Conformational effects on melting point depression of atactic polypropylene and ethylene–propylene copolymers

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The composition dependence of T_m is investigated for RIS models of a-PP and random E/P copolymers using a modified Flory's equation. The values of a(= 1 in the original equation) are 1.8∼1.9 and 1.3 for a-PP and E/P copolymers respectively. Values for the heat and entropy of transition due to quasi-crystals in the amorphous regions suggest that there is a high possibility of ordering in these regions in a-PP but there is a much looser packing in E/P copolymers.

INTRODUCTION

The melting temperature T_m of atactic polypropylene (a-PP) varies depending on its tacticity. A-PP is normally taken as being totally amorphous whereas in this paper it refers to imperfectly stereoregular material which can, however, still crystallize to some extent. Natta[1], Newman[2] and Pavan etc.[3] investigated the melting point depression of a-PP as a function of tacticity using an original Flory's equation (equation 1 with a = 1)[4]. However, it has been pointed out[5] that the application of an original Flory's equation to the T_m data of copolymers is inadequate, because the heat of fusion h_u of a polymer evaluated from an original Flory's equation is a third to a half of the magnitude of h_u from the diluent method[5] and the d.s.c. measurement. The results for a-PP by Natta etc.[1–3] should be reconsidered.

In this paper, a modified Flory's equation (1) is proposed and the composition dependence of T_m is investigated for the rotational isomeric state (RIS) models[6] of a-PP and random ethylene–propylene (E/P) copolymers.

THEORY

A modified Flory's equation (1), on the melting point depression of non-isomorphic binary random copolymers depending on the increase of minor component, is derived by considering the heat h_x and entropy s_x of transition due to quasi-crystals, for example, with short range ordered parts in the amorphous regions on the basis of the melting theory of copolymers by Flory[4].

$$\frac{1}{T_m}-\frac{1}{T_m^0}=-\frac{aR}{h_u}\ln X_A \qquad (1)$$

with

$$a\approx\frac{2h_u}{2h_u-h_x}$$

where T_m is the melting temperature of a copolymer, T_m^0 the melting temperature of a major component polymer, h_u the heat of fusion per molar structural unit of major component, X_A the mol fraction of major component units and R the gas constant.

Melting point depression of atactic polypropylene

The composition dependence of T_m is investigated for RIS models of a-PP generated using random numbers. Fortunately a modified Flory's equation (1) is available for a-PP, because a-PP can be treated as a binary random copolymer composed of meso and racemi diads[7]. *Figure 1* shows the relation between T_m and X_A for two RIS models

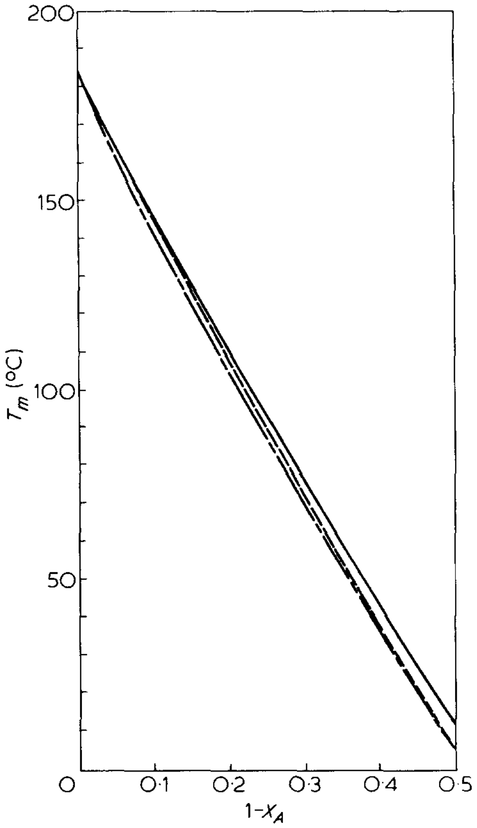

Figure 1 Relation between T_m and $1-X_A$ for a–PP (——), 3 states model, $\eta = 0.5$; (– – –), 3 states model, $\eta = 0.05$; (—— — ——), 5 states model

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Table 1 The values of a, h_x, s_x and h_x/s_x for RIS models of a-PP

Number of rotational isomeric states	h_x (cal mol^{-1})	s_x (cal mol^{-1} K^{-1})	h_x/s_x (°C)	a
5	1812.6	4.05	174.3	1.91
3(η = 0.5 at 25°C)	1712.1	3.83	173.9	1.82
3(η = 0.05 at 25°C)	1789.4	4.00	174.3	1.89

