Polymer 42 (2001) 8285–8288

polymer

www.elsevier.nl/locate/polymer

Studies on the minimum crystallizable sequence length of semicrystalline copolymers

Huijun Luo[a,b], Qun Chen[a,*], Guang Yang[a]

[a]*Analytical Center and The Key Laboratory of Education Ministry for Optical and Magnetic Resonance Spectroscopy, East China Normal University, Shanghai 200062, People's Republic of China*
[b]*Analytical Center, East China University of Science and Technology, Shanghai 200237, People's Republic of China*

Received 20 November 2000; received in revised form 19 February 2001; accepted 13 March 2001

Abstract

A novel method for determining the minimum crystallizable sequence length, ζ^*, of the semicrystalline copolymers was proposed recently. By applying it to several semicrystalline copolymer systems, the general applicability of the method was tested. The value of ζ^* was found to be dependent on the crystallization conditions and the size of the comonomer unit. The rationality of the present method comparing with that of Burfield's was demonstrated. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Semicrystalline copolymer; Minimum crystallizable sequence length; Comonomer units

1. Introduction

It is well known that the properties of semicrystalline copolymers depend greatly on the phase structures of the sample. For a copolymer constituted by one crystallizable monomer unit (c-unit) and one noncrystallizable monomer unit (nc-unit), the phase structures are closely associated with the relative contents and the sequence distribution of two monomer units in the copolymer sample. One reason for such a characteristic is, as suggested firstly by Flory [1], that there exists a minimum crystallizable sequence length ζ^* (counted with the number of the c-unit) at certain temperature. Only c-unit sequence equal to or longer than ζ^* can participate in crystallization. It has been recognized since then that ζ^* is one of the key parameters for establishing the quantitative correlation between the phase structure and chain structure of semicrystalline copolymers [2].

Several methods of estimating ζ^* were individually suggested by Natta [3], Jackson [4], Killian [5], Randall [6] and Burfield [7,8] in the studies with ethylene copolymers and LLDPE, where the c-unit is ethylene and the comonomer unit is assumed as unable to enter the crystalline region. The value of ζ^* obtained by them falls into the range from 4 to about 18 ethylene units and is believed to be a constant for copolymers crystallized under similar conditions. Among these methods, Burfield proposed the most applicable one. In his works, the enthalpy of fusion of a random ethylene copolymer, ΔH_m, is assumed to be related to the mole content of ethylene unit (P_E) by the relationship

$$\Delta H_m = kP_E^{\zeta^*}$$

where k is a constant related to the enthalpy of fusion of the parent homopolymer and is affected by the factors as molecular weight, molecular weight distribution, thermal history of the samples and so on. His assumption is supported by the linear relationship between the $\log(\Delta H_m)$ and the $\log(P_E)$ of several series of ethylene copolymer samples with different structure and different content of comonomers. ζ^* can then be attained directly from the slope of the straight line. Such a methodology has an obvious shortcoming as no clear physical meaning of the formula and the constant k can be visualized.

Recently, in studying the influence of chain structure on the crystalline structure of a series of ethylene–dimethylaminoethylmethacrylate (EDAM) copolymers [9], we suggested a new method for determining ζ^*. By introducing a new parameter, X'_c, which represents the degree of crystallinity of ethylene sequences equal to or longer than ζ^*, a quantitative relationship between the degree of crystallinity

---

* Corresponding author. Tel.: +86-21-62232494; fax: +86-21-62576217.

E-mail address: ac1@ecnu.edu.cn (Q. Chen).

PII: S0032-3861(01)00327-5

and ζ^* was established without introducing any assumptions as Eq. (1):

$$X_c = \frac{X'_c \sum_{n \geq \zeta^*}^{\infty} nf(n)}{\sum_{n=1}^{\infty} nf(n)/C\%} \tag{1}$$

where X_c represents the degree of crystallinity in its common meaning, $C\%$ denotes the overall weight fraction of c-units in the copolymer, $f(n)$ is the molar percentage of the c-unit sequences with a given length n in all kinds of c-unit sequences. It is obvious that the numerator of the right-hand side of Eq. (1) corresponds to the weight of the crystalline region and the denominator to the total weight of the sample. For random or first Markov chain copolymers, $f(n)$ can be expressed as

$$f(n) = p^{n-1}(1-p) \tag{2}$$

where p corresponds to the mole fraction of c-unit for random copolymers and to the conditional probability of the c-unit for copolymers with first-order Markov distribution. Eq. (1) can then be simplified as

