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Crystallization and melt behaviour of isotactic poly((4-α,α-dimethyl-benzyl) phenyl methacrylate)

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The crystallization and melting behaviour of practically 100% isotactic poly((4-α,α-dimethylbenzyl) phenyl methacrylate) has been studied by d.s.c. and light microscopy. Crystallization from the melt seemed to be non-spherulitic. The maximum crystallization rate, which could only be determined by d.s.c., was found to be 2% min^{-1} at a crystallization temperature T of 155°C. Assuming that the growth rate theory for small supercooling is valid and by taking the appropriate value 51.6 K for the constant c_2 of the WFL equation, the chain-folded surface free energy σ_e was estimated at $89 \times 10^{-2}\,\mathrm{J\,m^{-2}}$. The melting curves showed two melting endotherms. Crystallization from the melt produced a small melting endotherm just above T_c. This peak may originate from secondary crystallization of tie molecules melt trapped within the crystalline phase. The peak temperature of the second melting endotherm increased linearly with T_c, yielding an extrapolated value for the equilibrium melting temperature T_m^0 of 282°C. Avrami analysis showed for the exponent n non-integer values between 2 and 3, indicating at least a non-spherulitic growth process which is confirmed by the 'rod-like' morphology of the crystalline phase as determined by phase-contrast light microscopy. © 1997 Elsevier Science Ltd

(Keywords: isotactic poly((4-α,α-dimethylbenzyl) phenyl methacrylate); crystallization; melt behaviour)

INTRODUCTION

Poly(meth)acrylates containing aromatic groups in the side-chain, e.g. azobenzene, biphenyl, benzylidene-*p*-aminobenzene, etc. connected via a spacer to the backbone, can exhibit liquid-crystalline behaviour, but in order to form a crystalline phase highly stereoregular polymers, isotactic or syndiotactic, are required.

Crystallization kinetics and melt behaviour of isotactic and syndiotactic polymers with aromatic moieties in the side chain, e.g. isotactic polystyrene[1-7], syndiotactic polystyrene[8,9] and isotactic poly(2-vinylpyridine)[10] crystallized from the melt, has been the subject of investigations. As far as we know no detailed investigations on the crystallization and melt behaviour of stereoregular aromatic polymethacrylates have been reported in the literature. Several years ago we were able to synthesize pure poly((4-α,α-dimethylbenzyl)phenyl methacrylate), alternatively named poly(cumylphenyl methacrylate) (poly 1)[11]. In spite of the large bulky ester group the polymer was capable of crystallization. The results of a study on some aspects of the crystallization kinetics from the melt and the melt behaviour of bulk crystallized poly 1 are laid down in this paper (*Figure 1*).

EXPERIMENTAL

Poly 1 was synthesized and characterized as reported before[1]. Based on the isotactic triad content, tacticity of the used poly 1 was practically 100%! $M_n = 120\,000$ and $D = 3.17$. Crystallization kinetics and melt behaviour were studied by means of a Perkin Elmer DSC 7 apparatus, the first isothermally and the latter employing a scan speed of $10°\mathrm{C\,min}^{-1}$. For determination of melting temperatures, T_m, rates of crystallization and Avrami exponents after isothermal crystallization at different temperatures, T_c, the d.s.c. samples were first heated up to 270°C, annealed for 5 min, and quenched to T_c. Above the maximum growth rate temperature, $T_{G,\max}$ also heating curves of isothermally crystallized samples were used for determining the Avrami exponent. This latter method failed for T_cs below $T_{G,\max}$ because of extra crystallization during the subsequent heating run, resulting in a too large crystalline fraction which is not representative for the used crystallization time, especially for short crystallization times.

Films of about 10 μm thickness were obtained by evaporation of a 2 wt% solution of poly 1 in chloroform on a glass slide and used without a cover glass. Before crystallization films were first heated up to 270°C for 5 min after which they were cooled to the desired T_c. A Zeiss Axiophot polarizing microscope equipped with a hot stage (Mettler FP82) was used to visualize the crystalline texture. Growth rate measurements failed because no spherulites were formed (see also *Figure 4*).

RESULTS AND DISCUSSION

Crystallization behaviour

For calculating the crystalline fraction the enthalpy of crystallization and/or fusion for 100% crystalline poly 1

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*To whom correspondence should be addressed should be known. No enthalpic data are available from literature. Via the additive group contributions method from van Krevelen[12] it is possible to estimate the enthalpy of fusion leading to $\Delta H_f = 111\,\mathrm{J\,g^{-1}}$. This value is used in all the calculations concerning crystallinity. Experimentally determined crystallinities were generally around 15%, but never exceeded 30%.

