(2) Zeldin, M.; Wynne, K. J.; Allcock, H. R. *Inorganic and Organometallic Polymers*; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1987.
(3) Allcock, H. R. *Chem. Eng. News* **1985** *63* (Mar 18), 22.
(4) Allcock, H. R.; Brennan, D. J.; Allen, R. W. *Macromolecules* **1985**, *18*, 139.
(5) Allcock, H. R.; Brennan, D. J.; Graaskamp, J. M.; Parvez, M. *Organometallics* **1986**, *5*, 2434.
(6) Allcock, H. R.; Brennan, D. J.; Graaskamp, J. M. *Macromolecules* **1988**, *21*, 1.
(7) Allcock, H. R.; Brennan, D. J.; Dunn, B. S.; Parvez, M. *Inorg. Chem.* **1988**, *27*, 3226.
(8) Allcock, H. R.; Brennan, D. J. *J. Organomet. Chem.* **1988**, *341*, 231.
(9) Allcock, H. R.; Brennan, D. J.; Dunn, B. S. *Macromolecules*, in press.
(10) Wisian-Neilson, P.; Ford, R. R.; Neilson, R. H.; Roy, A. K. *Macromolecules* **1986**, *18*, 2091.
(11) Evans, T. L.; Fuller, T. J.; Allcock, H. R. *J. Am. Chem. Soc.* **1979**, *101*, 242.
(12) Allcock, H. R.; Evans, T. L.; Fuller, T. J. *Inorg. Chem.* **1980**, *19*, 1026.
(13) Allcock, H. R.; Fuller, T. J.; Evans, T. L. *Macromolecules* **1980**, *13*, 1325.
(14) Allcock, H. R.; Lavin, K. D.; Tollefson, N. M.; Evans, T. L. *Organometallics* **1983**, *2*, 267.
(15) Allcock, H. R. *Acc. Chem. Res.* **1979**, *12*, 351.
(16) Allcock, H. R.; Kwon, S.; Riding, G. H.; Fitzpatrick, R. J.; Bennett, J. L. *Biomaterials* **1988**, *9*, 509.
(17) Babic, D.; Souverain, D. M.; Stannett, V. T.; Squire, D. R.; Hagnauer, G. L.; Singler, R. E. *Int. J. Radiat. Appl. Instrum., Part C* **1986**, *28*, 169.
(18) Boileau, S. In *Ring Opening Polymerization*; McGrath, J. E., Ed.; ACS Symposium Series 286; American Chemical Society: Washington, DC, 1985; Chapter 2, pp 23-37.
(19) Wright, P. V. In *Ring-Opening Polymerization*; Ivin, K. J., Saegusa, T., Eds.; Elsevier: Amsterdam, 1985; Vol. 1, Chapter 14.
(20) Frye, C. L.; Salinger, R. M. *J. Org. Chem.* **1970**, *35*, 1308.
(21) However, polymer that retained some solvent did redissolve. Hence, purification by reprecipitation was possible.
(22) Exenrod, T. *NMR of Nuclei Other Than Proton*; Wiley: New York, 1974; Chapter 17.
(23) Silverstein, R. M.; Bassler, G. C.; Morril, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley Scientific: New York, 1981; Chapter 5, p 249.
(24) ^{29}Si NMR spectra of **15** contained four major signals at +7.5, −2.6, −20.6, and −20.9 ppm. A similar signal, corresponding to a siloxane cross-link, was detected at −21.7 ppm.
(25) Grignon-Dubois, M.; Laguerre, M.; Barbe, B.; Petraud, M. *Organometallics* **1984**, *3*, 1060.

Dependence of Miscibility on Copolymer Composition for Blends of Poly(vinyl chloride-*co*-vinyl acetate) and Poly(*n*-butyl methacrylate-*co*-isobutyl methacrylate)

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ABSTRACT: It has been so far reported that some polymer blends containing random copolymers can be miscible in a certain range of copolymer compositions even though the combinations of their corresponding homopolymers are immiscible. On the other hand, according to theory, there may exist some copolymer blends that are immiscible in a certain range of copolymer compositions even though their corresponding homopolymers are miscible with each other. For real blends with a possibility of such an immiscibility region, the dependence of miscibility on the copolymer composition was observed at the blend ratio 1/1. Poly(vinyl chloride-*co*-vinyl acetate) copolymers (VC·VAc) were immiscible with poly(*n*-butyl methacrylate-*co*-isobutyl methacrylate) copolymers (nBMA·iBMA) in a certain range of copolymer compositions of nBMA·iBMA, though every pair of VC·VAc copolymer/nBMA homopolymer, VC·VAc copolymer/iBMA homopolymer, and nBMA homopolymer/iBMA homopolymer was miscible.

