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Properties of thermoplastic elastomeric polypropylene

Simulations of the effects of molecular weight and molecular weight distribution

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Summary

The present investigation employs Monte Carlo techniques to model crystallization in stereoblock polypropylene. Of particular interest was determining how its properties might depend on the molecular weight and molecular weight distribution (polydispersity) of the chains. The simulations indicate that degrees of crystallinity and melting points should generally increase with increase in molecular weight and with decrease in polydispersity. The elongation modulus, based on the crystallites acting as temporary crosslinks in an elastomeric network, generally behaved similarly but were less sensitive to these variables. This decreased sensitivity is apparently due to the assumption that the elastic moduli depended only on the number density of the crystallites, without account for size effects, such as large crystallites, also functioning as filler particles.

Introduction

A variety of important forms of polypropylene (PP) now exist [1-5]. For example, stereoblock PP synthesized by using metallocene catalysts can consist of alternating isotactic and atactic sequences [6-9]. If the isotactic sequences are long enough to crystallize, the resulting PP crystals can act as crosslinks in a thermoplastic (reprocessible) elastomer [10]. The efficiency of the catalyst as well as the molecular weights of the polymers were found to be sensitive to reaction conditions [10,11]. For example, an increase in propylene gas pressure and a decrease in the polymerization temperature increased the molecular weight, presumabaly through increases in the monomer concentration and the slowing of ligand rotations in the catalyst.

High molecular weights could also be obtained by using metallocenes [12], a possible consequence of high regioselectivity [13]. However, the molecular weights of the resulting PP were lower than those produced using industrial catalysts [14]. This is probably due to increased rate of chain termination and/or decreased rate of olefin insertion [15].

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Polyolefins obtained with heterogeneous catalysts generally have large polydispersities $D \equiv M_w/M_n$ of ~5-10 [16], where the two molecular weights are the weight average and number average. In contrast, homogeneous catalysts produce polymers with lower D values, ~1.5-2.8 [9,17]. These results were predicted from Schultz-Flory statistics [18] for polymers generated from identical catalyst centers with fixed rates of chain propagation and chain termination. Molecular weights are very important in the case of these types of PP, since equilibrium melting points were shown [14] to increase with increasing molecular weight, and with decreasing breadth of the molecular weight distribution.

This study uses Monte Carlo simulations and sequence-matching algorithms to explore the effect of the molecular weight and molecular weight distribution on some characteristics of stereoblock PP.

Simulation Methodology

Generation of representative chains and sequence matching

Stereoblock chains were simulated using Monte Carlo methods, so as to resemble PP chains consisting of blocks of 15 (crystallizable) isotactic repeat units alternating with blocks of 100 (noncrystallizable) atactic units (85 in the case of the very shortest chain studied). Details are given elsewhere [8]. The simulations of the stereochemical structures were carried out for chains having degrees of polymerization DP ranging from 100 to 2000 units, to characterize the effects of molecular weight. The effects of molecular weight distribution were also modeled by assuming distribution values ranging from 1.5 to 2.8 [17]. Values of the polydispersity were chosen for a particular molecular weight, 84,000 g/mol, which corresponds to 2,000 repeat units. The lengths of the chains at a given polydispersity were simulated according to a normal (Gaussian) distribution function. One hundred chains were simulated for each chosen molecular weight or molecular weight distribution. They were placed in parallel two-dimensional arrangements and scrutinized for matches sufficiently long (14 or more units) to result in their crystallization [8,9].

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 [8,9]

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

where T^0_m and T_m are the melting points of the pure crystallizable polymer and the polymer under study, respectively. The melting point of isotactic PP [8] was determined to be 187.7 °C using extrapolation methods. ΔH_u is the enthalpy of fusion per mole of crystallizable units, 8.79 KJ/mol. R is the gas constant, and L is the crystallinity fraction determined with respect to the number of units with potential for crystallization.

Chain matching

Sliding the chains past one another longitudinally to search for the largest possible matching densities was done to model the annealed samples [8,9]. 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 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.