In *Figure 2* crystallization isotherms obtained by plotting percentage crystallized poly 1 against time are shown. Only the linear part of the curves were taken to calculate average growth rates, G, which are plotted against T_c in *Figure 3*. The maximum rate, G_{max}, of about $2\%\,\mathrm{min^{-1}}$ will be influenced by molecular weight and tactic purity of the polymer and is found at a temperature of 155°C ($T_{G,max}$) for the used poly 1. Investigations of growth rates by polarized light microscopy turned out to be unsuccessful, because no spherulites were formed and at temperatures below $T_{G,max}$ no crystalline morphology became visible at all, neither by phase contrast nor between crossed polars. *Figure 4* shows some typical micrographs of crystalline textures at different T_cs using phase contrast. 'Rod-like' structures growing radially from nuclei with decreasing dimensions at decreasing T_c ending in invisible crystallites below $T_{G,max}$. TEM and SEM confirmed the found textures. This 'rod-like' behaviour was also reflected by the high Mark–Houwink exponent of 1.46 in THF solution[13]. Formation of a helix structure in the crystalline phase is a possibility like the 10/1 double-stranded helix of crystalline isotactic poly(methyl)methacrylate[14]. Non-spherulitic crystallization was also found by Murphy *et al.*[15] for several polymers when these polymers were not heated beyond the Hoffman–Weeks T_m^0 but to temperatures between the found T_m and T_m^0. For poly 1 heating to 290°C (T_m^0 = 282°C, see *Figure 8*) had no influence on the crystalline texture. More investigations will be necessary to determine the crystal structure of poly 1. 'Rod-like' crystalline structures indicate a deviating crystallization mechanism. The Avrami exponent which provides qualitative information on the nature of nucleation and growth processes, is deduced from the equation

$$(1-\alpha) = \exp(Zt^n) \qquad (1)$$

where α is the crystalline fraction, Z is a rate constant, t is time and n is the Avrami exponent. By plotting $\ln[-\ln(1-\alpha)]$ vs. $\ln t$, n is derived from its slope. *Figure 5* shows Avrami plots for poly 1 crystallized at different T_c. The resulting initial slopes gave non-integer values for n between 2 and 3 which are independent of ΔH_f. Increasing values of ΔH_f only resulted in a decrease of Z. These values also found for the crystallization of syndiotactic polystyrene[8], are probably caused by mixed growth and nucleation mechanisms. Assuming that the initial primary nucleation rate is mainly sporadic, however, one can conclude that the growth process is in two dimensions in agreement with the morphology of *Figure 4*. Avrami plots derived from isothermal crystallization at T_c below $T_{G,max}$ are non-linear and the slope decreases continuously with increasing crystallinity probably due to a changing

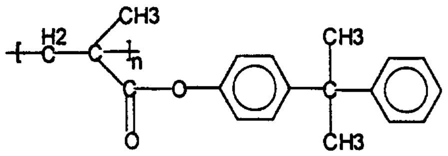

Figure 1 Poly((4-α,α-dimethylbenzyl)phenyl methacrylate)

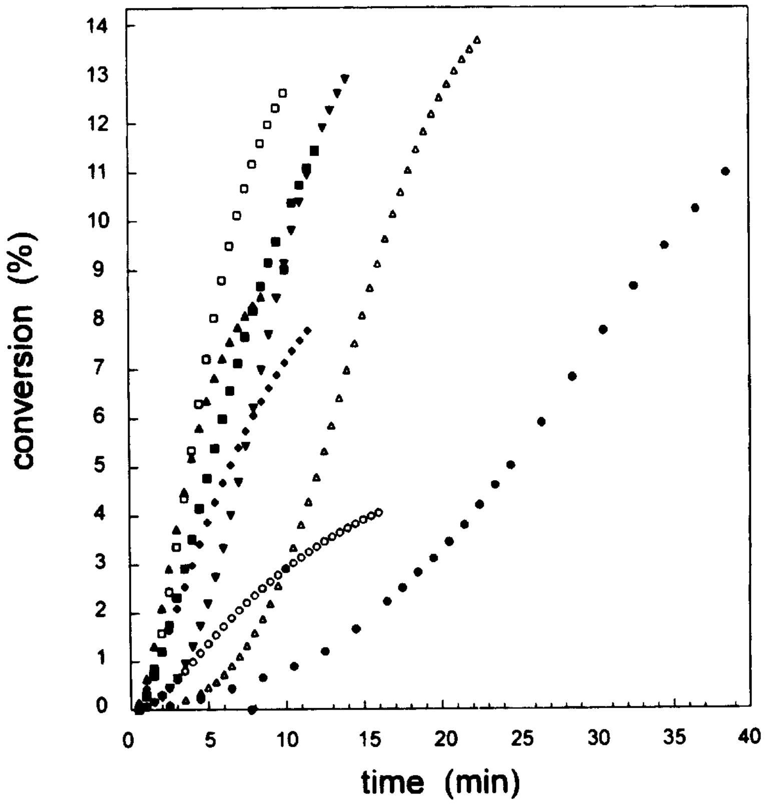

Figure 2 Conversion (% crystallinity) of the crystallization of poly 1 against time (min) for various T_cs. (○) 130°C; (◆) 135°C; (■) 140°C; (▲) 145°C; (□) 150°C; (▼) 160°C; (△) 165°C; (●) 170°C

