

POLYMORPHISM OF ISOTACTIC POLYBUTENE-1 AS REVEALED BY MICROINDENTATION HARDNESS – Part II: CORRELATIONS TO MICROSTRUCTURE

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Abstract.-

The influence of polymorphism on the micromechanical properties of isotactic polybutene-1 has been investigated by means of the microhardness technique. Hardness data, H , of Form I (hexagonal) are shown to be notably larger than those of Form II (tetragonal). The H values of both polymorphic forms are shown to depend on the molecular weight, M_w , and the crystallization temperature, T_c . The hardness behaviour with M_w and T_c has been correlated to the changes of degree of crystallinity and nanostructure as derived from SAXS. A hardness value for isotactic polybutene-1 infinitely thick crystals (H_c^∞), of forms I and II, is proposed. H_c^∞ of form I is shown to be notably larger than that of form II. This result is a consequence of the denser packing of the hexagonal crystal modification, and accounts for the large difference in H -values found for form I and II. Finally, the variation of the mechanical b -parameter, proportional to the surface free energy of the crystals, with molecular weight is discussed.

Introduction

The basis of the microhardness technique lies on the local deformation produced at a microscopic scale on a material surface. Microindentation hardness is widely recognized to provide fundamental information on the morphology and microstructure of polymer materials [1-3]. It is now well established and widely experimentally supported that the microhardness of a semicrystalline polymer is intimately related to the degree of crystallinity, chain packing, crystal thickness and surface free energy of the crystals [1, 4]. The sensitivity of microhardness to the polymer structural parameters makes this technique of great value in the study of the kinetics of solid state transformations such as those occurring upon crystallization from the glassy state or in the course of a polymorphic transition [5-9]. The influence of polymorphism on microhardness has been studied in the case of isotactic polypropylene (iPP) [10]. Here, it was demonstrated that the microhardness technique can be successfully used to evaluate the amount of α and β phases within an iPP sample. Moreover, microindentation hardness has been applied to follow stress-induced polymorphic transitions such as those taking place in polybutylene terephthalate, its block copolymers and blends [7-9].

Isotactic polybutene-1 exhibits a tetragonal crystal cell (form II) when crystallized from the melt at atmospheric pressure [11]. This crystal modification is gradually transformed at room temperature into the thermodynamically favoured hexagonal form I [12, 13]. This peculiar polymorphic transformation is completed after approximately ten days storage. Despite the II \rightarrow I transformation of polybutene was soon recognized, its mechanism and the influence of polymorphism on the mechanical properties of this material is still not fully understood.

The present paper is the second of a series of two concerning the study of the polymorphism of isotactic polybutene-1 by means of microindentation hardness. Part I was devoted to the study of the kinetics of the above mentioned polymorphic transformation. The present work describes the

microhardness-microstructure correlation in both crystal modifications. The influence of molecular weight and crystallization temperature is discussed.

Basic equations

It is now widely accepted that the microhardness of a semicrystalline polymer can be described in terms of a parallel model of alternating crystalline and amorphous regions following [1, 4]:

$$H = H_c \alpha + H_a (1-\alpha) \quad (1)$$

where H_c is the hardness of the crystals, H_a is the hardness of the amorphous regions and α is the fraction of crystalline material. The crystal hardness can be expressed in terms of [14]:

$$H_c = \frac{H_c^\infty}{1 + \frac{b}{l_c}} \quad (2)$$

where H_c^∞ is the hardness of an infinitely thick crystal, l_c is the crystal thickness, and b is a parameter related to the surface free energy of the crystal, σ_e , and to the energy required for plastic deformation of the crystal blocks, Δh , following [14]:

$$b = \frac{2\sigma_e}{\Delta h} \quad (3)$$

Equation 2 describes the deviation of the crystal hardness from that of an infinitely thick crystal due to the limited size of the crystals and the occurrence of entanglements and other defects located at their boundaries. On the other hand, the H_c^∞ value is mainly controlled by chain packing.

