Polymer Vol. 39 No. 24 pp. 6085–6091, 1998
0032-3861/98/$ – see front matter

PII: S0032-3861(98)00056-1

Modelling of crystallization in stereoblock polypropylene. Idealized structures showing the effects of isotactic block lengths and their polydispersity

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(Received 22 April 1997; revised 3 November 1997; accepted 23 December 1997)

Characterizing partially crystalline isotactic polypropylene can be carried out by extractions which are based on decreases in solubility with increased crystallinity, which in turn increases with increased isotactic block length. The present investigation employs Monte Carlo techniques to model how crystallization in polypropylene might depend on increase in isotactic block length (with the overall isotacticity either increasing or being held constant), and on its distribution (polydispersity). While isotactic block length was found to have a strong effect on the characteristics of crystallization, it should have less effect on elastomeric moduli calculated from the number density of crystallites (when functioning as volume-less cross-links). In contrast, block-length polydispersity had little or no effect on the crystallization, but a rather unusual effect on mechanical properties. These dependences may be due to the assumption that the elastomeric moduli depended only on the number density of the crystallites, without account for size effects such as large crystallites also functioning as filler particles. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: Monte Carlo simulations; polypropylene; crystallization)

INTRODUCTION

Stereoblock polypropylene (PP) generated using Ziegler-type catalysts or metallocene catalysts consists of stereo-irregular and stereoregular sequences alternating along the polymeric chains[1–6]. A particularly interesting class of catalysts in this regard are the metallocenes in which the unbridged molecules isomerize between chiral (racemic-like) and an achiral (*meso*-like) geometries by rotation of the indenyl ligands about the metal–ligand bond axis[7–9]. These two arrangements produce atactic and isotactic stereosequences, respectively. The microstructure of the PP produced is therefore thought to be blocks of atactic and isotactic sequences, with the latter being of sufficient length to crystallize with similar sequences on neighbouring polymeric chains.

Whole polymers produced using these catalysts consist of several fractions that can be separated using a series of boiling solvents, and the various fractions vary greatly in their physical properties. For example, the heptane-insoluble fraction is typically a semi-crystalline thermoplastic (with a ‘yield point’) and has the highest isotactic content, while the ether-soluble fraction is a weak, gummy material with almost no isotacticity at all. In contrast, the intermediate hexane-soluble or heptane-soluble fractions show good elastomeric properties, indicating the presence of the stereoblock isotactic sequences forming crystallites that act as physical cross-links. The fraction [mmmm] of isotactic (*meso*) pentads increases in each successive fraction, reaching a maximum of ca 70% for the hexane-insoluble fractions. The crystallinity of the ether-soluble fraction which contains the smallest number of isotactic sequences seems to increase with molecular weight[10]. This is surprising from the kinetics point of view, since increases in molecular weight increase chain entangling and reduce molecular mobility. An offsetting increase in the probability for occasional long isotactic blocks could be facilitating the crystallization.

The fractional number of monomers in isotactic blocks containing four or more monomers is $n(\geq 4) = 2[\mathrm{rmmm}] + [\mathrm{mmmm}]$[10,11], and the fractional number of isotactic blocks containing four or more repeat units is $b(\geq 4) = [\mathrm{rmmm}]/2$. Therefore, the average length of isotactic blocks having four or more monomer units is $N(\geq 4) = n(\geq 4)/b(\geq 4) = 4 + 2[\mathrm{mmmm}]/[\mathrm{rmmm}]$. Using the above equation, Collette *et al.*[10] reported a number-average length of isotactic blocks in highly isotactic PP to be approximately 100 repeat units. They also reported average block lengths for the ether-soluble and heptane-soluble fractions to be 6 and 15 units, respectively. Since the minimum length required for an isotactic sequence to crystallize was reported to be 14 units[9,12,13], this explained both the ability of the heptane-soluble fractions to crystallize, and the inability of the ether-soluble ones to do so.

The distribution of block lengths is also known to affect the mechanical properties of stereoblock PP. For example, Natta[1] reported that stereoblock PP with crystallinity values of 25% showed good elastomeric properties and exhibited reversible elongations up to 200%. This is in contrast to

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mixtures of amorphous and isotactic polymers having the same overall crystallinity, which do not exhibit such properties. In more detail, stress–strain isotherms of stereoblock PP[14] show low initial elastic moduli, reversible elongations, and relative high tensile strengths. Creep is also relatively low, which is consistent with the isotactic crystallites acting as cross-links opposing the irreversible flow of the chains[1,14].

The present investigation uses Monte Carlo methods to generate PP chains having illustrative stereoblock sequences, and then looks for matches in arrays of such chains that might lead to the formation of crystallites. Of particular interest was the way in which thermodynamic and mechanical properties of PP increase with increase in isotactic block length (with the overall isotacticity either also increasing, or being held constant by corresponding increases in atactic block length), and on the corresponding block length distribution (polydispersity).