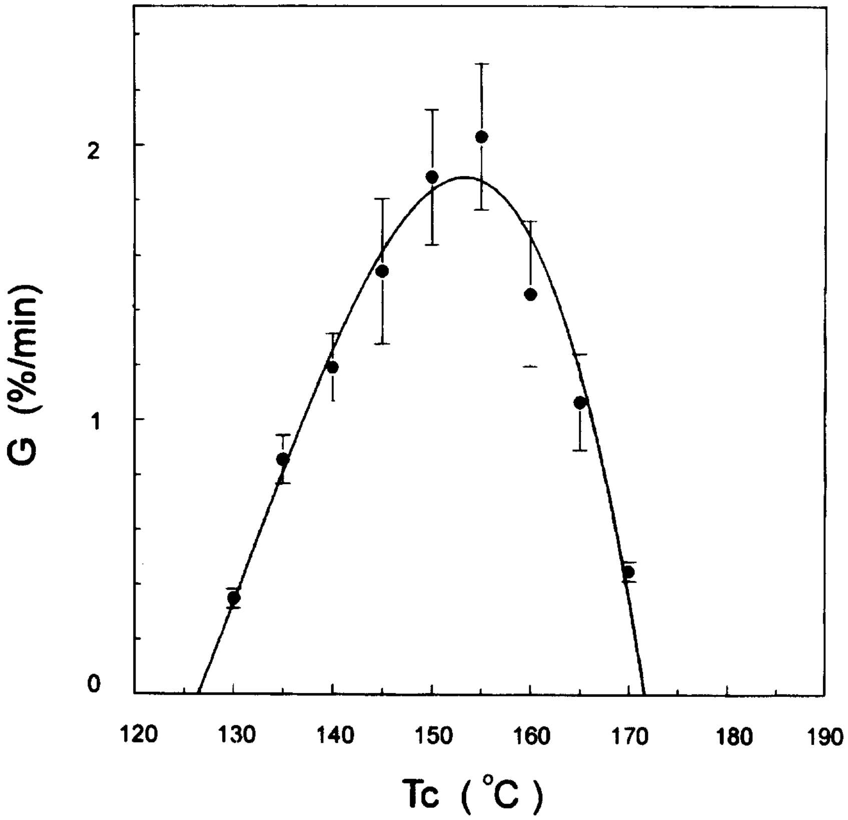

Figure 3 Growth rate G (% min^{-1}) of poly 1 as a function of the crystallization temperature T_c (°C)

primary nucleation process, e.g. when only a limited number of nuclei will be formed. Further studies on this subject will be necessary to establish the nucleation process of the material.

Melting behaviour

Figure 6 shows heating curves of a quenched sample (curve 1) and a sample crystallized on lengthy annealing of the melt (curve 2). From curve 1 one can distinguish a glass transition, a crystallization exotherm and one melting endotherm (HM). For the isothermally crystallized sample (curve 2) a second endotherm (LM) is seen at a lower temperature just above T_c, which resembles the small extra melting peak of melt crystallized isotactic polystyrene[16]. This low temperature melting endotherm (T_{LM}) shifts toward the high temperature melting endotherm (T_{HM}) at increasing T_c as can be seen in *Figure 7*.

The melting points, T_m, from the isothermally melt crystallized samples are collected in a T_m vs. T_c diagram (*Figure 8*). Extrapolating the T_{HM}-line with a slope of 0.275 to $T_m = T_c$ yields $T_m^0 = 282$°C. Because of the extrapolation over a large distance this T_m^0 is only an approximation. The T_{LM}-line (after melt crystallization for at least 14 days) with a slope of 0.88 runs almost parallel to $T_m = T_c$. This behaviour is similar to that of the small melting peak just above T_c of isotactic polystyrene. Lemstra *et al.*[16] proposed that during crystallization numerous tie molecules are formed, especially at rather large supercooling. Aggregation of these tie molecules can form locally intercrystalline links of imperfect crystals with a low melting point. In the case of poly 1 a lot of tie molecules may be present because of the low overall crystallinity. The melting point of these crystallites seemed to be strongly dependent on annealing time, as can be seen in *Figure 9*. Increase of melting temperature as a function of time is due to thickening of the intercrystalline links, a process which is diffusion and hence time dependent. Lamellar thickening could not be established for T_{HM}.

