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MOLECULAR WEIGHT DEPENDENCE OF LATERAL GROWTH RATE OF A SINGLE CRYSTAL OF POLYETHYLENE

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INTRODUCTION

Molecular weight dependence of crystallization rate of polyethylene (PE) crystallized from the melt at 1atm. was studied by Hoffman et al.[1] and Fatou et al.[2] Hoffman et al .observed the lateral growth rate (V) on polycrystals, such as spherulites, axialites and so on. As there has been some ambiguity whether V observed on a polycrystal is the same as that on a single crystal or not, it is interesting to observe V on a single crystal. Fatou et al. observed overall crystallization rate also on polycrystals by using differential scanning calorimetry (DSC). In this case it is difficult to obtain V separately. Toda and Keller found that single crystals of PE can be classified into two types which they named type A and type B[3]. They observed on two kinds of materials, number average molecular weight (Mn) of which are 11400 and 28900 (denoted as 11K and 29K, respectively). They also observed V on single crystals[4]. It is important in the study of crystallization to determine correct equilibrium melting temperature (Tm^0). In Hoffman et al.'s and Toda and Keller's studies Tm^0 was estimated theoretically. It is well known that the theoretical one is much higher (about 5K) than that estimated from the melting temperature of an extended chain crystal (ECC) (Tm(ECC)) by Wunderlich.[5] They are shown in Fig.1. Purpose of this study is to observe the molecular weight dependence of lateral growth rate of single crystals of PE crystallized from the melt. In this study the Tm^0 is estimated from Tm(ECC) observed at 1atm.

EXPERIMENTAL

Materials used in this study were fully fractionated polyethylene (PE), a 11K fraction (NIST, SRM1482, Mn=11400, Mw/Mn=1.19), a 29K fraction (NIST, SRM1483, Mn=28900, Mw/Mn = 1.11) and a 100K fraction (NIST, SRM1484, Mn=100500, Mw/Mn=1.11). Samples were isothermally crystallized at 1atm. from the melt to a crystallization temperature (Tc) and the crystallization behavior was observed by polarized optical microscope. V was observed on single crystals. Tm^0 was determined by applying the relation, Tm^0 = Tm(ECC) + 0.3K. Tm(ECC) was observed at 1 atm. on extended chain single crystals crystallized at 0.4GPa. 0.3K in the above equation is estimated from Gibbs Thomson's equation shown in Fig.10 of ref.5, assuming that the lamella thickness is about 1 μm. Degree of supercooling (ΔT) and V are defined by the relations $\Delta T = Tm^0 - Tc$ and $V=(1/2)(da/dt)$, respectively, where a is lateral length of a single crystal and t is time, respectively.

RESULTS and DISCUSSION

Tm° determined in this study is plotted against Mn in Fig.1. Tm° obtained in this study was very close to one reported in Wunderlich's text, therefore it was much lower than Hoffman et al.'s theoretical one. Single crystals were formed only at the early stage of crystallization and then they changed to polycrystals through overgrowth. Onset time of overgrowth strongly depends on both △T and molecular weight Mn. It was rather long time for 11K and 29K, whereas very short time for 100K. Obtained logarithmic V is plotted against 1/(Tc ・△T) in Fig.2. The temperature where morphology of single crystals changed from type A to type B is also shown in Fig.2. The temperature for 100K was not sufficiently reliable because of difficulty in distinguishing morphology due to very short onset time of overgrowth. V vs. 1/(Tc ・△T) for type A showed straight lines for all samples, therefore the experimental formula was given by V=Aexp (-B/Tc・△T) where A and B are constants. It should be noted that B=14.5 [K²] was nearly independent of Mn, while A significantly decreased with increase of Mn, which is shown in Fig.3.

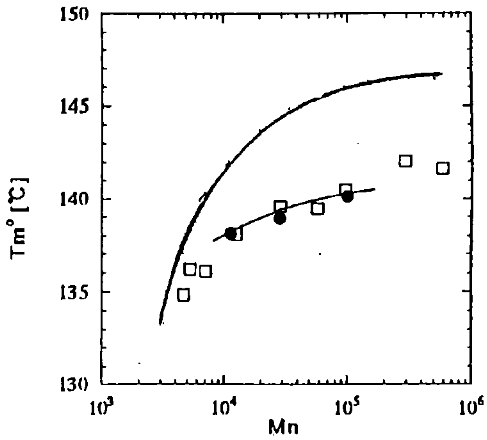

Fig.1 Tm°(●) plotted against Mn along with the data(□) in textboox of Wunderlich(1977). Solid line represents the theoretical curve determined by Hoffman et al.(1975).

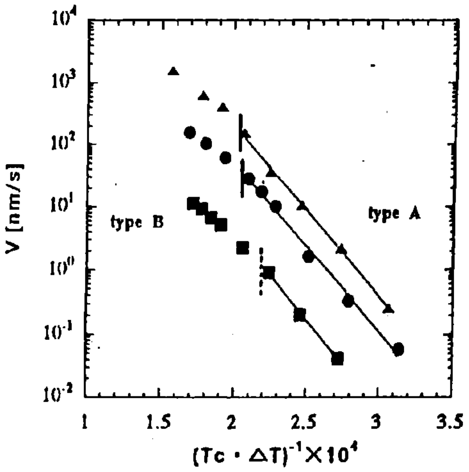

Fig.2 (Tc・△T)⁻¹-dependence of V for Mn=11400(▲), 28900(●), and 100500(■).

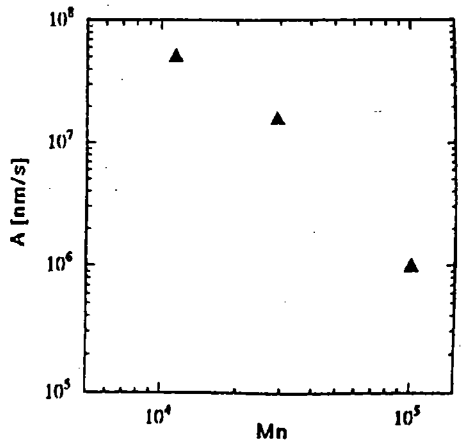

Fig.3 Mn-dependence of A.

CONCLUSION

Degree of super cooling dependence of the lateral growth rate of single crystals of PE was observed on three kinds of number average molecular weitht (Mn=11400, 28900 and 100500). It significantly decreased with increase of Mn.

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