SIMULATION METHODOLOGY

General aspects

The present application of Monte Carlo methods involves generating PP chains consisting of sequences of either *meso* (m) placements or racemic (r) placements. The stereoregular sequences with capability of crystallization were taken to be isotactic (m), whereas stereoirregular ones (m or r at random) represent the atactic. Some of the simulations were designed to model the type of stereoblock PP generated using metallocene catalysts. Each simulated chain was divided into sections of equal length, and every section consisted of an isotactic and an atactic sequence. The stereo-configuration of the first unit of any given isotactic block, (*d*) or (*l*) as defined in the older terminology, was chosen randomly by comparing a computer-generated random number with 0.5[9] This initial unit was followed by a chosen number of repeat units of the same atomic configuration for the length of this particular isotactic block. A p_r replication probability value of 0.5 was also used to produce the entire atactic sequences following the isotactic ones, and was chosen to produce the desired stereochemical randomness. The atactic sequences were generated in such a way that the fraction of isotactic placements (replications) within the atactic sequences equalled[15] the value chosen for p_r. All simulations were carried out for chains having degrees of polymerization DP of 2000 units.

Block lengths

The effects of block length were studied in two ways, but in each simulation of this type all the isotactic blocks had the same length, as did the atactic blocks. In other words, both types of block had monodisperse length distributions, with the question of polydispersity considered separately below. In the first series of the present simulations, the increase in length of the isotactic sequences was at the expense of the length of the atactic ones, so as to keep the section length constant[12]. The stereochemical structure could thus be represented by the placements $[(\mathrm{m})_x(\mathrm{m\ or\ r})_{y-x}]_{2000/(y+1)}$. This increase in the number of repeat units x in the isotactic blocks is accompanied by a subsequent decrease in the number of units $y - x$ in the atactic sequences, and is directly characterized by increasing values of the fractional isotactic pentad content [mmmm].

In the second approach, the lengths of both the isotactic blocks and atactic blocks were increased approximately proportionally, with corresponding increases in total section length and decreases in the number of sections. The stereochemical structure is now represented by the placements $[(\mathrm{m})_x(\mathrm{m\ or\ r})_{xz}]_{2000/(x+xz+1)}$, where the parameter z controls the relative lengths of the isotactic and atactic sequences. Examples of numbers of isotactic units and atactic units, respectively, are 15 and 35, 20 and 40, 24 and 50, 30 and 70, 40 and 80, 60 and 140, and 120 and 280. All of these combinations correspond to atactic sequences approximately twice as long as the isotactic ones, and gave polymers having approximately 30% isotacticity, but with varying block length (in a monodisperse distribution).

Polydispersity

The effect of polydispersity was also modelled, again at an approximately constant value of 30% isotacticity. For example, the average length of 30 isotactic units (29 placements) described above was alternatively modelled as two alternating isotactic sequences of 40 and 20 units, or as two sequences of 50 and 10 units, for every pair of 100 repeat units. The stereochemical structure $[(\mathrm{m})_x(\mathrm{m\ or\ r})_{y-x}]_{2000/(y+1)}$ for the monodisperse distribution was thus replaced by an alternating bimodal distributions of $[(\mathrm{m})_{x+y}(\mathrm{m\ or\ r})_{99-x-y}]$ sequences alternating with $[(\mathrm{m})_{x-y}(\mathrm{m\ or\ r})_{99-x+y}]$ sequences in the case of the isotactic blocks. The limiting case of 60 and 0 units, represents isotactic blocks of 60 units every 200 section repeat units.

Crystallization

One hundred chains thus simulated were placed in parallel two-dimensional arrangements in order to search for crystallinity, using the Windle approach[15,16] for copolymers with two crystallizable components. Since the simulations are for two dimensional arrangements, they thus represent only slices through an actual three-dimensional sample. The present approach for stereochemical polymers parallels that taken earlier for some chemically-copolymeric[17] and stereochemically-copolymeric polysiloxanes[18].

Each unit in the chains was given the opportunity to be involved in the crystallization process so long as it occurred in a sequence of minimum length suitable for crystallization, and was adjacent to other isotactic sequences on neighbouring chains[19]. The most common crystallographic form of isotactic PP was simulated here; in it, the neighbouring helical sequences must have opposite chirality or handedness[4,19]. They also have to have sufficient sequence length to be expected to crystallize[9,10,13]. The minimum number of units in a sequence required for crystallization was taken to be fourteen units, which corresponds to the thickness of the smallest crystallite (3.0 nm)detected for the ether-soluble elastomeric PP of low isotacticity. Crystallites formed during crystallization would grow longitudinally until meeting a unit of the other type, and laterally so long as sequences of the crystallizable component of a minimum sequence length were available from the amorphous regions[20]. Possible kinetic complications are not taken into account, making the results most reliable for relatively short blocks of crystallizable component.