ROUGH ESTIMATION OF THE GROWTH RATE PARAMETERS

The growth rate of polymer spherulites can be theoretical given by[17,18]

$$G = G_0 \exp\,[-C_1/R(c_2 + T_c - T_g)]$$
$$\exp\,(-nb_0\sigma\sigma_e T_m^0/k\Delta H_f T_c \Delta T) \qquad (2)$$

G is a preexponential factor which is in general assumed to be constant or proportional to T_c. The first exponential factor, the transport factor, is similar in form to the definition of the Williams–Landel–Ferry (WLF) activation energy for viscous flow of a polymer[19] and contains two empirical constants C_1 and c_2. In the second exponential factor, n is a parameter that depends on the 'regime' of crystallization, b_0 is the thickness of a growth layer (i.e. stem thickness), σ and σ_e are interfacial free energies per unit area of the lateral surface and the fold surface of the growing crystal respectively, T_m^0 is the equilibrium melting temperature, k is the Boltzmann constant, ΔH_f is the heat of fusion per unit volume and ΔT is the supercooling, $T_m^0 - T_c$. Accordingly a plot of $\ln G + C_1/R(c_2 + T_c - T_g)$ vs. $1/T\Delta T$ should yield a straight line provided that appropriate values for C_1 and c_2 are chosen. Usually $C_1/R = 2060$ K and $c_2 = 51.6$ K[19]; for poly 1 $T_m^0 = 555$ K and $T_g = 387$ K. *Figure 10* shows the resulting plots using four different c_2 values from which