$$X_c = X'_c C\% p^{\zeta^*-1}[\zeta^*(1-p)+p] \tag{3}$$

and then

$$X'_c = X_c/C\% p^{\zeta^*-1}[\zeta^*(1-p)+p] \tag{4}$$

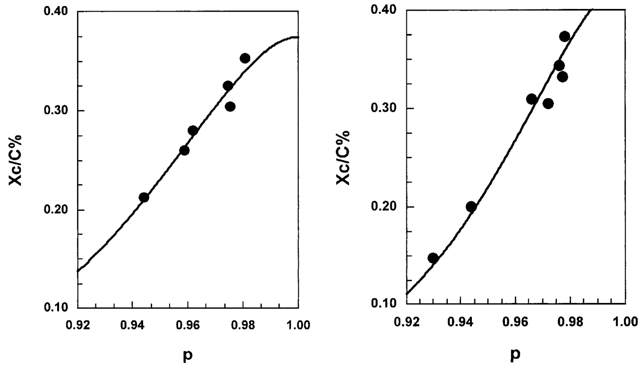
Because X_c, $C\%$ and p are experimentally measurable, a plot of X'_c against ζ^* can be drawn. For a set of copolymers crystallized under similar conditions, it is reasonable to assume that X'_c is a constant. If such an assumption is correct, curves of X'_c against ζ^* for copolymers in the set should converge. In our previous work, we have demonstrated that the curves of X'_c against ζ^* for most EDAM samples do intersect at the same point, indicating the correctness of the assumption. From the x- and y-coordinates of the cross-point, X'_c and ζ^* are obtained as 70% and 25 ethylene units for EDAM samples. The value of ζ^* is obviously larger than the previously reported data [3–8] and is close to the value expected from Flory's equilibrium theory [1,2]. Such a value is also comparable to the least lamellar thickness observed by TEM [9,10].

In this approach, by making further analysis on some published data, we aim to testify the general applicability of the above methodology, to discuss the factors which may have influence on the value of ζ^* and to make comparison with Burfield's method.

2. Results and discussion

2.1. Calculations according to the published data

As introduced above, in our previous work, the procedure of getting ζ^* and X'_c is to plot curves of X'_c against ζ^* for samples with different comonomer content and then to acquire the value of ζ^* and X'_c from the x- and y-coordinates of the cross-point of the curves. In this work, we introduce an equivalent manipulation procedure, which is easier to operate comparing with the previous one. Fig. 1a and b shows the plots of $X_c/C\%$ against the mole fraction of ethylene unit of a series of ethylene–butene (EB) and a series of ethylene–hexene (EH) copolymers with molecular weights ranging from 53 000 to 125 000 and from 488 000 to 69 400, respectively. Both series of samples were all melt-quenched at −78°C. The experimental data of X_c, $C\%$ and the mole fraction of ethylene unit were reported by Kennedy et al. [11]. The sequence distribution of these two copolymer series are random and therefore the mole fraction of ethylene unit equals to p in Eq. (3). The real lines in Fig. 1a and b correspond to the fitting results of Eq. (3), by assuming the constancy of ζ^* and X'_c. It is obvious that the fitting results agree well with the experiment data, yielding ζ^* of 26 ethylene units and X'_c of 0.37 for EB and ζ^* of 32 ethylene units and X'_c of 0.43 for EH. The larger ζ^* of EH comparing with that of EB indicates that larger side group may lead to larger critical crystallizable sequence length for copolymers crystallized under similar conditions. Such kind of factor has been inappropriately omitted in previous works. The values of ζ^* for EB and EH are larger than that of EDAM samples, suggesting that during the short period of melt-quenching, only long ethylene sequences with higher crystallization ability can participate in the crystallization. The large value of ζ^* is one of the causes of low crystallinity values of the melt-quenched ethylene copolymer samples.



(a) (b)

Fig. 1. Plots of $X_c/C\%$ against the mole fraction of ethylene unit (p): (a) for EB copolymers; (b) for EH copolymers.

Although the opinion that for random copolymers, the degree of crystallinity is constant with molecular weight had prevailed for many years, a comprehensive study of the crystallization kinetics of random ethylene copolymers recently reported by Alamo et al. [12] revealed clearly that the molecular weight does influence the crystallization behavior and the degree of crystallinity of random copolymers to a certain extent. For this reason, EB and EH samples

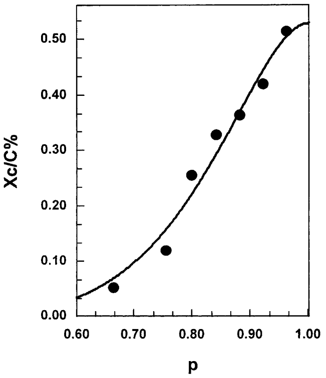


Fig. 2. Plot of $X_c/C\%$ against the mole fraction of ethylene oxide unit (p) for ethylene oxide/propylene oxide copolymers.

with similar molecular weight were chosen for the above calculation.