Modeling Results

Degrees of crystallinity

Values of the degree of crystallinity of the simulated samples were determined by counting the units involved in the crystallization relative to the total number of units of the samples. The resulting values are shown in Figure 1 as a function of PP molecular weight, with the vertical bars representing standard errors. As was found experimentally [19], the degree of crystallinity increased with increase in molecular weight, but levelled off after approximately a dozen pairs of blocks. Apparently the matching leading to identification of crystallites is facilitated when the numbers of isotactic blocks become representative, and the search routine has more sequences to work with in looking for matches. This simple scheme, however, does not take into account kinetic complications resulting from increases in chain entangling and deceases in chain mobility.

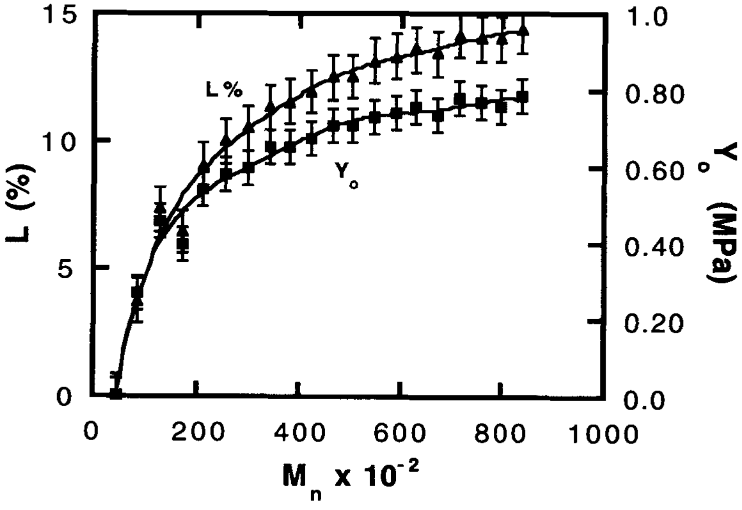

Figure 1. Degree of crystallinity and Young's modulus as a function of molecular weight.

The effect of the molecular weight distribution is shown in Figure 2. Apparently, the wider the dispersion, the lower the probability for the crystallizable isotactic sequences to match with other isotactic sequences for crystallization.

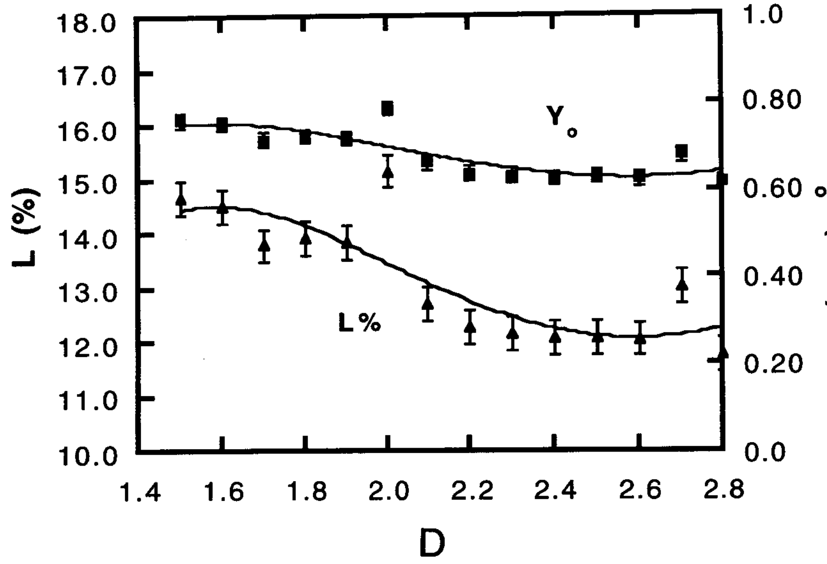

Figure 2. Degree of crystallinity and Young's modulus as a function of polydispersity in molecular weight.

Melting points

The second columns in Tables 1 and 2 give melting point values simulated for various molecular weights and molecular weight distributions, respectively. Increases in molecular weight and decrease in polydispersity generally increased the predicted values of the melting points, paralleling the increases in degrees of crystallinity, both dependences being in agreement with experiment [14].