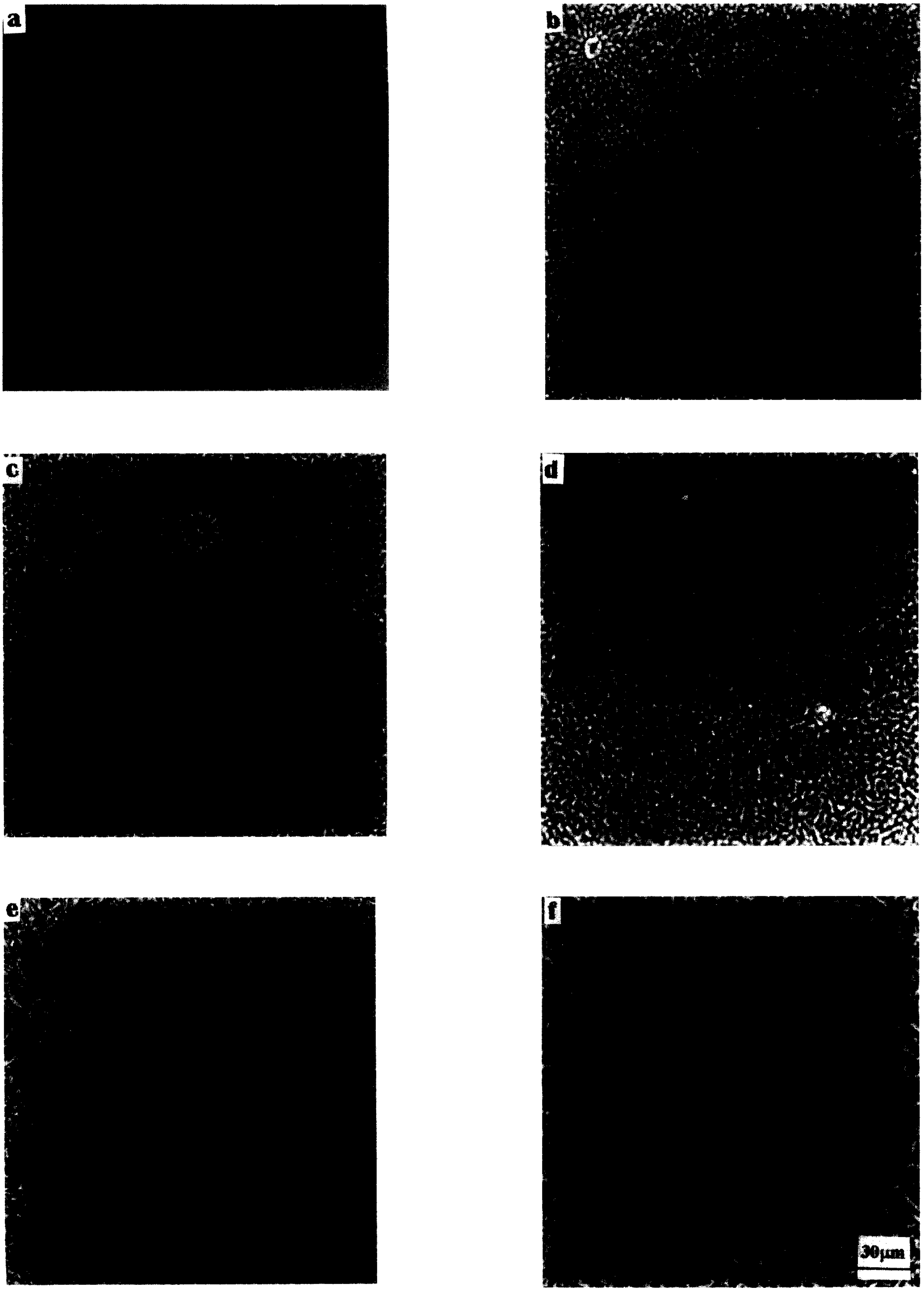

Figure 4 Phase-contrast photographs of the crystalline morphology as a function of crystallization temperature: (a) 165°C; (b) 170°C; (c) 175°C; (d) 180°C; (e) 185°C; (f) 190°C. Bar on f: 30 μm; valid for all the photographs

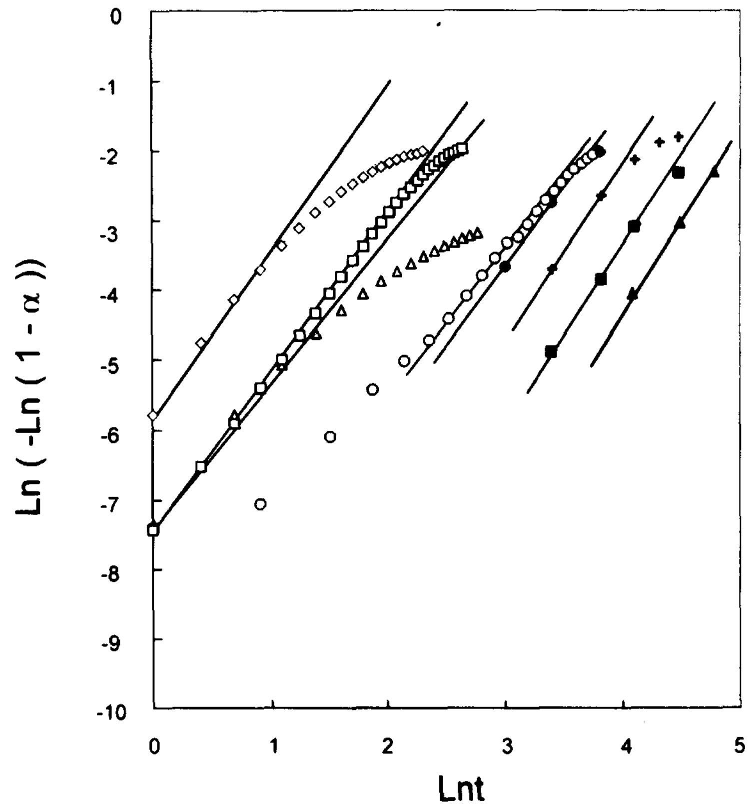

Figure 5 Avrami plots for the crystallization of poly 1 at various temperatures. (◇) 150°C; (□) 160°C; (△) 130°C; (○) 170°C, determined from the crystallization exotherm; (●) 170°C; (+) 180°C; (■) 185°C; (▲) 190°C, determined from heating curves of isothermally crystallized samples