Melting points

The extent to which the melting point of the crystallizable units in a polymer is depressed by the presence of the other units is given by:[15–18,20]

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

where T_m^0 and T_m are the melting points of the pure crystallizable polymer and the polymer under study, respectively. The melting point of isotactic PP was determined to be 187.7°C using extrapolation methods[10] and ΔH_u is the enthalpy of fusion per mole of crystallizable units, 8.79 kJ mol^{-1}. R is the gas constant, and L is the degree of crystallinity determined with respect to the number of units with potential for crystallization.

Modelling of the annealing process

Annealing was modelled by sliding the chains past one another longitudinally to search for the largest possible match densities[15–18]. The longitudinal movement of the chains relative to one another, out of register, approximately models the lateral sorting out of sequences in polymeric chains during slow crystallization. In sliding the chains by one another in these searches, protruding sections were relocated from one end of the array to the other so as to keep the number of comparison pairs constant. The use of the idealized structures described above creates an artificial situation for the chosen reference state, however. Starting with the isotactic sequences exactly in register maximizes the number of sufficiently long sequences to crystallize. This is somewhat unrealistic as a reference point, however, since the random nature of the crystallization process makes it exceedingly unlikely that such an arrangement would ever actually occur. It is referred here as the ‘quenched’ state only to facilitate comparisons with other simulation results on PP[9,13]. In addition, this highly idealized arrangement does not maximize the total number of matches of any arbitrary length, which is what the program seeks[15–18], since the matches lost in the isotactic blocks by the sliding could be more than made up for by new matches found using units in the atactic blocks. These new matched sequences would generally be too short to crystallize, however, which means that the searching procedure for these illustrative simulations should result in reduced amounts of crystallinity. A refinement of the search algorithm would be to maximize instead the number of sequences long enough to crystallize, or to use as a starting point the single longest matched sequence. Also, keeping two neighbouring chains in parallel arrangements artificially increases the likelihood of additional crystallites forming between this particular pair of chains, but this should not be a major problem. Finally, it should also be mentioned that in actual crystallizations the initial crystallites formed would impede large translations of the chains and thus thwart their increasing the number of matches.

MODELLING RESULTS

Stereochemical structures

Figure 1 represents graphical representations of the initial sequences of the simulated chains, laid down in horizontal rows. The numbers on the left of the figure refer to the length of the sections comprising the chains, with the shortest isotactic block at the bottom. The black squares represent the (*d*) isomer, and the white squares the (*l*) isomer. Vertical stacks of three chains having the same section length are shown together to provide easier visualization. Every chain of the simulated PP would thus contain one or more isotactic blocks, of varying length. The relative or normalized isotactic pentad content [mmmm] increases with increase in the length of the isotactic sequences (moving upward in the diagram). *Figure 2* indicates the change in the values of the various pentads as a function of the lengths of the isotactic blocks. Error bars shown in all the figures are based on four simulations and represent the standard errors of the modelling results. As expected, the number of mmmm pentads increases essentially linearly with increase in isotactic block length, while the other pentads decrease linearly to zero.

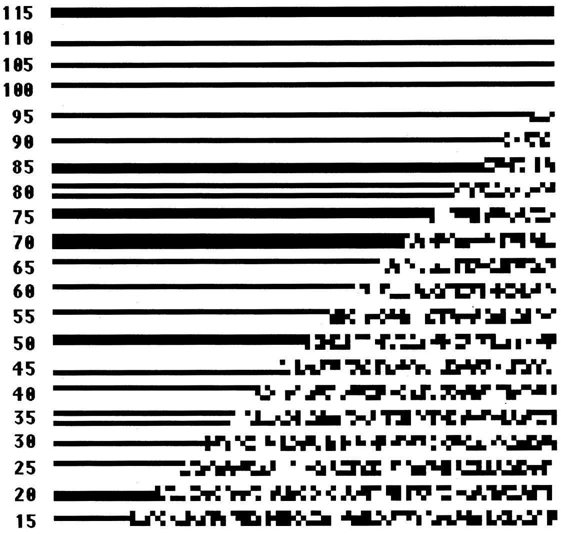

Figure 1 Graphical representations of simulated chains of stereoblock polypropylene having various isotactic block lengths. Black and white squares represent the (D) and (L) stereoisomers of the units, respectively