Experimental

Materials

We used four different isotactic polybutene-1 grades with different molecular mass, within the range $200.000 \text{ g/mol} \leq M_w \leq 850.000 \text{ g/mol}$, kindly supplied by Montell Polyolefins, Louvain la Neuve (see table 1). C^{13} NMR analysis reveals that the fraction of isotactic pentads (≈ 0.8) is independent of molecular weight.

Quenched films were obtained by compression moulding as described in the preceding paper [15]. The final film thickness is of $\approx 300 \text{ }\mu\text{m}$. In addition, portions of the high molecular weight film ($M_w = 850.000 \text{ g/mol}$) were isothermally crystallized at temperatures in the range 80°C - 110°C (see table 2), as described in detail in reference 15.

Techniques

Differential Scanning Calorimetry (DSC), Small Angle X-ray Scattering (SAXS) and Microhardness (H) data for form II were derived from measurements performed immediately after the samples were, either quenched from the melt, or isothermally crystallized. This procedure ensures that no incipient II \rightarrow I transformation takes place. The data for form I were derived on samples where a complete transformation of form II into form I has occurred, according to our previous results [15].

DSC measurements were performed as described in the preceding paper [15]. Tables 1 and 2 collect the melting temperature, T_m , and the degree of crystallinity, α , of form II and I, for the quenched and the isothermally crystallized samples respectively. It is worth noting that the melting temperature of form I is about $10 \text{ }^\circ\text{C}$ higher than that of form II, in agreement with previous published work [16]. On the other hand, α values seem to remain constant upon the polymorphic transformation.

Small Angle X-ray Scattering patterns were obtained using the synchrotron radiation source of the Advanced Polymers Beamline (X27C) in the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). Scattering patterns were recorded using a one-dimensional detector. A wavelength λ of 0.1366 nm was used. The sample to detector distance was 193.5 cm. The data were corrected for the detector response and beam intensity. SAXS patterns were calibrated against a standard of silver Behenate. Application of Bragg's equation to scattering maxima was adopted to derive the long period, L . The crystal lamellar thickness, l_c , was estimated using: $l_c = \alpha L$.

Microhardness was measured at room temperature, using a Leitz tester equipped with a Vickers diamond pyramid. Microhardness values, H , were derived from the optical measurement of the residual impression left behind upon load release, according to: $H = 1.854 P/d^2$; where d is the length of the indentation diagonal and P is the applied load. A loading cycle of 6s was used in order to minimize the sample creep under the indenter. Loads of 49, 98 and 147 mN were employed to correct for the instant elastic recovery. For each load, at least eight measurements were averaged.

Results and discussion

Crystallinity dependence

Tables 1 and 2 collect the T_m , α , L , l_c and H values of forms II and I, for the quenched and isothermally crystallized samples respectively. The H values of form I are shown to be remarkably higher than those of form II. This result is a consequence of the denser chain packing in the hexagonal crystal modification (form I) with respect to the tetragonal crystal structure (form II) [17], as already suggested in the preceding paper [15]. The H variation with M_w (see table 1) and the conspicuous H -increase with increasing T_c (see table 2) can be explained in terms of the hardness dependence on α , l_c and the mechanical b -parameter (see equations 1 and 2), as will be shown below.

Figure 1 illustrates the linear increase of H with α for forms II and I (solid and open symbols respectively), for the quenched (circles) and isothermally crystallized (triangles) samples. There is a tendency of H to increase with increasing α for both forms II and I. The straight lines in Figure 1 follow the microhardness additivity law according to equation 1, where $H_a \approx 0$, since the glass transition temperature of iPBu-1 is below room temperature. In the case of form II, the crystal hardness values, calculated using equation 1 and represented in Figure 1 as the intercept with the right-hand y-axis, lie in the range 10-13 MPa. On the other hand, H_c values for samples in form I lie in the range 56-79 MPa. The spread in the H_c values of form II and I could be immediately attributed to changes in the thickness of the lamellar crystals (see equation 2, tables 1 and 2). The microhardness-lamellar thickness correlation is discussed in detail below.