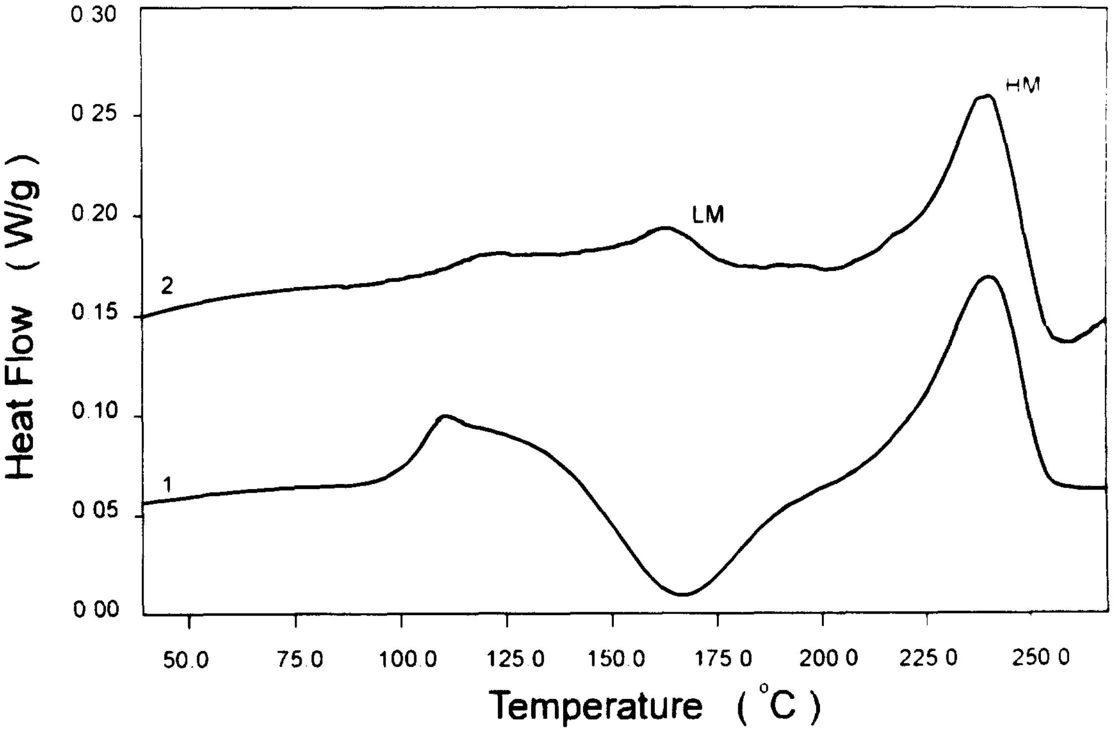

Figure 6 D.s.c. thermograms of poly 1. Curve 1 is quench cooled from the melt; curve 2 is already isothermally crystallized

$c_2 = 51.6\,\mathrm{K}$ gives the best fit with theory and leads to a slope of $23.1 \times 10^5\,\mathrm{K}^2$. This value for the slope

$$K = n\sigma\sigma_e T_m^0 / k\Delta H_v \qquad (3)$$

enables us to estimate the free energies. For large supercoolings mostly $n = 4$. $\Delta H_v = 139 \times 10^6\,\mathrm{J\,m^{-3}}$ as calculated via the groups contribution method of van Krevelen ($\rho_c = 1.25\,\mathrm{g\,m^{-3}}$)[12]. To obtain values for $\sigma\sigma_e$ or even σ and σ_e separately, b_0 should be determined by an independent method which has been unsuccessful as yet. A rough estimate is possible by taking literature values for b_0 which range from $4\text{–}10 \times 10^{-10}\,\mathrm{m}$. Then σ can be calculated by using the Thomas–Stavely relation[20]

$$\sigma = \alpha\beta_0\Delta H_v \qquad (4)$$

with $\alpha = 0.1$ for the lateral surface of a chain type crystal.

