STUDIES ON THE GROWTH RATES OF POLYETHYLENE SINGLE CRYSTALS

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Abstract. A study has been made on the growth rates of intermediate molecular weight fractions of linear polyethylene as a function of solution concentration, molecular weight and crystallization temperature. In agreement with earlier work, the growth rate was found to be proportional to the concentration raised to a power less than unity and the magnitude of the concentration exponent at a given crystallization temperature decreases as the molecular weight increases. Furthermore, at a given molecular weight the exponent tends to increase as the crystallization temperature increases. These results agree qualitatively with the predictions of Sanchez and DiMarzio. These observations could be satisfactorily accounted for when considering the mechanism of the folded deposition of the chains, and in particular the situation, unique for polymers, that a given chain can be partly attached to the crystals while parts of it remains in solution, i.e. forming cilia.

Introduction

A recent theory proposed by Sanchez and DiMarzio[1,2] suggests the effect of concentration, molecular weight and the crystallization temperature on the crystallization of polymers from dilute solution. Fractionated samples of polyethylene were used in most of the experiments of polyethylene single crystal formation because of the low molecular weight fractions which may exist in the unfractionated sample. The single crystals formed from low molecular weight samples possibly contain the extended-chain crystals which, in turn, may influence the strict measurement of the fold length. On the contrary, with too high molecular weight samples, well shaped crystals were hardly obtained. On account of the reason mentioned above the present experiments were carried out with moderate molecular weight fractions of polyethylene.

The rate at which a crystal grows from solution is of fundamental importance, for the final structure of the crystal in terms of its fold length, fold surface and the degree of crystallinity is dependent on the growth rate. The major steps in the growth of a crystal are the formation of the primary nucleus and the secondary nucleation of each growth step needed for the continuing growth of the crystal.

It should be noted that the measurement of the total rate of transformation, such as by dilatometry, involves both nucleation and growth, and these processes must be separated to obtain information about the growth only. The effect of solvents on the crystallization of polymers,[3] the relation between the crystal size and the crystallization temperature,[4,5] and between the dissolution temperature and the mature crystal[6-8] have been studied extensively.

Blundell and Keller[9] reported concentration dependence of growth rate and argued that the weak concentration dependence may be associated with the shielding of the crystal face by chains which are still in solution but accumulated along the face. Such chains could be full molecules or portions of molecules where the rest is already attached to the crystal. They used unfractionated sample and the work only covered a small temperature range which obviously needed extension.

Experimental

The polyethylene used in this work was a commercial Marlex 6050 polymer (kindly supplied by Phillips Petroleum Co., USA) which had been fractionated by the method described by Henry.[10] This technique utilizes a solvent-non solvent extraction procedure with xylene and butyl cellosolve as the respective liquids. The extration is carried out at about 127° in a column packed with polymer coated celite. Five fractions of weight average molecular weights of 5,200,000; 6,600,000; 7,800,000, 8,200,000, and 9,400,000 were used for single crystal experiments. The electron microscopic studies were carried out by using electrom microscope, model JEM-7 manufactured by Japan Electron Optics Laboratory Co., Ltd.

Crystallization Kinetics

It is extremely difficult to observe the growth of the crystal directly *in situ*. Instead, it is necessary to follow the growth by sampling at various stages of crystallization. Such a procedure is only really successful when all the crystals have a simple morphology and are of a uniform size so that the whole

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crystal population can be characterized by observing any one crystal. These requirements are satisfied in the present studies where uniform population of single-layer crystals are grown using self-seeding techniques.[11], [12]

The essential feature of the self-seeding method is that a solution of polyethylene in xylene is dissolved by slowly heating to a temperature, T_s, close to 100°. In this way a very large number of submicroscopic seeds are obtained which on cooling to T_c can act as centres for immediate crystal growth. Right from the beginning the growth rate of the crystals is uniform throughout the preparation so that at any instant of time all the crystals have attained the same size. Any one crystal can therefore be used to characterize the whole preparation. The number of seeds and hence the ultimate crystal size could be controlled by an appropriate choice of T_s. Values of T_s were chosen such that the growth rate was linear during the initial 1-4 μ of growth as measured from the centre of a crystal to any (110) face. For any one molecular weight fraction it was found that satisfactory results could be obtained when the values of T_s were within 0.2° of the most suitable temperature.