Influence of lamellar thickness

Quenched samples: Hardness for infinitely thick crystals (form II)

It is convenient to write equation 2 as:

$$\frac{1}{H_c} = \frac{1}{H_c^\infty} \left(1 + \frac{b}{l_c} \right) \quad (4)$$

In this way, we can derive the H_c^∞ and b values from a linear plot of $1/H_c$ versus $1/l_c$. Figure 2 shows this plot for the quenched samples with different molecular weight (form II). From this representation, a b-value of 110 Å and $H_c^\infty = 27$ MPa are induced. While the b-value obtained lies in the range of those reported in the literature for other polymers [18, 19], it is to be noted the low H_c^∞ value derived for form II of iPBu-1 in contrast to that found for other systems (for example: for polyethylene oxide, $H_c^\infty = 150$ MPa; for polyethylene, $H_c^\infty = 170$ MPa and for polyethylene terephthalate, $H_c^\infty = 392$ MPa [1]).

Isothermally crystallized samples: comparison of mechanical parameters of forms I and II

Figure 3 presents the plot of $1/H_c$ versus $1/l_c$ for the high molecular weight sample, crystallized at different temperatures at the beginning and after the end of the polymorphic transformation (forms II and I respectively). The data for form II have been fitted to a straight line, assuming $H_c^\infty = 27$ MPa (see Figure 2). The b-value obtained in this case is significantly larger ($b = 260 \text{ \AA}$) than the one derived for the quenched samples ($b = 110 \text{ \AA}$, see figure 2). The b-parameter is known to be proportional to the surface free energy of the crystals (see equation 3). Hence, crystals developed in the course of an isothermal crystallization seem to contain a larger number of defects and molecular entanglements at their surface boundary, with respect to the crystals developed during quenching from the melt. During isothermal crystallization, defects are segregated more efficiently to the crystalline-amorphous interphase. Similar results have previously been reported for polyethylene samples quenched and slowly crystallized from the melt [18].

Concerning the linear fit of data for form I (see figure 3), results yield values of $H_c^\infty = 104$ MPa and $b = 78 \text{ \AA}$. It is noteworthy the high H_c^∞ value of form I with respect to that derived for form II ($H_c^\infty = 27$ MPa). This result supports our foregoing contention, that the notable enhancement observed in the H values upon the II→I transformation (see Figure 1) is mainly attributed to the different chain packing, and hence to different H_c^∞ values, in both crystal modifications.

Influence of molecular weight (form I): The role of the b-parameter

We have derived for the isothermally crystallized samples of form I, a H_c^∞ value of 104 MPa (see figure 3). Assuming the same H_c^∞ value for the quenched samples, we have obtained the b-values for the various molecular weights (see table 3). Figure 4a illustrates the variation of the b-parameter with the molecular weight of the samples in form I. One can see an initial b-increase with

increasing M_w , followed by a conspicuous drop in the b -values for the high molecular weight sample. The initial b -rise could be attributed to an increase in the entanglement density at the crystal surface with increasing chain length. A similar b -behaviour with M_w has been reported for a range of molecular weight polyethylene samples ($56.000 \leq M_n \leq 173.000$ g/mol) [18]. On the other hand, the significant decrease in the b -value for the high molecular weight sample could be explained in terms of an increase in the number of tie molecules interconnecting adjacent crystals. This number would tend to increase with increasing molecular weight.

Correlation between the mechanical b -parameter and the thermodynamic b^ -parameter.*

It has already been suggested the analogy between equation 2 and Thomson-Gibbs equation [20]. While the former describes the crystal hardness depression due to the finite size of the crystals and the mechanical parameter b , the latter expresses the melting temperature in terms of:

$$T_m = T_m^\infty \left(1 - \frac{b^*}{l_c} \right) \quad (5)$$

Where T_m^∞ is the equilibrium melting temperature and b^* is a thermodynamic parameter, related to σ_e and to the equilibrium heat of fusion Δh_f^∞ ($b = 2\sigma_e / \Delta h_f^\infty$).