Thermodynamics of crystallization

The Flory theory [20] provides equations for several physical quantities associated with crystallization [7-9]. For example, the probability P_ζ of finding a unit residing adjacent to a terminal unit of a crystallite and belonging to a sequence of ζ units is 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 $P_\zeta = P^e{}_\zeta = \exp(-\Delta F_\zeta / RT)$. This probability was calculated from the simulated results by counting the units adjacent to a crystallite, with potential for crystallization. Values of ΔF_ζ were calculated as described. The interfacial free energy per unit, σ_e, which represents the excess free energy per mole associated with a unit at the end of a crystallite could also be calculated from the simulation results. Specifically, the standard free energy of fusion per mole of units ΔF_u was

Table 1. Effects of Molecular Weight on the Crystallization Characteristics of Stereoblock Polypropylene

M_n (g mol^{-1})	T_m	P^e_ζ	ΔF_ζ	σ_e
4,208	-	-	-	-
8,416	-64.6	0.002	3.872	6.297
12,624	-33.4	0.009	2.797	5.815
16,832	-40.0	0.009	2.790	6.035
21,040	-21.6	0.022	2.280	5.690
25,248	-15.8	0.023	2.224	5.527
29,456	-13.1	0.027	2.137	5.482
33,664	-8.1	0.034	1.999	5.388
37,872	-6.8	0.035	1.992	5.351
42,080	-4.5	0.036	1.984	5.278
46,288	-1.7	0.042	1.883	5.238
50,496	-1.4	0.042	1.878	5.229
54,704	1.9	0.047	1.803	5.161
58,912	2.6	0.046	1.826	5.125
63,120	4.1	0.051	1.765	5.107
67,328	3.2	0.051	1.768	5.137
71,536	7.1	0.056	1.713	5.036
75,744	6.4	0.055	1.717	5.057
79,952	6.4	0.054	1.729	5.052
84,160	8.1	0.058	1.685	5.017

Table 2. Effects of Molecular Weight Distribution on the Crystallization Characteristics of Stereoblock PP

D[a]	T_m	P^e_ζ	ΔF_ζ	σ_e
1.5	9.0	0.066	1.606	5.027
1.6	8.2	0.061	1.658	5.026
1.7	4.7	0.051	1.759	5.093
1.8	5.3	0.054	1.729	5.086
1.9	4.8	0.056	1.716	5.109
2.0	11.5	0.058	1.684	4.907
2.1	-1.1	0.047	1.815	5.252
2.2	-3.5	0.043	1.861	5.309
2.3	-4.1	0.039	1.926	5.295
2.4	-4.5	0.047	1.819	5.363
2.5	-4.5	0.043	1.875	5.333
2.6	-4.6	0.043	1.870	5.339
2.7	0.5	0.036	1.974	5.122
2.8	-6.3	0.038	1.937	5.362

[a] Polydispersity $D \equiv M_w / M_n$, for $M_n = 84{,}000$ g mol^{-1}.

calculated from $\Delta F_u = \Delta H_u - T\Delta S_u$ and σ_e from $\Delta F_\zeta = \zeta\Delta F_u - 2\sigma_e$.The interfacial free energy is an important variable since it takes into account the decreased stability of the shorter crystallites. Values for P^e_ζ, ΔF_ζ, and σ_e for different molecular weights and molecular weight distributions are shown in columns 3, 4, and 5 of Tables 1 and 2, respectively. The increase in P^e_ζ indicates the formation of larger crystallites, whereas the decrease in σ_e indicates decrease in the stability of the shorter crystallites.

Elongation moduli

According to the theory of rubberlike elasticity, the modulus of elasticity can be calculated from the number of crystalline sequences υ_c acting as cross links, with the sequences in the amorphous state contributing the elastomeric chains. The basic relationship is $Y_0 = 3RT(\upsilon_c/N_1)$, where Y_0 is Young's modulus at infinitesimal elongation and N_1 is the number of the units in the crystallites [20,21]. Figures 1 and 2 show the dependence of Young's modulus on the molecular weight and its distribution, respectively. Values of the elongation modulus generally paralleled the changes in degree of crystallinity, but were less sensitive to these variables. This decreased sensitivity is apparently 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.

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