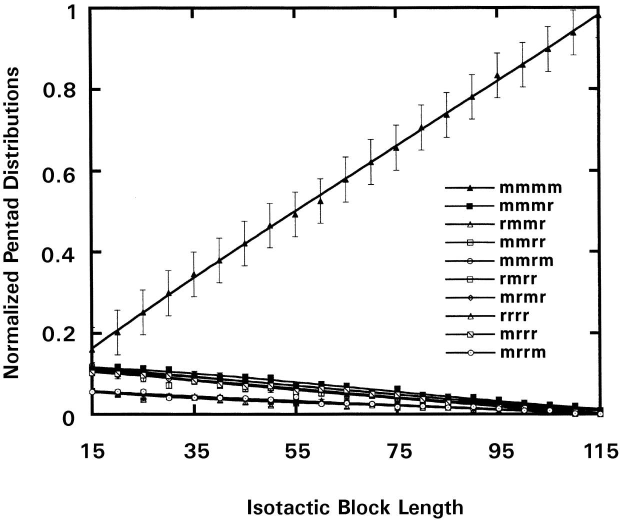

Figure 2 The dependence of the pentad distribution of PP on the isotactic block length, which increases at the expense of the atactic blocks so as to keep the combined length at 115 repeat units

Identification of crystalline regions

Some graphical representations of the simulated results are shown in *Figures 3* and *4*. The figures are for initial illustrative regions of stereoblock PP with isotactic sequences of fifty units. They were obtained using the repeat unit matching procedure, and represent quenched (Q) and searched (S) PP, respectively. In the (a) sections of the

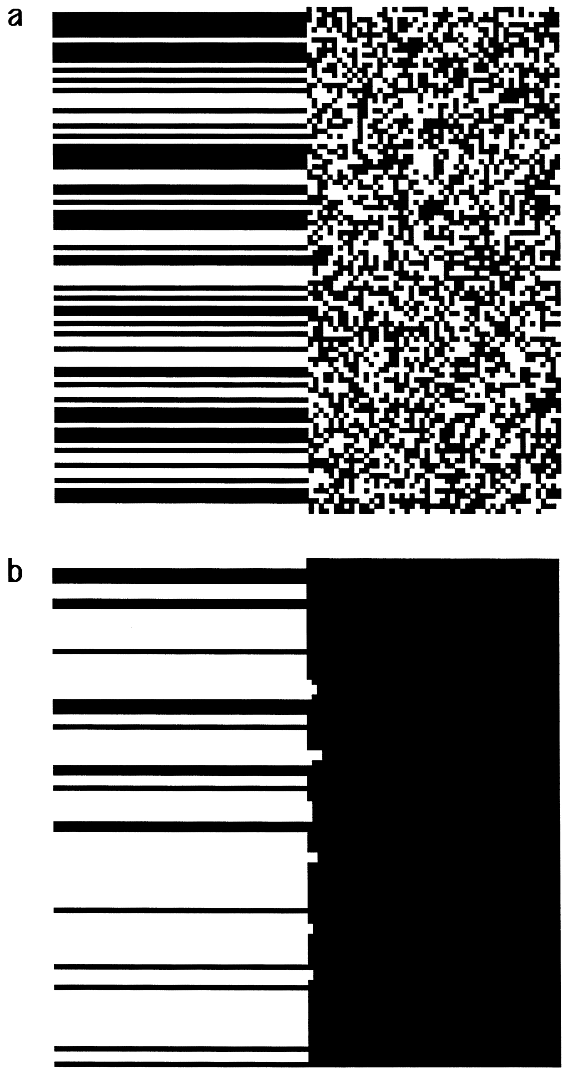

Figure 3 Simulated results for the quenched polymers: (a) stereochemical structures and (b) corresponding crystalline regions. See text