A similar calculation based on published data has also been made for a series of random ethylene oxide/propylene oxide copolymers with different comonomer contents [13]. The crystallinities were measured by wide-angle X-ray scattering. Fig. 2 shows the plot of $X_c/C\%$ against the mole fraction of ethylene oxide and the fitting result (the real line) according to Eq. (3). The agreement between the experimental data and the fitting results shows the general applicability of our methodology. The ζ^* value of nine ethylene oxide units and X'_c of 0.53 were obtained. By considering the bigger size of the ethylene oxide comparing with ethylene unit, the relative small value of ζ^* of this series of copolymer is acceptable.

It is worthy to point out that as the values of the degree of crystallinity influence greatly the value of ζ^*, for a same series of copolymers, calculations based on the data of crystallinity measured by different methods may lead to different results for both ζ^* and X'_c.

2.2. Comparison with Burfield's method

It is evident that when p is close to 1, or in other words, when the content of nc-unit is very low, Eq. (3) can be further simplified as

$$X_c = X'_c C\% p^{\zeta^*} \tag{5}$$

It has obviously the same style as Burfield's equation. As the establishment of Eq. (3) has introduced no assumption and no approximation, it can be understood then that Burfield's equation is an approximation of Eq. (3) and could be correct only when p is close to 1. Because the enthalpy of fusion ΔH_m in Burfield's equation corresponds to experimentally determined enthalpy of fusion divided by $C\%$, the constant k in his equation, thus equals to X'_c multiplied by the enthalpy of fusion of the parent homopolymer of c-unit. Therefore, it can be said that k is related to the degree of crystallinity of c-unit sequence equal to or longer than ζ^*.

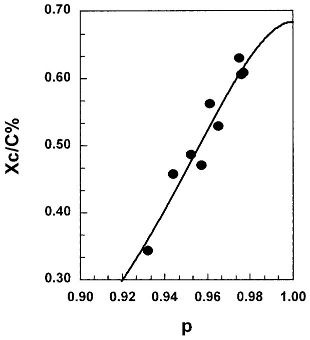


Fig. 3. Plot of $X_c/C\%$ against the mole fraction of ethylene unit (p) for ethylene–propylene, EB and ethylene–4-methyl-1-pentene copolymers.

Fig. 3 shows the curve of $X_c/C\%$ versus p for random ethylene copolymers with propylene, 1-butene or 4-methyl-1-pentene comonomer units, which possess the similar molecular weight, i.e. 1×10^4–2×10^4 and were crystallized at ambient temperature [7,8]. The data of this series of copolymers had been employed in Burfield's calculation. The value of ζ^* obtained by Burfield is 14 ethylene units. For the purpose of comparison, computer fitting according to Eq. (3) was made on this series of data (real line). ζ^* of 23 ethylene units and X'_c of 0.694 were obtained. Both values are close to those of EDAM and the value of ζ^* is much higher than that obtained by Burfield. In fact, the degree of crystallinity of a copolymer is not only determined by the critical crystallizable sequences, but also by the distribution of crystallizable sequences. However, the effect of sequence distribution is not considered in Burfield's equation. This is the reason, we believe, the underestimation of ζ^* in Burfield's work.

3. Conclusions

A novel method for determining the minimum crystallizable sequence length, ζ^*, was established. The general applicability of the method was demonstrated by applying it to several semicrystalline copolymer systems with different nc-unit size and different crystallization condition. The value ζ^* was found to be dependent on the crystallization conditions and the size of the nc-unit. The previously suggested method of acquiring ζ^* by Burfield was demonstrated to be a simplification of present method and could lead to reliable results only when the mole content of the c-unit is close to 1.

Acknowledgements

This work is supported by the KUASHIJI RENCAI foundation of Education Ministry of China and by QIMINGXING project of the Committee of Science and Technology of Shanghai Municipality.

References

[1] Flory PJ. Trans Faraday Soc 1955;51:848–57.
[2] Domszy RC, Alamo R, Mathieu PJM, Mandelkern L. J Polym Sci, Polym Phys Ed 1984;22:1727–44.
[3] Natta G, Mazzanti G, Valvassori A, Sartori G, Morero D. Chim Ind (Milan) 1960;42:125.
[4] Jackson JF. J Polym Sci, Part A 1963;1:2119–26.
[5] Killian HG. Kolloid-Z 1963;189:23–36.
[6] Randall JC, Ruff CJ. Macromolecules 1988;21:3446–54.
[7] Burfield DR. Macromolecules 1987;20:3020–3.
[8] Burfield DR, Kashiwa N. Makromol Chem 1985;186:2657–62.
[9] Chen Q, Luo HJ, Yang G, Xu DF. Polymer 1997;38:1203–5.
[10] Luo HJ, Chen Q, Yang G, Xu DF. Polymer 1998;39:943–7.
[11] Kennedy MA, Peacock AJ, Failla MD, Lucas JC, Mandelkern L. Macromolecules 1995;28:1407–21.
[12] Alamo RG, Mandelkern L. Macromolecules 1991;24:6480–93.
[13] Yao N, Li X, Li Y, Nu X, Xie H. Eur Polym J 1992;28:831–4.