Introduction

Recently, it has been demonstrated[1-4] that polymer blends containing random copolymers can be miscible in a certain range of copolymer compositions even though the combinations of their corresponding homopolymers are immiscible. Kambour et al.,[3] Paul and Barlow,[5] and ten Brinke et al.[6] explained such a miscibility, which is called a "miscibility window", by expressing the Flory–Huggins intermolecular interaction parameter, χ, in terms of the respective intersegmental parameters, χ_{ij}.[7] Shiomi et al.[4] showed various theoretical patterns of dependence of miscibility on the copolymer composition (miscibility map) for the copolymer blends having a common monomer, and they reported some experimental results corresponding to the theoretical miscibility maps.

The dependence of miscibility on the copolymer composition has been interpreted as follows.[3,5,6] For a mixture of two general random copolymers, **1** ($[(A1)_{x_1}(A2)_{x_2}\cdots(Am)_{x_m}]_{r_1}$) and **2** ($[(B1)_{y_1}(B2)_{y_2}\cdots(Bn)_{y_n}]_{r_2}$), we can write the interaction parameter, χ, per segment between copolymers **1** and **2** as

$$\chi = \sum_{i=1}^{m}\sum_{j=1}^{n} x_i y_j \chi_{AiBj} - \sum_{i=1}^{m-1}\sum_{j=i+1}^{m} x_i x_j \chi_{AiAj} - \sum_{i=1}^{n-1}\sum_{j=i+1}^{n} y_i y_j \chi_{BiBj} \quad (1)$$

where χ_{AiBj}, etc., are the segmental interaction parameters between the different segments Ai and Bj, etc., respectively, and x_i and y_j are the copolymer compositions expressed as the volume fraction for copolymers **1** and **2**, respectively. When the intermolecular χ at a certain temperature is smaller than that at the critical point, χ_{crit}, that is,

$$\chi < \chi_{crit} \quad (2)$$

two polymers are miscible with each other at that temperature, while they are immiscible when

$$\chi > \chi_{crit} \quad (3)$$

According to the Flory–Huggins theory, χ_{crit} is given by

$$\chi_{crit} = 1/2(r_1^{-1/2} + r_2^{-1/2})^2 \quad (4)$$

where r_1 and r_2 are the numbers of segments for polymers **1** and **2**, respectively, when the segment is taken to be of

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Table I
Copolymer Compositions and Molecular Weights[a] for Poly(vinyl chloride-*co*-vinyl acetate)

sample	source[b]	VC content, wt %	VC content, mol %	$10^{-5}\bar{M}_w$	$10^{-5}\bar{M}_n$
PVC-1	A			1.5	0.84
PVC-2	A			2.8	1.0
VC·VAc-97.5	B	97.5	98.2	1.6	0.94
VC·VAc-90	B	90.0	92.5	0.91	0.43
VC·VAc-87	B	87.0	90.2	0.26	0.13
VC·VAc-81	B	81.0[c]	85.4[c]	0.37	0.23

[a] Determined by GPC measurement. [b] Source: A, Shin-Etsu Chemical Co., Ltd.; B, Scientific Polymer Products Inc. [c] Including 2 wt % maleic acid.

equal volume between the two polymers. Equation 4 gives $\chi_{crit} = 0$ when the molecular weights of both polymers are infinite. Therefore, even though all the segmental interactions, χ_{ij}, are positive, i.e., all the combinations of the corresponding homopolymers are miscible, there is a possibility that χ expressed by eq 4 may satisfy $\chi < \chi_{crit}$ or $\chi < 0$ in a certain range of the copolymer composition. Such a miscibility window may occur when χ_{ij}'s for pairs of different monomer segments in the same copolymer are significantly large, namely due to the "repulsion effect".[5,6]

According to eq 1, on the other hand, the intermolecular χ can be positive even though all χ_{ij}'s are negative. Then the copolymer blends may have an immiscibility region (immiscibility window) with respect to the copolymer composition even though the combinations of the corresponding homopolymers are miscible. A real system in which all χ_{ij}'s may be negative was first reported by Fernandes et al.[8] They showed that miscibility for the poly(epichlorohydrin-*co*-ethylene oxide)/poly(methyl methacrylate) (ECH·EO/PMMA) blend, in which every combination of the homopolymers corresponding to their constituent monomers was miscible, was less than that for homopolymer blends of either ECH/PMMA or EO/PMMA. In this paper we will present the dependence of miscibility on the copolymer composition for such a blend.