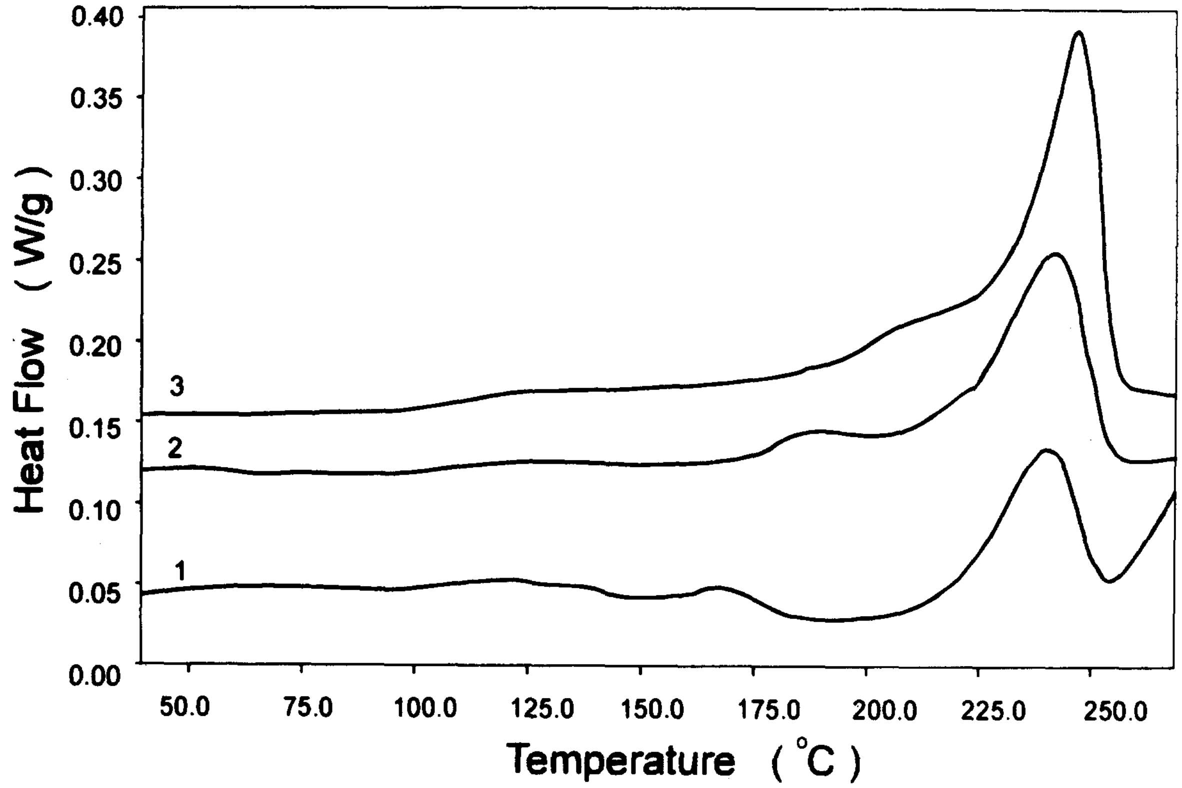

Figure 7 Three thermograms of poly 1 at different temperatures isothermally crystallized. Curve 1 at 130°C; curve 2 150°C; curve 3 170°C

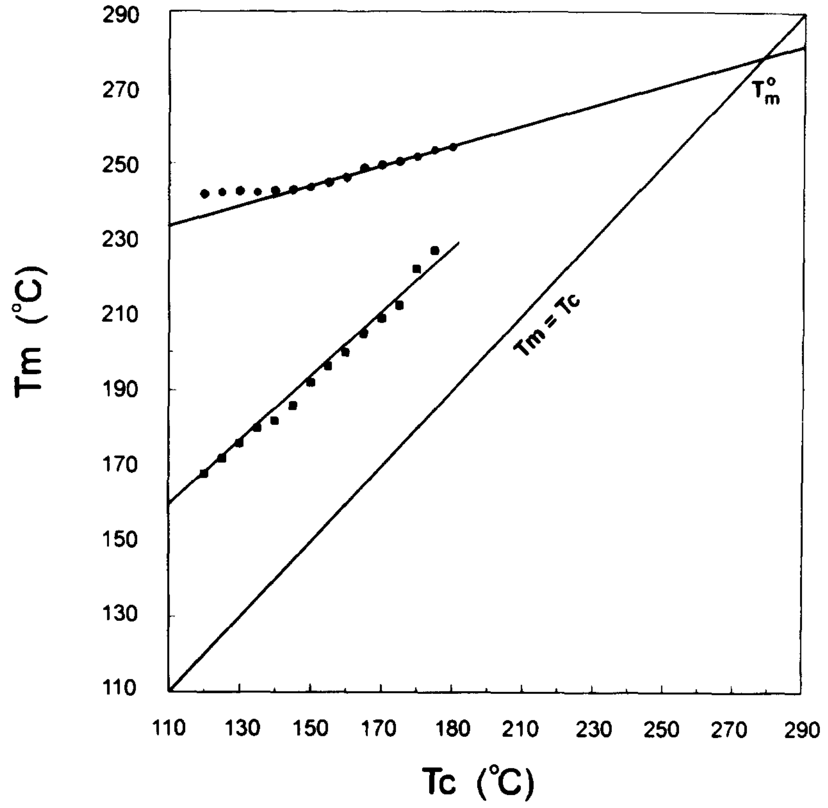

Figure 8 Peak melting temperatures of poly 1 as a function of crystallization temperature. (●) High melting (HM) endotherms; (■) low melting (LM) endotherms