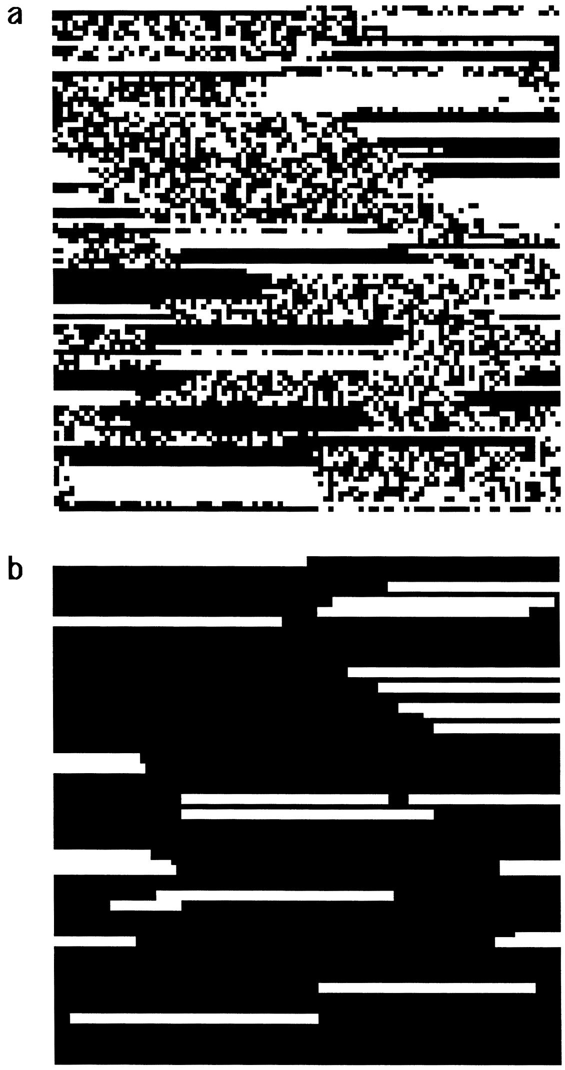

Figure 4 The results of *Figure 3*, after modelling of the annealing process

figures, the black squares represent the (d) isomer, and the white squares the (l) isomer. The (b) sections show the extent of the crystallized regions obtained from number of 'like' squares neighbouring one another, and thus coalescing into blocks of sufficient length to crystallize. 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 chains in *Figure 3* were slid by one another to maximize the number of such matchings in an attempt to model annealing, with the results shown in *Figure 4b*. The results indicate that the chain searching procedure did not improve the crystallinity significantly. This may be partly due to the fact that the chain-matching process includes not only isotactic sequences too short to crystallize, but also matching units found in various atactic sequences not contributing at all to the crystallinity. In any case, the lack of much improvement in the matching is consistent with experimental observations that extended crystallization times (annealing) have little or no effect on the extent of crystallinity in these polymers[13].

Degrees of crystallinity

Values of the degree of crystallinity of the various simulated samples were determined by counting the units

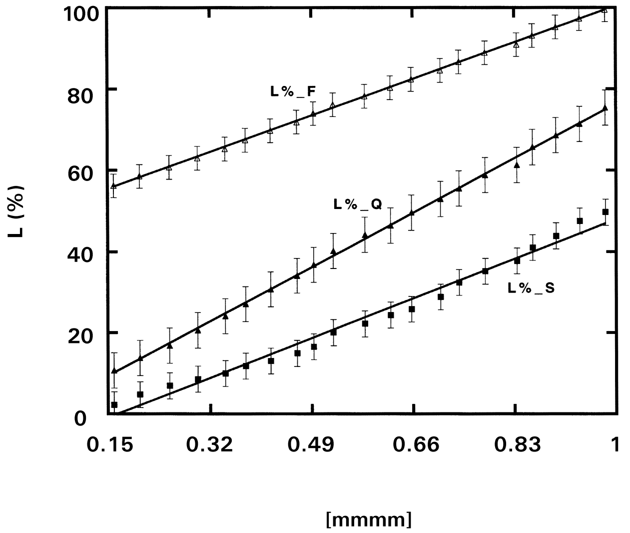

Figure 5 Degree of crystallinity of the polymers as a function of the fractional isotactic pentad content [mmmm]

involved in the crystalline sequences relative to the total number of units in all the chains. The results are shown in *Figure 5* as a function of the isotactic pentad content [mmmm], with F representing the Flory relationship between degree of crystallinity and p_r, and Q and S the simulated results for quenched and searched (annealed) samples, respectively. As expected, the degree of crystallinity increases with [mmmm] as a consequence of the increase of the crystallizable isotactic content. In this case, the chain-searching process resulted in decreases in the percent crystallinity, presumably because increase in total number of matches came at the cost of decreased numbers of sequences of sufficient length to crystallize. Crystallinity values predicted for the quenched and searched (annealed) cases are seen to be less than those predicted using the Flory melting point depression relationship, and are more comparable with values determined experimentally[21]. It should be noted that for almost the entire range of [mmmm], significant crystallinity is predicted for these stereoblock modifications. This is in contrast to the usual atactic samples of PP having moderate replication probabilities, which do not show any crystallinity at all[13]. These predicted crystallites would act as cross-links in a network structure, which explains the attractive properties of the stereoblock PP first described by Natta[1].

Melting points

Table 1 presents the melting points of some PP polymers simulated using different [mmmm] values. Column two of the table gives the melting points predicted by equation (1), the melting point depression relationship[22], using the number of units with potential for crystallization in place of the degrees of crystallinity. As expected, the predicted melting points using this relationship are much higher than those determined experimentally. This is, of course, due to the fact that only part of the crystallizable component could have undergone crystallization. Using our simulated values of the percent crystallinity in equation (1) should therefore provide more appropriate predicted values of the melting points. The resulting values are given in columns three and four of the table for the quenched and searched (annealed) samples, respectively.