Experimental Section

The characteristics of poly(vinyl chloride-*co*-vinyl acetate) (VC·VAc) and poly(vinyl chloride) (PVC) are shown in Table I. The PVC homopolymers were supplied by Shin-Etsu Chemical Co., Ltd. (Tokyo, Japan), and the VC·VAc copolymers were purchased from Scientific Polymer Products, Inc. (Ontario, NY). In Table I, the vinyl chloride contents in VC·VAc are nominal, and the respective molecular weights were determined by GPC using polystyrene standards. Table II shows the characteristics of poly(*n*-butyl methacrylate) (PnBMA), poly(isobutyl methacrylate) (PiBMA), and their copolymers (nBMA·iBMA). The PiBMA homopolymer was purchased from Aldrich Chemical Co., Inc. (Milwaukee, WI), and other polymers were synthesized by radical polymerization in the bulk at 80 °C using AIBN as an initiator (conversion, 20–30%). In the copolymerization of each copolymer, the composition of the resulting copolymer was almost the same as that of the feed monomer mixture. The copolymer composition and tacticity were determined by ^{1}H NMR (270-MHz) and ^{13}C NMR (67.8-MHz) measurements, respectively, using the JEOL JNM-GX270 NMR apparatus.

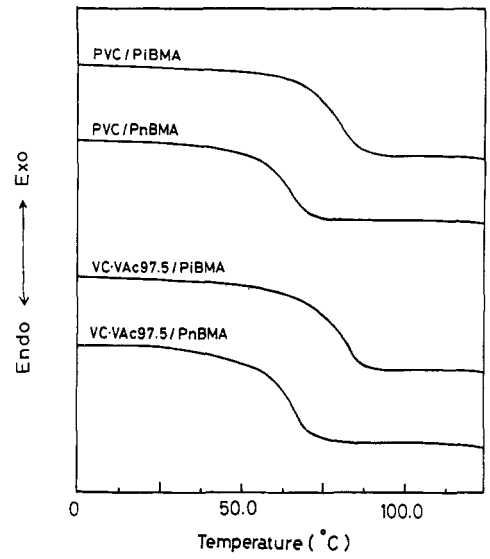

Figure 1. DSC thermograms for the blends of PVC/PiBMA, PVC/PnBMA, VC·VAc-97.5/PiBMA, and VC·VAc-97.5/PnBMA annealed at 180 °C.

All blends were prepared by casting from a common solvent, THF. The two constituent polymers were dissolved in the solvent (5 wt %) at a blend ratio of 1/1 by weight. All the solutions were clear. The solvent was allowed to evaporate at room temperature, and the resulting film was dried in vacuo for at least 3 days at 60 °C. The compatibility of the blends were determined by observations of one or two glass transition temperatures with DSC (SEIKO I & E Ltd., DSC 20 with SSC/580 thermal controller and data system). The samples were annealed for 2 h at the desired temperature in the DSC apparatus and then were rapidly cooled to an initial temperature of scanning. The heating rate was 20 °C/min for all the samples, and the sample sizes were about 20 mg for the blends and about 10 mg for the pure polymers.

Results and Discussion

Figure 1 shows the DSC thermograms for the blends of PVC/PnBMA, PVC/PiBMA, VC·VAc-97.5/PnBMA, and VC·VAc-97.5/PiBMA annealed at 180 °C. These blends did not show the double glass transition temperatures at least up to this temperature. Also, both PVC and VC·VAc-97.5 were miscible with a series of the nBMA·iBMA copolymer at all the annealing temperatures investigated here. As in the examples shown in Figure 2, on the other hand, every blend of a series of nBMA·iBMA with VC·VAc-90, -87, and -81 changed from miscibile to immiscibile with increasing temperature. This suggests that these systems are LCST types.