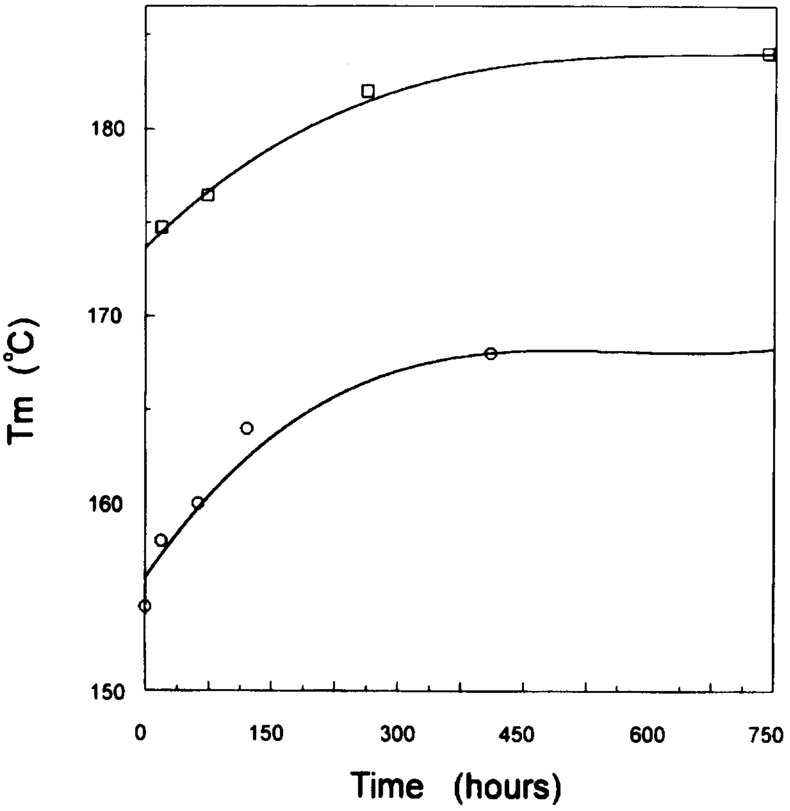

Figure 9 Melting temperatures of the low melting enodtherm of poly 1 as a function of crystallization time. (○) 120°C; (□) 140°C

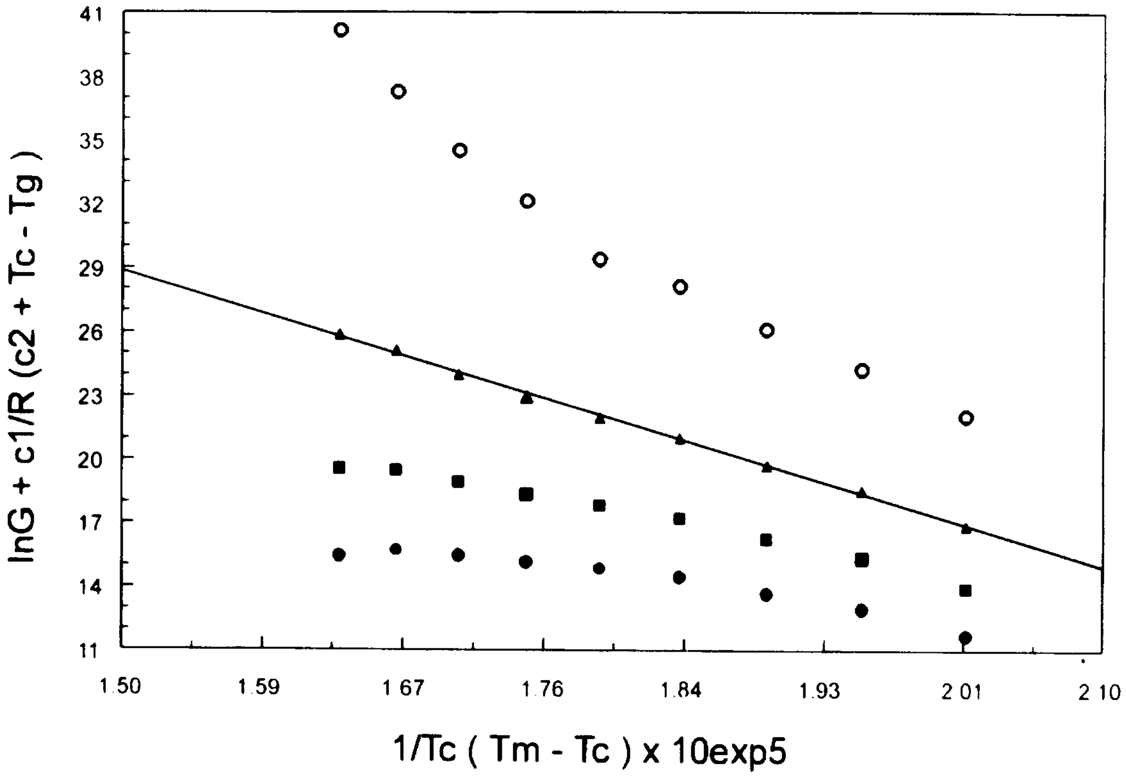

Figure 10 Plots in $\ln G + C_1/R(c_2 + T_c - T_g)$ vs. $1/T_m(T_m - T_c)$ for four different values of c_2: (▲) $c_2 = 51.6$ K; (■) $c_2 = 75$ K; (●) $c_2 = 100$ K; (○) $c_2 = 25$ K. $C_1/R = 2060$ K; $T_g = 378$ K; $T_m^0 = 555$ K

Substitution in equations (3) and (4) yields for $\sigma\sigma_e = (5.0–12.4) \times 10^{-3}\,\mathrm{J^2\,m^{-4}}$, $\sigma = (5.6–13.9) \times 10^{-3}\,\mathrm{j\,m^{-2}}$ and $\sigma_e = 894 \times 10^{-3}\,\mathrm{J\,m^{-2}}$.

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