MELTING POINT PREDICTION OF ATACTIC POLYPROPYLENE AND PROPYLENE/ETHYLENE COPOLYMERS WITH \((A-B)_n\) TYPE CONFIGURATIONS

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ABSTRACT

By using the modified Flory's equation on the melting of copolymers, the relationships have been investigated between the melting temperature and the composition for the rotational isomeric states models of atactic polypropylene, ethylene/propylene and propylene/ethylene copolymers of \((A-B)_n\) and random types. Atactic polypropylene may be treated as a binary copolymer composed of meso and racemi units. For these models, the common characters are found in the \(T_m\) vs. composition curves. For models with \(n=1\), the depression of \(T_m\) is negligibly small. The larger the \(n\), the larger the \(T_m\) depression, approaching to the curves for the random type models. The conformational contribution to the melting point depression of copolymers is correlated with the sequential probability of crystallizable unit in a chain as functions of number and length of sequences of major component units.

1. INTRODUCTION

For many random copolymers, the melting temperature \(T_m\) from Flory's theory\(^1\) is higher than the experimental values. This tendency is especially significant for nylon and polyester copolymers\(^2-8\). The conflict on this apparent discrepancy was already resolved by considering the quasi-crystals in the amorphous regions\(^2\). After that, the modified Flory's theory has been expanded to the melting of copolymers with various configurations\(^9\).

In this paper, on the basis of the modified Flory's theory\(^9\), the relationships between the \(T_m\) and the composition for the rotational isomeric states (RIS) models\(^10\) of atactic polypropylene (a-PP), ethylene/propylene (E/P) and propylene/ethylene (P/E) copolymers of \((A-B)_n\) and random types are investigated under the particular attention to the conformational contribution on melting point depression. a-PP may be treated as a binary copolymer composed of meso and racemi units\(^7\).

2. THEORETICAL AND DISCUSSIONS

The new proposal of equation (1) on the probability \(p_c\) of continuation from a crystallizable unit \(A'\) to the next unit \(A'\) in a copolymer chain progressed the study on the melting point depression of binary copolymers\(^9\).

\[
p_c = \frac{p_{cR}}{p_{cB}} = \left(\frac{X_A}{X_B}\right)^{1/\alpha} \frac{1}{\frac{1}{p_{cR}} + \frac{1}{p_{cB}}} \quad (1)
\]

where \(\alpha (\equiv \text{crystal length } \zeta)\) is a constant relating to the number and the mean length of blocks composed of crystallizable units (described below), \(p_{cR} = \frac{X_A}{X_B}\) and \(p_{cB}\) are \(p_c\) for a random copolymer \((\alpha/\zeta = 1)\) and an \(A-B\) type block copolymer \((\alpha/\zeta = 0)\), respectively and \(X_A\) is the structural mole fraction of major component unit \(A'\). By using equation (1), the relationship between the \(T_m\) and the composition for the binary copolymers with various configurations is derived as

\[
\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{2h_A - h_A'} \ln \frac{X_A}{X_B} \frac{p_{cR}}{p_{cB}}  \quad (2)
\]

with

\[
h_A' = h_A + \frac{2\alpha}{\zeta} ,
\]
where \( T_m \) is the melting temperature of a copolymer, \( T_m^0 \) is that of a homopolymer consisting of major component, \( h_u \) is the heat of fusion per molar structural unit of major component, \( h_x \) is the heat of transition per molar structural unit due to quasi-crystals in the amorphous regions, \( \sigma_e \) is the molar surface free energy at the ends of a crystal and \( R \) is the gas constant. When \( T_m \) is almost equal to the equilibrium melting temperature \( T_m^* \) of a copolymer, \( 2\sigma_e/\zeta \approx 0 \), i.e., \( h_x \approx h_u \) may be obtained, according to the well-known equation (3).

\[
\frac{2\sigma_e}{\zeta} = h_u \left( 1 - \frac{T_m}{T_m^*} \right) \tag{3}
\]

From the equation (2) with \( 2\sigma_e/\zeta \approx 0 \), the free energy of transition \( f_x \) per molar structural unit due to quasi-crystals in the amorphous regions is given as

\[
f_x = \frac{a}{\zeta} f_R + (1 - \frac{a}{\zeta}) f_B + RT_m \frac{\alpha}{\zeta} \left( 1 - \frac{\alpha}{\zeta} \right) \ln \frac{X_A}{P_B} \tag{4}
\]

where \( f_R \) and \( f_B \) are \( f_x \)'s for a random copolymer \((\alpha/\zeta = 1)\) and an A-B type block copolymer \((\alpha/\zeta = 0)\). In the \( f_x \) in equation (4) with \( \alpha/\zeta \approx 0 \) and 1, the interaction free energy difference \( -\frac{a}{\zeta} \left( 1 - \frac{\alpha}{\zeta} \right) \)

\((f_x - f_B)\) inevitable for copolymers with blocks of units should be contained, as understood from

\[
RT_m (X_A/P_B) = (1/2)(f_R - f_B).
\]

\( f_k \) is the interaction free energy per molar structural unit in the amorphous regions without the quasi-crystals. When \( \alpha/\zeta = 0 \) and 1, \( f_k = f_x \) (subscript \( x \) is B or R). The energy of each free energy \( f (f_x, f_R, \text{and} f_B) \) in equation (4) to the conformational contribution \( f^e \) and the intermolecular contribution \( f^v \) leads to the following relation.