In Figure 3 are shown the thermograms for the PiBMA homopolymer, PnBMA homopolymer, VC·VAc-90 copolymer, and their blends annealed at 130 °C. The thermograms for three kinds of blends suggest that these blends are miscible at this temperature. Particularly, the

Table II
Copolymer Compositions,[a] Molecular Weights,[b] and Tacticities[c] for Poly(*n*-butyl methacrylate-*co*-isobutyl methacrylate)

sample	iBMA content, wt %	$10^{-5}\bar{M}_w$	$10^{-5}\bar{M}_n$	triad tacticity, % mm	mr	rr
PnBMA	0.0	1.9	0.72	4.6	35.2	60.2
nBMA·iBMA-12.7	12.7	1.8	0.48			
nBMA·iBMA-25.2	25.2	1.9	0.75			
nBMA·iBMA-47.1	47.1	1.5	0.69	5.7	36.4	57.9
nBMA·iBMA-71.4	71.4	1.9	0.77			
PiBMA[d]	100.0	3.0	1.4	4.0	32.0	64.0

[a] Determined by ^{1}H NMR (270-MHz) measurement in $CDCl_3$. [b] Determined by GPC measurement. [c] Determined by ^{13}C NMR (67.8-MHz) measurement in $C_6D_5NO_2$. [d] Purchased from Aldrich Chemical Co., Inc.

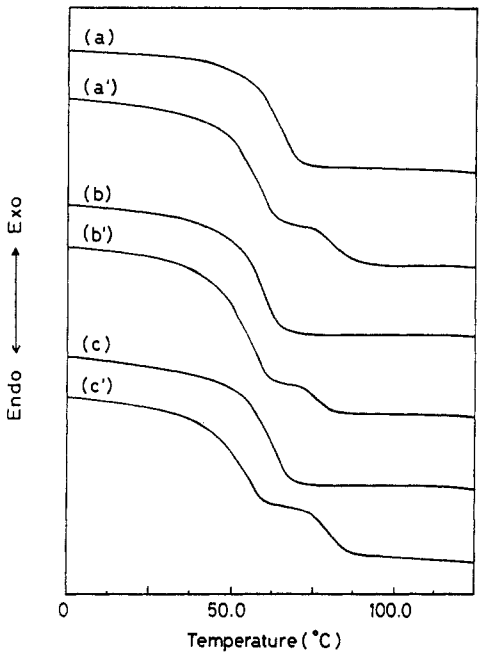

Figure 2. DSC thermograms for blends of nBMA·iBMA-25.2 with VC·VAc. VAc content in VC·VAc: (a, a') 10 wt %, (b, b') 13 wt %, (c, c') 19 wt %. The samples a, b, and c were annealed at 130 °C and the samples a', b', and c' at 180 °C.

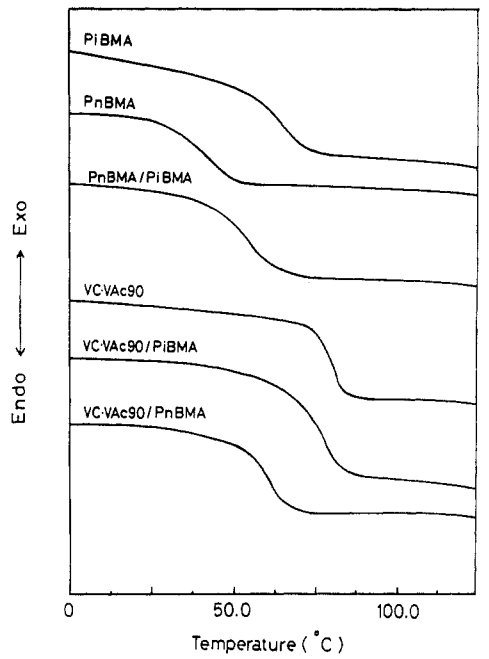

Figure 3. DSC thermograms for VC·VAc-90, PnBMA, and PiBMA and for their combinations. All the samples were annealed at 130 °C.

film of the PnBMA/PiBMA blend remained clear up to the temperature (ca. 230 °C) at which the blend became brown. Here, if the VC·VAc copolymers can be regarded as a homopolymer consisting of a monomer with characteristics averaged with respect to those of the vinyl chloride and vinyl acetate monomers, then every binary combination of the three "homopolymers" of iBMA, nBMA, and VC·VAc is miscible at 130 °C.

