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ESRF	**Experiment title:** **Investigation of the Early Stages of Crystallization and Melting of Linear Polyethylene Fractions by Ultra-Small Angle X-Ray Scattering.**	**Experiment number**: SC726
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Report:

It is well known that the growth of semi-crystalline polymers starts on nuclei stable at the crystallization temperature. These nuclei are frequently impurities, traces of catalyst,… i.e. heteregeneous nuclei. The self-seeding technique allows to initiate the starting of the growth of all crystals at the same time and to obtain crystals of the same size. The self-seeding technique developped for crystallization of polymers from dilute solution[1], has been up-graded for crystallization from the melt[2]. Small angle X-Ray scattering (SAXS) can delivery important insights into the crystallization and melting processes of semi-crystalline polymers when performed simultaneously with WAXD. It is generally accepted that crystallization proceeds by a primary process where spherulites grow until they impinge on each other and finally fill the whole available space. Each spherulite is made of lamellar stacks containing crystalline and amorphous layers. Within the spherulites, an additional very slow process, called secondary crystallization, occurs. Several possible processes can contribute to the secondary crystallization : thickening of the crystals, growing of new lamellar stacks, formation of new crystals between the already existing crystals…

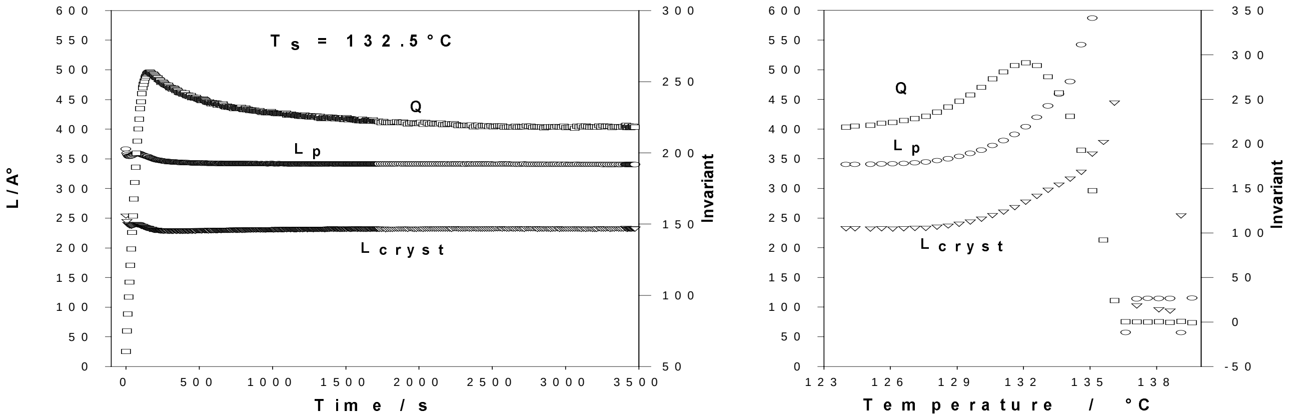
The crystallization of narrow molecular weight fractions of linear polyethylene from the melt using the self-seeding technique has been investigated by ultra small angle X-ray scattering (USAXS). The used LPE samples cover a wide range of average molecular weights and are characterized by different degrees of polydispersity ($p = \langle M_w \rangle / \langle M_n \rangle$). Their molecular characteristics are given hereafter.

Sample	1482a	1483	1475a	1484a	-
$\langle M_w \rangle$	13600	32100	52300	119600	264800
p	1.15	1.15	2.90	1.15	1.15

. The USAXS curve of LPE 32k exhibits a maximum arising from density variations due to the alternation of crystals and amorphous regions. The application of the Bragg's law to the position of this maximum gives the long period $L_p = L_{cryst} + L_{am}$, The lamellar thickness or the long spacing Lp of the used narrow molecular weight LPE fractions ranges between 30 and 70 nm. The total integrated SAXS intensity Q also called the invariant is given for a two-phase system by $Q = K \Phi v_c^l (1 - v_c^l) (\Delta\rho)^2$ where K is a constant, Φ is the fraction of lamellar crystals stacks, v_c^l is the linear degree of crystallinity in stacks of lamellae ($v_c^l = L_{cryst}/L_p$), Δρ is the difference between the densities of the crystalline (ρ_c) and amorphous (ρ_a) layers. The invariant, the long spacing and the thickness of the crystalline layers of LPE32k samples crystallized isothermally from the melt at 124 °C after self-seeding at 132, 132.5 and 133 °C, respectively have been determined. For T_s = 133 °C, the invariant Q progressively increases on about 3600 s from the early stages of the isothermal crystallization. The thicknesses of the lamellar crystals L_p and of their crystalline layers L_{cryst} decrease during the first 400 s of isothermal crystallization and afterwards sligthly increase with time. For lower values of the seeding temperature T_s, the evolution of the invariant Q is quite different : Q very quickly increases to reach a maximum value and afterwards decreases with time. The long spacing L_p and the thickness of the crystalline layers decrease with time to reach a constant value after 120 and 300 s for seeding temperatures of 132 and 132.5 °C, respectively. As we don't have any information about the change of the fraction of lamellar crystals stack i.e. the macroscopic degree of crystallinity with respect to the crystallization time, we can only suggest the following proposals to explain our results :

a) With low values of the seeding temperatures T_s (122 and 122.5 °C), the primary crystallization proceeds very quickly due to the large number of nuclei initially present in the melt. The fraction of lamellar crystals stacks increases quickly to reach its maximum value. It results into poor packing in the lamellar stacks. Therefore the increase of v_c^l during the larger times of isothermal crystallization induces a decrease of Q due to the term $v_c^l(1 - v_c^l)$.

b) For high values of the seeding temperature (133 °C), the number of nuclei is extremely low which limits the number of spherulites. The macroscopic degree of crystallinity therefore increases slowly. It results in well packed stacks of lamellar crystals. The value of the linear degree of crystallinity is therefore approximately equal to its maximum value. The contribution of $v_c^l (1- v_c^l)$ keeps approximately a constant value and the only reason of the increase of Q during the isothermal crystallization is due to the fraction Φ of lamellar crystals stacks, i.e. the macroscopic degree of crystallinity.



Lamellar thickness, thickness of the crystalline layers and invariant Q of LPE32.1k :a) Isothermal crystallization at 124 °C after self-seeding at 132.5°C; b) Melting

LPE samples having weight average molecular weights equal to 13600, 32100 an 119600 have been crystallized at 124 °C using the self-seeding technique. The values of the lamellar thickness at the early stages of crystallization (L_p*) and after 10 min of isothermal crystallization as well as the thickness of the crystalline layers in the same conditions are given hereafter. It appears that the lamellar thickness increases with molecular weight as well as the thickness of the crystalline layer. The net result is an approximately constant value for the linear degree of crystallinity in the stacks of lamellae for measurements made at the crystallization temperature.

$\langle M_w \rangle$	L_p*/nm	L_p/nm	L_c/nm	v_c^l
13600	58.7	30.1	21.8	0.72
32100	60	34.6	23	0.66
119600	66.4	46.1	33.1	0.72

References

1. D.J. Blundell, A. Keller, A.J. Kovacs, J. Polym. Sci., Polym. Let.,**4**, 481 (1966).
2. B. Fillon, J.-C. Wittmann, B. Lotz, A. Thierry, J. Polym. Sci., Polym. Phys. Ed., **31**,1383 (1993).