In order to study the growth rate at higher undercooling, the hot seeded suspension was poured into a suitable volume of the pure solvent held at T_c. On using this method the shape and intercept of crystal size vs. time curve indicated that the initial growth was linear and growth began within sec. of the moment of transfer. The method of sampling the crystal population at any time was that of Blundell and Keller.[12] After regular intervals, a previously warmed teat pipette was used to sample and quench a few drops of the solution into a tube containing pure xylene, held at some suitable temperature which is mainly determined by the molecular weight of the fraction under study. On allowing the crystal to complete the growth they could then be spotted onto grids, shadowed and observed in the electron microscope.

The linear crystal dimensions as measured from the centre of a crystal up to the step on (110) growth face were plotted as a function of time of the corresponding crystallization. Linear growth with time, during the initial stages of growth, was observed in all cases. The slope of the plot of crystal size vs. time gave the growth rate which was studied under varying conditions of temperature, concentration and molecular weight.

Results and Discussion

The concentration dependence of the growth rate of a crystal may be described by the relation :

$$G \propto C^\alpha \qquad (1)$$

where G is the growth rate, C is the concentration and α is a constant known as the concentration exponent.

In the Table, the results obtained for the growth rates of the (110) faces in single crystals from the five molecular weight fractions, under different conditions of crystallization temperature and solution concentration, are shown together with the values for α obtained from the slopes of the curves. As noted elsewhere for unfractionated polythylene from xylene solution,[13], [14] the growth rate is proportional to concentration raised to a power less than unity. Unlike previous reports,[15-18] the present work, as shown in the Table, indicates that α increases slightly as the crystallization temperature is raised, and that α has higher values for the lower molecular weight sample. Both results agree qualitatively with the predictions of Sanchez and DiMarzio and suggest that a self-nucleating mechanism contributes to the overall nucleation, for it has been shown that α would be expected to retain a value of about 1 if solution molecule nucleation were the only means by which growth were propagated. As seen in Table I, the change in concentration at a given T_c does not have a large effect on the growth rate in the case of high molecular weight fraction while in the case of low molecular weight fractions the change is appreciable.

In the present study it has been confirmed that the value of α increases with crystallization temperature for all but the samples of higher molecular weight (Fig. 1). Also α increases as the molecular weight decreases (Fig. 2). Both these findings are in agreement with the theory of Sanchez and DiMarzio in which they proposed that the secondary nucleation may involve cilia as well as solution molecules.

The growth rate increases with increasing molecular weight. Furthermore, at higher concentrations the growth rate tails off with decreasing molecular
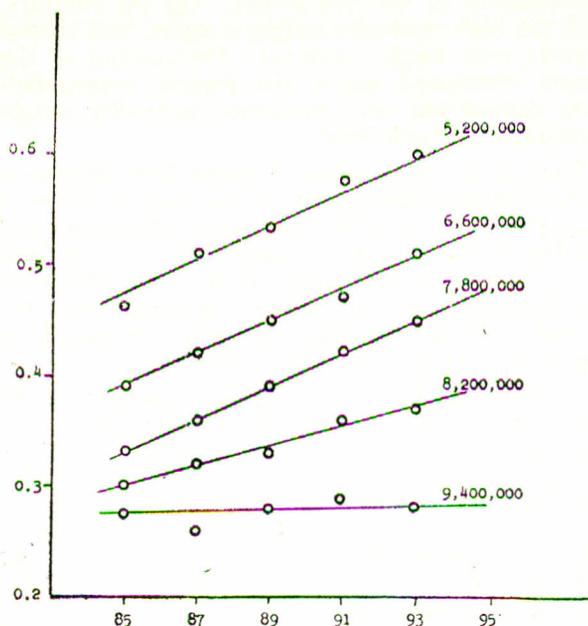
Fig. 1. Plot of the concentration exponent, α, versus temperature of crystallization T_c, for the five molecular weight fractions.