\[
f_x = \frac{a}{\zeta} f_R + (1 - \frac{a}{\zeta}) f_B + RT_m \frac{\alpha}{\zeta} \left( 1 - \frac{\alpha}{\zeta} \right) \ln \frac{X_A}{P_B} \tag{5}
\]

if the first term of the right hand side in equation (5) is taken as zero, the next relation is obtained.

\[
f_x = \frac{a}{\zeta} f_R + (1 - \frac{a}{\zeta}) f_B \text{ or } \frac{a}{\zeta} = \frac{f_x - f_R}{f_B - f_R} \tag{6}
\]

The conformational free energy \( f^e \left( = h^e - Ts^e \right) \) \( (f^e, f^v_R \text{and} f^v_B) \) may be calculated by

\[
h^e = (RT^e \frac{d \ln Z}{d T^e}) x^{-1} \tag{7}
\]

and

\[
s^e = (RT \ln Z + RT \frac{d \ln Z}{d T}) x^{-1} \tag{8}
\]

where \( h^e \) and \( s^e \) are the conformational enthalpy and the entropy per molar structural unit, \( Z \) is the conformational partition function for a copolymer and \( x \) is the degree of polymerization.

Figure 1 shows the relationship between the \( P_c \) from equation (1) with (6) and \( P_c \left( = 1 - 1/y \right) \) \((y: \text{sequence length composed of major component units})\) for RIS models of a-PP. For a-PP, the values of \( P_c \) from equation (1) with (6) are a little smaller than \( P_c \left( = 1 - 1/y \right) \). The difference between the both values of \( P_c \) increased in proportion to the \( 1 - P_c \left( = 1 - 1/y \right) \). According to this result, the equation (6) should be revised for a-PP.

Figure 2 shows the relationship between \( f^e - ((\alpha/\zeta)f_R^e + (1 - \alpha/\zeta)f_B^e) \) and \( P_c \left( = 1 - 1/y \right) \) for a-PP. With increasing \( 1 - P_c \left( = 1 - 1/y \right) \), the \( f^e - ((\alpha/\zeta)f_R^e + (1 - \alpha/\zeta)f_B^e) \) increased linearly. Its cause may
be contributed to the intramolecular interaction between the neighboring meso and racemi units at a turning point of sequences, because of \( Q = 2X_A(1-\rho) \), where \( Q \) is the number of turning points of sequences. Such tendency is small for E/P copolymers\(^8\). Substituting the \( \frac{f^e_* - \left( \frac{\alpha}{\zeta} f^e_{\text{R}} \right)}{f^e_{\text{B}} - f^e_{\text{R}}} \) for \( e(Q) \) as a function of \( Q \), \( \frac{\alpha}{\zeta} \) is represented by

\[
\frac{\alpha}{\zeta} = \frac{f^e_* - \left( \frac{\alpha}{\zeta} e(Q) \right)}{f^e_{\text{B}} - f^e_{\text{R}}} \tag{9}
\]

The composition dependence of the \( T_m \) depression is investigated for the RIS models of a-PP, E/P and P/E copolymers with \( x = 100 \). Each model has a relation of \((y + z)n = 100\), where \( y \) is the sequence length of major component, \( z \) is the sequence length of minor component and \( n \) is a number of alternating repetition of major and minor component sequences. Figures 3 and 4 show the relationships between \( T_m \) and \( 1-X_A \) for the RIS models of a-PP, E/P and P/E copolymers with \( n = 1, 2 \) and \( 5 \), and of random type. For these models, the common characters are found in the \( T_m \) vs. \( 1-X_A \) curves. For models with \( n = 1 \), the depression of \( T_m \) is negligibly small in the range of \( X_A > 0.5 \). The larger the \( n \), the larger the \( T_m \) depression, approaching to the curves of random type models, where the curves for E/P copolymers in Figure 4 were taken from ref. 9.

![Fig. 3 Relation between \( T_m \) and composition \((1-X_A)\) for the models of a-PP with \( x = 100 \). a: \( n = 1 \), b: \( n = 2 \), c: \( n = 5 \) and d: random. Major component; ----- : meso unit, ------ : racemi unit.](image1)

![Fig. 4 Relation between \( T_m \) and composition \((1-X_A)\) for the models of E/P and P/E copolymers with \( x = 100 \). a: \( n = 1 \), b: \( n = 2 \), c: \( n = 5 \) and d: random. Major component; ----- : E unit, ------ : P unit. The curves for E/P copolymers were taken from ref. 9.](image2)

P.S.: Numerical calculations in this paper were carried out on the HITAC M-240H computer at the computer center of Gunma University.

REFERENCES

(A-B)_n 型コンフィギュレーションをもつアタックックポリ
プロピレンおよびプロピレン-エチレン共重合体の融点予測

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共重合体の融解の拡張フローリ式を用いて、アタックックポリプロピレン (a-PP), E/P および P/E 共重合体の RIS モデルについて、融解温度と組成の関係を調べた。a-PP は、メソ単位とラセミ単位からなる二成分系
共重合体とみなされた。これらのモデルの融点降下におよぼすコンホメーション寄与は、主成分単位の連鎖の長さの関数である主成分単位の連続確率関係していること
とが示された。いずれのモデルについても、融点降下は、A-B 型では小さく、また、(A-B)_n 型 (n > 1) (n はくり返し数) では、n の增加とともに増大し、T_m は、ラン
ダム型モデルの T_m - 組成曲線に近づいていく。