The temperature dependences of the miscibility for the blends of VC·VAc-90, -87, and -81 with a series of nBMA·iBMA are summarized as a function of the copolymer composition of nBMA·iBMA in Figures 4–6, respectively. In these figures, the circles indicate miscibility or immiscibility obtained by observing the glass transition

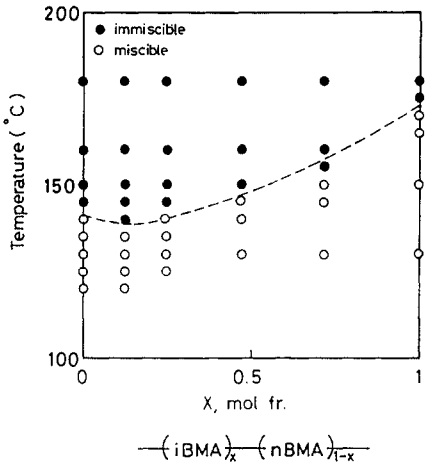

Figure 4. Compatibility for the nBMA·iBMA/VC·VAc-90 blends. The VC content in VC·VAc is 90 wt %.

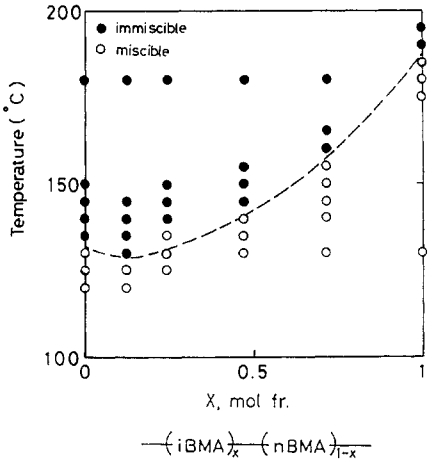

Figure 5. Compatibility for the nBMA·iBMA/VC·VAc blends. The VC content in VC·VAc is 87 wt %.

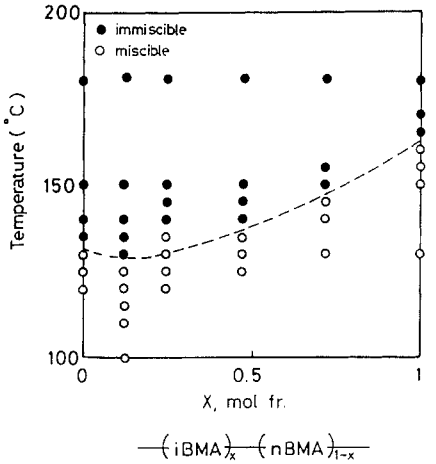

Figure 6. Compatibility for the nBMA·iBMA/VC·VAc blends. The VC content in VC·VAc is 81 wt %.

temperatures for the samples annealed at the respective temperatures. As seen in these figures, the experimental boundary line has a minimum for all the systems; there may exist an immisibility region with respect to the copolymer composition at the temperature corresponding to the minimum point even though any combinations of the corresponding *homopolymers* are miscible. These immiscibility regions for the present systems may not have been caused by the effects of either molecular weight or tacticity, which are important factors for miscibility. As shown in Table II, the molecular weight of the nBMA·

iBMA-12.7 copolymer, at whose copolymer composition a minimum point appears, is smaller than those of the two copolymers neighboring with respect to the copolymer composition; this may lead to good miscibility with respect to molecular weight compared to the respective neighboring blends. Also, the tacticities of the nBMA·iBMA copolymers used here are scarcely dependent on the copolymer composition as shown in Table II.

Concerning the dependence of miscibility on the VAc content, miscibility should be less as the VAc content increases. However, Figures 4–6 do not explicitly show such a behavior. The phase separation temperature is determined by the molecular weight as well as the copolymer composition. The molecular weights of VC·VAc-87 and -81 are considerably small compared to that of VC·VAc-90 and also the molecular weight of VC·VAc-81 is larger than that of VC·VAc-87. Therefore, the wider miscibility region with respect to temperature for the VC·VAc-87 blends may be due to the comparably low molecular weight of VC·VAc-87.