Thermodynamics of crystallization

The Flory theory[20] 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 neighbouring chains 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:

(1) the availability of neighbouring sequences in the amorphous regions, and
(2) the decrease in standard free energy gained by incorporation of amorphous polymer units into the crystalline state.

The probability P_ζ of finding a unit residing adjacent to a terminal unit of the crystallite and belonging to a sequence of ζ units will be related to the standard free energy of fusion ΔF_ζ of a sequence of ζ units from a crystallite of length ζ. It is given by[20]

$$P_\zeta = P_\zeta^e = \exp(-\Delta F_\zeta/RT) \qquad (2)$$

Here, ΔF_ζ is expressed in molar units and $P^e{}_\zeta$ is measured under equilibrium conditions (as indicated by the superscript). This probability was calculated from the simulated results by counting the units adjacent to a crystallite, with potential for crystallization, as a function of [mmmm]. The values of this probability are shown in *Figure 6*. As expected, the values increase with [mmmm]. This is an important factor when discussing the morphology of the chains since it gives an indication of the average crystallite sizes, with low $P^e{}_\zeta$ values associated with small sizes. Large $P^e{}_\zeta$ values, on the other hand, will indicate a higher probability of additional terminal crystallizable units and subsequently larger crystallites. The values of ΔF_ζ calculated from equation (2) are similarly shown in *Figure 7*. The results indicate a decrease in the standard free energy of fusion for a sequence of ζ units upon increase in the number of the crystallizable units, which is probably again related to crystallite size.

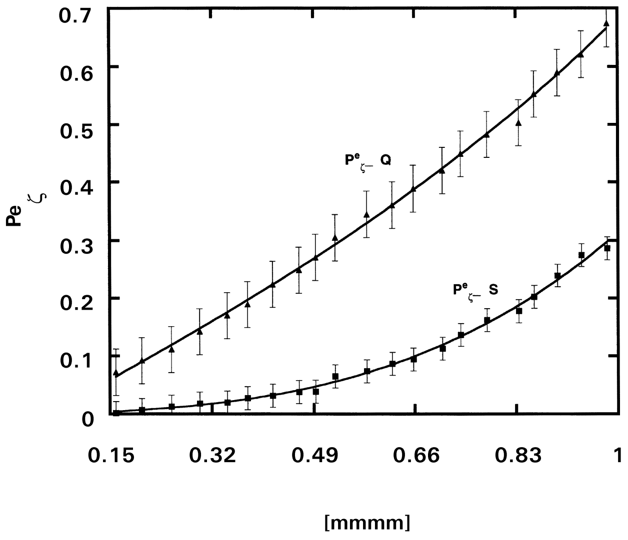

Figure 6 Probability of additional crystallizable units in the polymers

Table 1 Melting points of stereoblock polypropylene structures of different isotactic block lengths, as predicted from melting-point depression theory and from the simulations for the quenched and annealed cases

No of units in isotactic blocks	T_m (/°)		
	equation (1)[a]	Simulation	
		Quenched[b]	Annealed[c]
20	102.2	12.1	−49.8
30	111.9	39.2	−23.7
40	121.5	58.7	−8.4
50	130.9	76.6	3.0
60	139.9	89.2	20.6
70	148.5	100.6	32.3
80	157.1	111.1	42.9
90	165.8	118.8	57.3
100	174.2	128.0	68.5
110	182.6	133.9	80.0

[a] Melting point depression equation[22]
[b] Calculated for the simulated chains
[c] Calculated after chain-sliding process was performed on the simulated chains

Interfacial free energies

Another important crystallization variable is σ_e, 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_u was calculated from