Figure 4b illustrates the variation of the b^* -parameter, as derived from calorimetric measurements, as a function of molecular weight, for samples isothermally crystallized (form I) (see table 3). We have assumed that the T_m^∞ value of form I is about 10° higher than that of form II [16], the latter value being derived from Marand's approach [21, 22]. Figure 4b reveals that the b^* -parameter values follow the same trend as that shown in Figure 4a for the b -parameter. This result seems to support that the behaviour of b with M_w is a consequence of the variation of the surface free energy with molecular mass. It is noteworthy the high b^* -values with respect to the b data. This result has already been observed for other polymers and suggests that the energy required for plastic deformation of the crystals is significantly lower than the melting enthalpy.

Conclusions

- The hardness values of the tetragonal and the hexagonal crystal modifications of isotactic polybutene-1 are a function of both, the molecular weight and the crystallization temperature. This is a consequence of the variation of the degree of crystallinity and the thickness of the lamellae with M_w and T_c .
- From the analysis of the $1/H_c$ versus $1/l_c$ plot it is possible to derive the crystal hardness of an infinitely thick crystal H_c^∞ for both, forms I and II. Results reveal that H_c^∞ for form II ($H_c^\infty = 104$ MPa) is substantially larger than that of form I ($H_c^\infty = 27$ MPa).
- Analysis of the microhardness-nanostructure correlation for the high molecular weight sample crystallized at different temperatures reveals that the mechanical parameter b is significantly larger than that derived for the quenched samples. This result could be attributed to a more efficient segregation of the defects and entanglements to the crystalline-amorphous interphase for the isothermally crystallized samples.
- Results indicate that the b -value is constant at the beginning of the transformation (form II) while for the completely transformed material (form I) b shows an initial increase with increasing molecular weight, followed by a conspicuous drop for the high molecular weight.

References

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Table 1. Molecular weight, crystal modification, melting temperature, degree of crystallinity, long period, crystal lamellar thickness and microhardness values for the quenched samples with different molecular weight. The l_c data for form II were derived assuming $l_c(\text{II}) = l_c(\text{I})/1.16$ (see text).

Sample	M_w	Crystal	T_m	α	L	l_c	H
Code	(10^3 g/mol)	Form	($^{\circ}\text{C}$)		(\AA)	(\AA)	(MPa)
PBu 110	850	II	109.8	0.44		97	5.40
PBu 200	525	II	106.9	0.40		94	5.22
PBu 300	400	II	108.5	0.40		86	4.75
PBu 800	200	II	108.0	0.41		67	4.20
PBu 110	850	I	119.8	0.43	262	112	34.5
PBu 200	525	I	116.9	0.40	273	109	22.4
PBu 300	400	I	115.9	0.38	262	99	21.4
PBu 800	200	I	117.0	0.39	196	78	26.4

Table 2. Crystal modification, melting temperature, degree of crystallinity, long period, crystal lamellar thickness and microhardness values for the high molecular weight sample crystallized at different temperatures.

T_c (°C)	Crystal Form	T_m (°C)	α	L (Å)	l_c (Å)	H (MPa)
80	II	117.5	0.53		169	5.10
100	II	122.2	0.56		144	5.85
105	II	124.9	0.63		182	7.7
110	II	126.7	0.70		224	8.30
80	I	127.3	0.50	393	195	38.2
100	I	132.9	0.56	300	167	38.4
105	I	133.3	0.64	331	210	49.5
110	I	137.1	0.68	370	259	54.6

Table 3. The b , b^* values and the b/b^* ratio for samples in form I with different molecular weight.