TABLE. VALUES OF THE GROWTH RATE OF (110) FACES AS A FUNCTION OF CONCENTRATION AND TEMPERATURE FOR EACH OF THE POLYETHYLENE FARACTIONS STUDIED, TOGETHER WITH THE CONCENTRATION EXPONENT AS A FUNCTION OF CRYSTALLIZATION TEMPERATURE.

Crystallization temperature, T_c (°C)	Concentration (wt. %)	5,200,000		6,600,000		7,800,000		8,200,000		9,400,000	
		G	α	G	α	G	α	G	α	G	α
85	0.003	1.11		2.42		2.60		2.63		3.01	
	0.012	1.92		3.83		3.70		3.66		3.32	
	0.048	3.43	.46	5.15	.39	5.81	.33	5.78	.30	4.63	.27
	0.1	5.00		7.62		7.53		7.60		7.92	
87	0.003	0.52		1.34		1.44		1.42		1.14	
	0.012	1.17		1.55		1.62		1.54		1.65	
	0.048	2.00	.51	2.70	.42	2.72	.36	2.80	.32	2.73	.26
	0.1	3.05		4.00		3.90		3.65		2.51	
89	0.003	0.17		0.28		0.27		0.26		0.29	
	0.012	0.38		0.59		0.58		0.56		0.50	
	0.048	0.74	.53	0.90	.45	0.91	.39	0.88	.33	0.67	.28
	0.1	1.20		1.80		1.60		1.40		1.46	
91	0.003	0.09		0.17		0.15		0.15		0.14	
	0.012	0.20		0.35		0.37		0.36		0.28	
	0.048	0.40	.58	0.48	.47	0.50	.42	0.50	.36	0.55	.29
	0.1	0.60		1.20		0.08		0.66		0.00	
93	0.003	0.03		0.06		0.05		0.05		0.05	
	0.012	0.09		0.16		0.16		0.15		0.06	
	0.048	0.20	.60	0.30	.51	0.31	.45	0.30	.37	0.28	.28
	0.1	0.34		0.37		0.36		0.36		0.39	
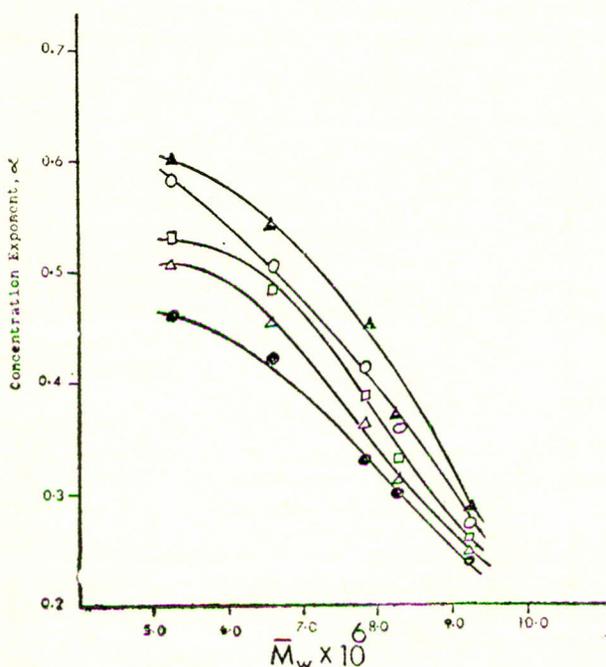
Fig. 2. Plot of the concentration exponent α, versus M_w for the five crystallization temperatures. ▲: 93; ○: 91; □: 89; △: 87; ●: 85°.

weight more rapidly as the crystallization temperature is increased. A possible explanation for this is as follows. As the molecular weight of the polymer decreases, so the lengths of the cilia they produce decrease and hence the number of stems that a molecule can contribute to the growth strip is reduced. A certain amount of strip growth is required to stabilize a nucleus on a crystal. A long cilium would be able to stabilize itself by chain folding, whereas one that is short would require molecules from solution to aid in the stabilization process. Since the availability of these molecules depends upon the concentration of the solution, the cilia nucleation rate is expected to fall markedly at low concentration for the shorter molecules.

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