$$\Delta F_u = \Delta H_u - T\Delta S_u \qquad (3)$$

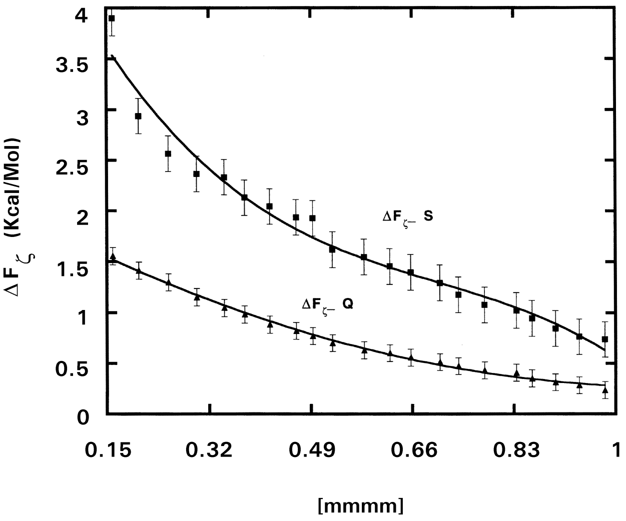

Figure 7 Standard free energy of fusion of a sequence of ζ units

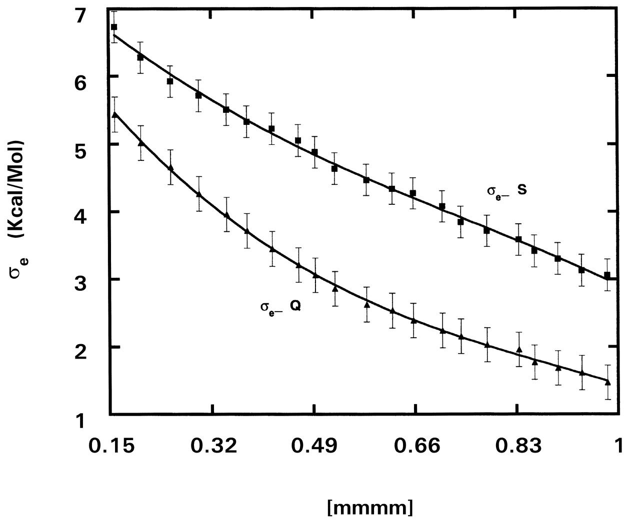

Figure 8 Interfacial free energy per mole of units

and σ_e from

$$\Delta F_\zeta = \zeta \Delta F_u - 2\sigma_e \tag{4}$$

Estimates of the required values of ΔH_u and ΔS_u were obtained from the literature[10]. Values of σ_e thus obtained are shown in *Figure 8*. This interfacial free energy is an important variable since it takes into account the decreased stability of the shorter crystallites, and can be used to characterize the predicted crystallinity in the polymers. For example, it identifies the conditions under which even the shorter crystallites should be stable.

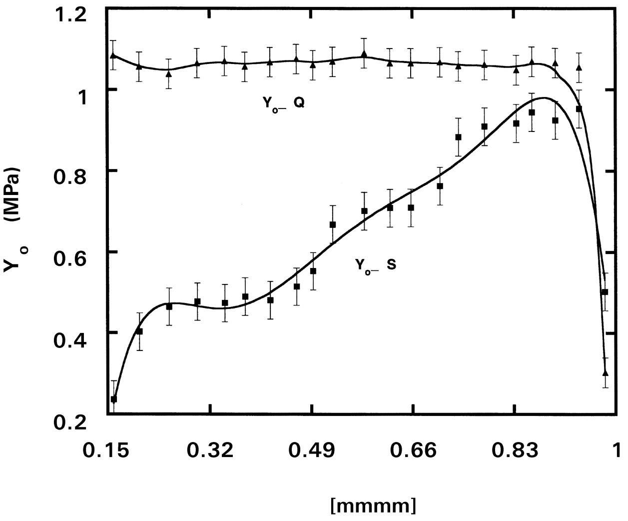

Figure 9 Young's modulus at infinitesimal extension

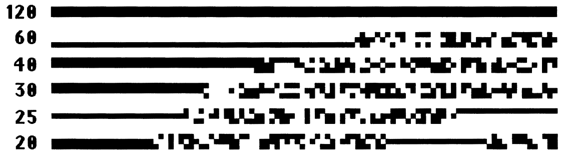

Figure 10 Graphical representation of simulated chains of stereoblock PP in which the isotactic and atactic lengths are increased approximately proportionately

Moduli of the elastomeric networks

The theory of rubber-like elasticity[18,20,23–26] relates 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 υ_c, then Young's modulus at infinitesimal deformation is given by

$$Y_o = 3RT(\upsilon_c/N_1) \tag{5}$$

where N_1 is the number of the units actually participating in the formation of the crystallites. Values of Young's modulus predicted from the simulated values of υ_c are shown in *Figure 9*. It is seen that for the idealized, artificial case of the quenched samples, increase in isotactic block length had essentially no effect on Young's modulus for almost the entire range of isotactic content. This is in marked contrast to the marked effects the block length had on the thermodynamic properties related to crystallization. The near constancy of the calculated modulus may be due to the assumption that the elastomeric moduli depended only on the number density of the crystallites. For most of the range in [mmmm], the crystallization may involve more growth in the sizes of the crystallites, with the number of crystallites subsequently plummeting as already-formed crystallites are connected into a smaller number of larger crystallites. In the case of the searched samples, the increase in modulus is presumably due to the increased number of sequences sufficiently long to crystallize. More realistic portrayals of the effect of crystallization could probably be obtained by taking into account size effects, such as large crystallites also functioning as filler particles.