M_w (10^3 g/mol)	b (Å)	b^* (Å)	b/b^*
200	45	7.5	6
400	84	8.1	10.4
525	94	6.8	13.8
850	34	4.4	7.73

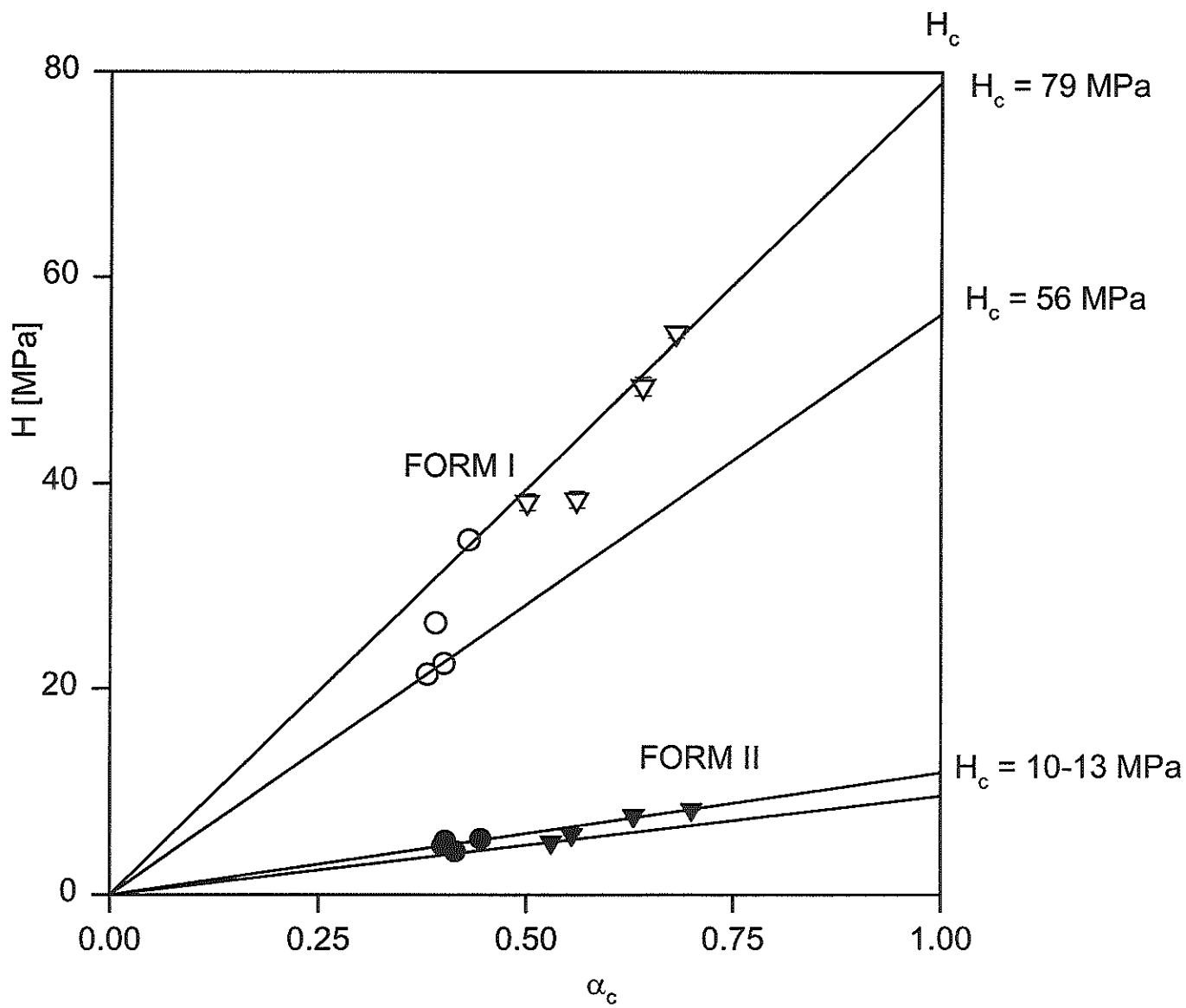


FIGURE 1

- $M_w = 850.000$ g/mol
- $M_w = 525.000$ g/mol
- ▲ $M_w = 400.000$ g/mol
- ▼ $M_w = 200.000$ g/mol