For the present systems, if the respective VC·VAc copolymers are regarded as homopolymers as described above, the present systems are the blends of an A_{r_1} and $(C_xD_{1-x})_{r_2}$ type, where A, C, and D correspond to the VC·VAc, iBMA, and nBMA *monomers*, respectively. Then, the intermolecular χ can be written from eq 1 as

$$\chi = x\chi_{AC} + (1-x)\chi_{AD} - x(1-x)\chi_{CD} \quad (5)$$

As is clear from eq 5, the intermolecular χ can be positive in a certain range of the copolymer compositions even though all the segmental χ_{ij}'s are negative. Then, the following relation is satisfied at that temperature:[1,2,4,8]

$$|\chi_{CD}| > (|\chi_{AC}|^{1/2} + |\chi_{AD}|^{1/2})^2 \quad (6)$$

In the present systems, $|\chi_{CD}|$ between iBMA and nBMA appears to be considerably large compared to both $|\chi_{AC}|$ and $|\chi_{AD}|$ because miscibility for the PiBMA/PnBMA blend is much more than those for the VC·VAc/PiBMA and Vc·VAc/PnBMA blends except the blend with VC·VAc-97.5. Therefore, if the blend ratio, 1/1, investigated for the present systems is very close to the critical concentration, there may be a possibility of an immiscibility region in the present systems. Then, around the temperature corresponding to the minimum point in the miscibility–immiscibility boundary line, the intermolecular χ changes from negative to positive and again to negative values with the copolymer composition.

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Registry No. (VC)(VAc) (copolymer), 9003-22-9; (*n*BMA)-(*i*BMA) (copolymer), 9011-53-4.

References and Notes

(1) Chiou, J. S.; Paul, D. R.; Barlow, J. W. *Polymer* **1982**, *23*, 1543.
(2) Vuković, R.; Karasz, F. E.; MacKnight, W. J. *Polymer* **1983**, *24*, 529.
(3) Kambour, R. P.; Bendler, J. T.; Bopp, R. C. *Macromolecules* **1983**, *16*, 753.
(4) Shiomi, T.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1986**, *19*, 2274, 2644.
(5) Paul, D. R.; Barlow, J. W. *Polymer* **1984**, *25*, 487.
(6) ten Brinke, G.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1983**, *16*, 1827.
(7) Scott, R. L. *J. Chem. Phys.* **1949**, *17*, 279.
(8) Fernandes, A. C.; Barlow, J. W.; Paul, D. R. *J. Appl. Polym. Sci.* **1986**, *32*, 5481.

Origin of the Long Period and Crystallinity in Quenched Semicrystalline Polymers. 1

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ABSTRACT: The long periods of quenched polymers [in particular linear polyethylene (PE)] of various molecular weight distributions have been determined by small-angle X-ray scattering according to the correlation function, Porod, DAB, and paracrystalline analysis. It is shown that neither of the average molecular weights M_n nor M_w governs the morphology of the semicrystalline state of polymers. The weight-average dimension $r_w \sim M_r^{1/2}$, of the coils in the melted state before crystallization is the main parameter that controls the morphology of the solid state, including long periods, amorphous layer thickness, and crystallinity. This correlation law between the melted and solid states is general, and comparisons between PE, poly(ethylene terephthalate), poly(tetrahydrofuran), and polypropylene are discussed. The role of entanglements during crystallization is clearly analyzed by measurements of the crystallinity $\chi(M_r)$, which is a linear function of $1/r_w$ and which extrapolates to 1 for a molecular weight of the order of M_c, the critical mass between entanglements. Models of crystallizations involving a balance between the enthalpy of crystallization and the energy of distortion of the entangled amorphous chains explain the dependence of the long period and the amorphous layer thickness on supercooling and molecular weight. Finally, the different behavior of amorphous chains of semicrystalline polymers crystallized by slow cooling (relaxed chains) and rapid cooling (constrained chains) is pointed out. The transition between the two regimes of crystallization at high and low supercooling is analyzed in terms of chain dynamics rather than nucleation.

1. Introduction

It is well-known that all properties of bulk-crystallized polymers are drastically dependent on the molecular weight and crystallization temperature.[1,2] The influence of these parameters on the morphology of the semicrystalline state[2-4] and on the kinetics of crystallization[5,6] is well documented. It has been recognized only recently that the morphology on a lower scale, the lamellar arrangment, is also dependent on the molecular weight distribution.[7-16] In monodisperse fractions and mixtures of monodisperse fractions of polyethylene (PE) the long period deduced from the maximum intensity of small-angle X-ray scat-

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