Table 2 The values of a, h_x, s_x and h_x/s_x for PE copolymers

Copolymer	h_x (cal mol^{-1})	s_x (cal mol^{-1} K^{-1})	h_x/s_x (°C)	a
Model of E/P copolymer	454.4	1.11	136.5	1.31
E/VA$_c$ copolymer	228.4	0.56	135.5	1.14
n-propyl branched copolymer of PE	787.9	1.92	136.9	1.70

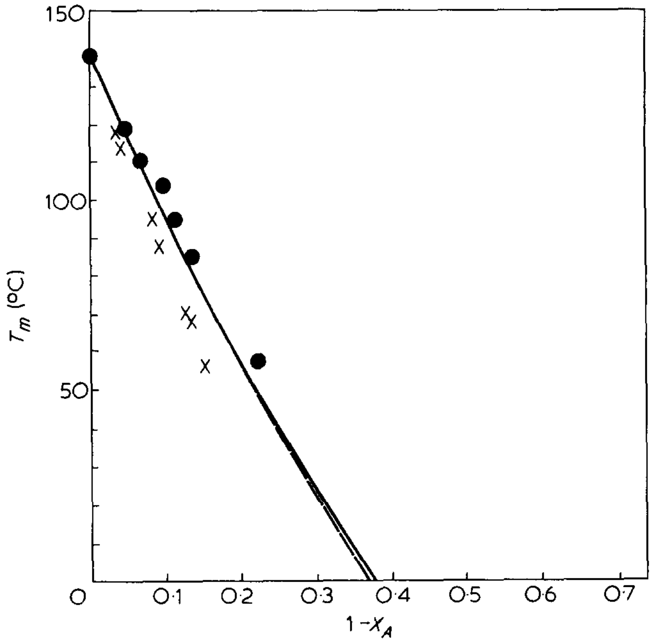

Figure 2 Relation between T_m and 1 $-X_A$ for E/P copolymer (——), η = 0.5, (– – –), η = 0.05; (●), E/VA$_c$ copolymer[10], (X), n-propyl branched copolymer of PE[11]

with three and five states of a-PP (major component is meso diad unit and the degree of polymerization $x = 100$). For an RIS model with three states, the two values of the 1st order interaction parameter η, expressing the statistical weight of *gauche* relative to the *gauche* state 0.05 and 0.5 at 25°C, were used[6]. Pavan's results[3] are plotted in the vicinity of T_m vs. X_A curves for models of a-PP. In *Table 1*, the values of a, h_x, s_x and h_x/s_x for these models are listed. For any model of a-PP, the values of h_x and s_x are a little smaller than h_u(1900 cal mol^{-1})[8] and s_u(4.2 cal mol^{-1} K^{-1})[8] for isotactic PP(i-PP) and the values of h_x/s_x are by 10 K smaller than T_m(184°C)[8] of i-PP. The values of a are in the range of 1.8 ~ 2.0. The high values of h_x and s_x for these models may be related to the high possibility of the presence of the ordered regions with the short helical structure in the amorphous regions[9].

Melting point depression of ethylene–propylene copolymer

For random E/P copolymer, the mol fraction X_A of major component units (ethylene units) should be given by $1-2n/N$, where n is the total number of skeletal carbon atoms with a hydrogen atom and another substitution residue (–CH$_3$), and N the total number of bonds. *Figure 2* shows the relation between T_m and X_A for an RIS model of random E/P copolymer with $x = 100$. The experimental data of T_m for ethylene–(vinyl acetate) (E/VA$_c$) copolymer[10] and alkyl branched copolymer of PE[11] lie in the vicinity of the calculated curves for an RIS model of random E/P copolymer. In *Table 2*, the values of a, h_x, s_x and h_x/s_x for E/VA$_c$ copolymer, n-propyl branched copolymer of PE and a model of E/P copolymer are listed. For E/VA$_c$ copolymer and n-propyl branched copolymer of PE, the melting point data by Nielsen[10] and Richardson[11] were used. In these copolymers, the values of a are smaller than 2. The values of h_x and s_x are smaller than h_u (960 cal mol^{-1})[5] and s_u(2.34 cal mol^{-1} K^{-1})[5] of PE. For an RIS model of E/P copolymer, these values are 0.47 times as much as h_u and s_u of PE respectively. The value of h_x/s_x for each copolymer is almost equal to T_m(137.5°C)[5] of PE. These results suggest that there is a much looser packing in E/P and E/VA$_c$ copolymer.

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