FORM II, quenched samples

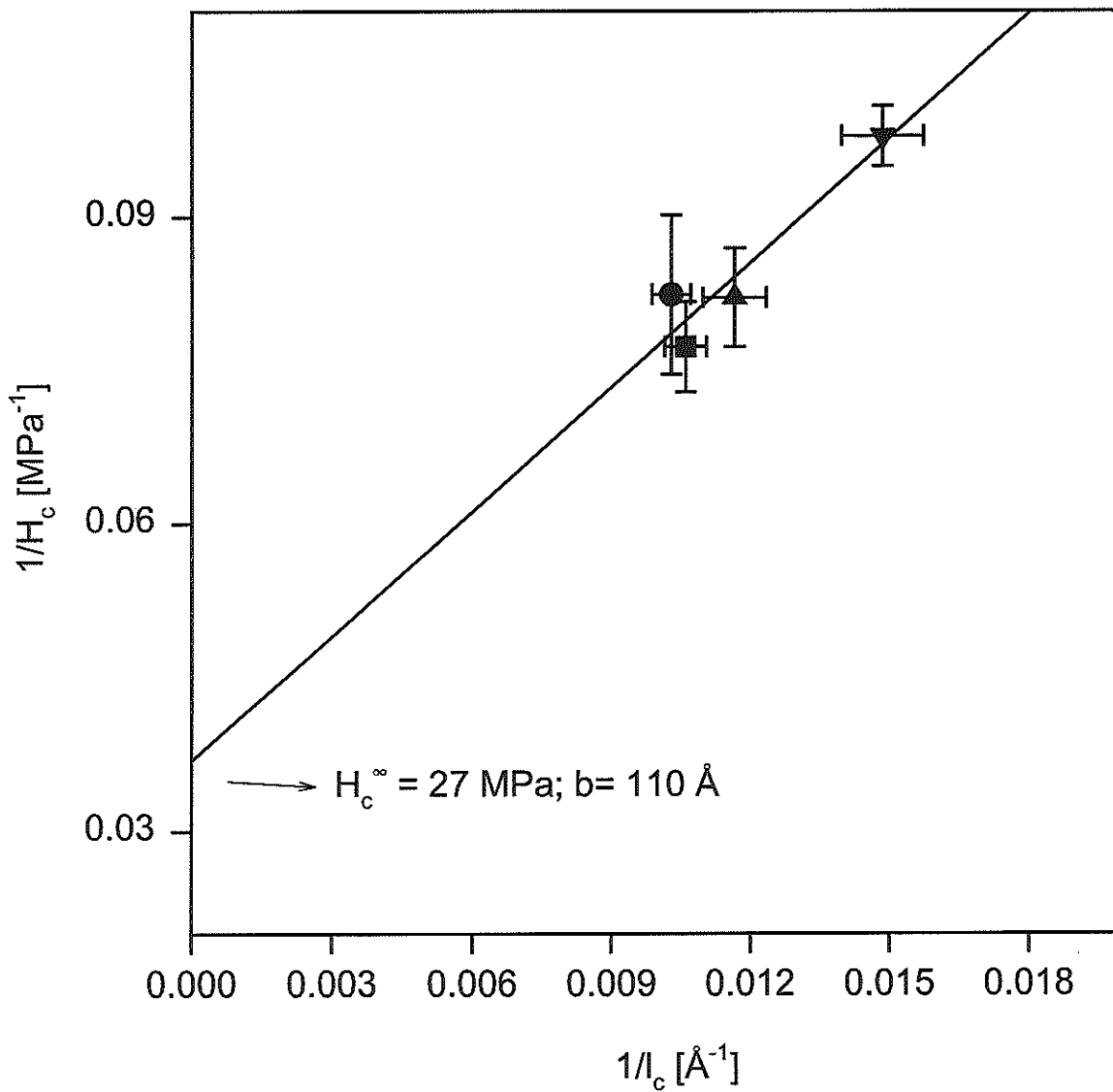


FIGURE 2