Effects of increased lengths of both blocks

Figure 10 is a graphical representation of the distribution of the blocks when the isotactic and atactic lengths are increased proportionally, so as to keep the isotactic content at approximately 30%. Each number on the left of the figure refers to the length of the isotactic blocks in that particular run. Moving upward in the rows corresponds to increasing the lengths of both the isotactic and the atactic blocks, with corresponding increases in section length and decreases in their number.

The effects of such increases in block sizes on various properties are shown in *Figure 11*. In this depiction,

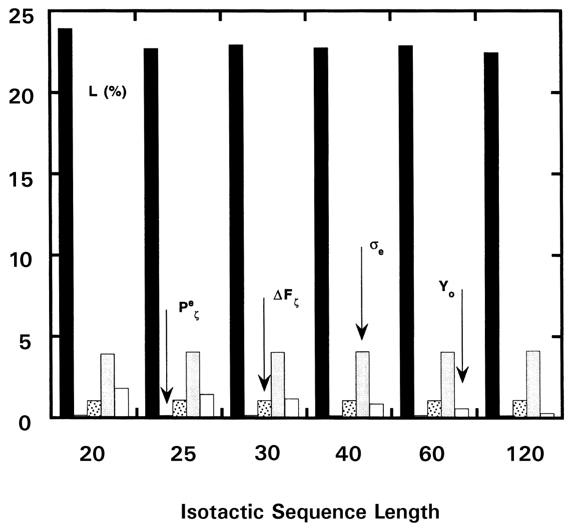

Figure 11 Various thermodynamic and mechanical properties of the PP samples described in *Figure 10*

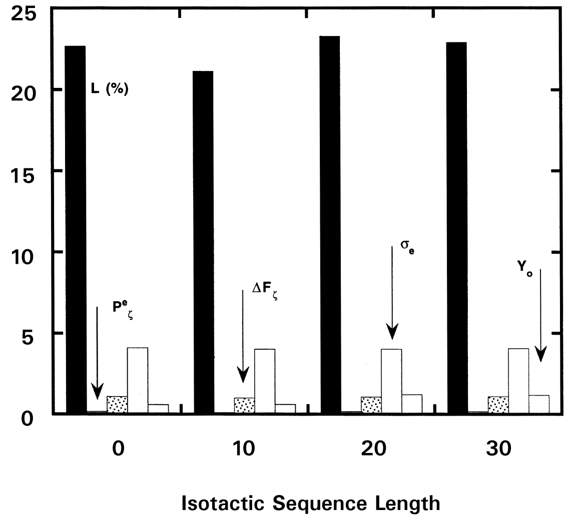

Figure 12 Various thermodynamic and mechanical properties of PP samples in which the polydispersity of the isotactic block lengths decreases from left to right

increasing the lengths of both the isotactic and the atactic blocks corresponds to moving from left to right along the abscissa. In this and the following figure, there is a grouping of five vertical bars for each value of the isotactic sequence length. As marked in the figures their heights correspond, from left to right, to the fraction of crystallinity *L* (%), the adjacent-unit probability $P^e{}_\zeta$, the standard free energy of fusion ΔF_ζ, the interfacial free energy σ_e, and the Young's modulus Y_0. In this figure and the following one, the scale is such that the bars for $P^e{}_\zeta$ were barely discernible; in any case this probability was small and quite independent of these changes in sequence length. In fact, as can be seen, most properties do not show much dependence at all on the proportionally scaled lengths of the two blocks. This is presumably because these lengths are all sufficient for the isotactic blocks to crystallize. The simulated values of the modulus show an interesting decrease as the isotactic length goes up, however, apparently because of the already mentioned fusing of crystallites, with corresponding increases in size but decreases in number.

Effects of polydispersity

The effects of polydispersity are shown in *Figure 12*, in which the abscissa shows the length of the shorter of the two isotactic blocks in the pair averaging to a length of 30 repeat units. Most properties do not show much dependence on polydispersity, with the modulus again representing an interesting exception. The largest values of Y_0 occur when all isotactic blocks have the same value, specifically 30 units in the case illustrated. Having pairs such as 10 units and 50 units is detrimental in this regard, since now only one of the two sequences is of sufficient length to participate in the crystallization process. The decrease in the effective number of cross-links decreases the modulus correspondingly, as would be expected.

ACKNOWLEDGEMENTS

It is a pleasure to acknowledge the financial support provided by the National Science Foundation through Grant DMR-9422223 (Polymers programme, Division of Materials Research), and by Amoco Chemicals. We also wish to thank R. M. Waymouth and M. D. Bruce of Stanford University and C. L. Myers of Amoco Chemicals for very helpful discussions, and the Fulbright programme for a Senior Scholar Award (#413/96) to TMM.

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