$M_w = 850.000 \text{ g/mol}$

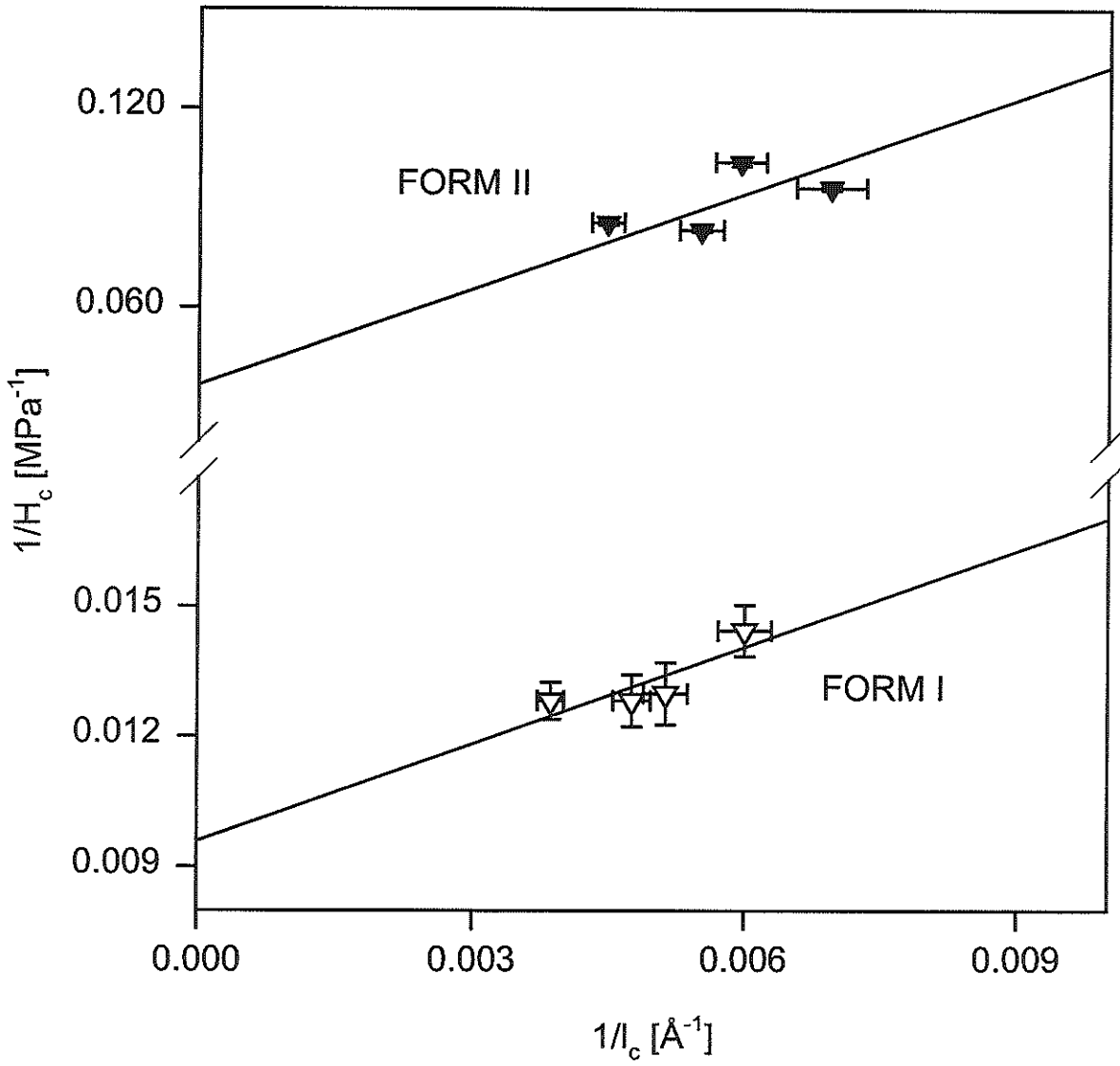


FIGURE 3

FORM I, $T_c = 20^\circ\text{C}$

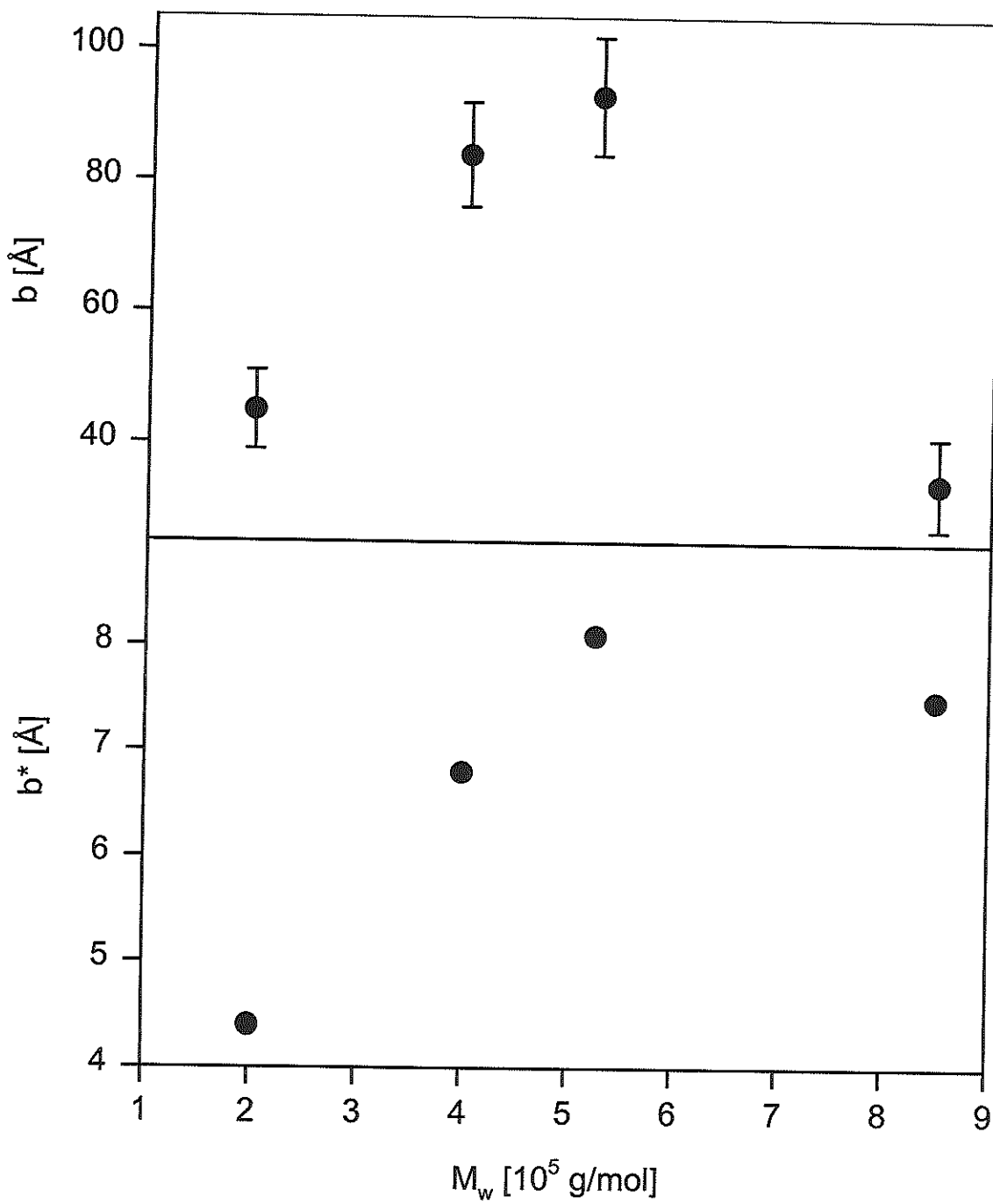


FIGURE 4

