Glass transition and cold crystallization in 'even' and 'odd' ω-amino-acid polyamides

K. -H. Illers
Mess- und Prüflaboratorium, BASF Aktiengesellschaft, D-6700 Ludwigshafen/Rhein, West Germany
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In a recent paper it was concluded from d.s.c. measurements that neither a glass transition nor cold crystallization occurs in quenched samples of 'odd' ω-amino-acid polyamides. This unusual behaviour has been attributed to complete hydrogen bonding, leading to a high rate of crystallization, while the existence of unbonded --NH groups was postulated in the 'even' polyamides. The present d.s.c. investigation demonstrates that under appropriate quenching conditions glass transition and cold crystallization are present for 'even' as well as 'odd' polyamides. The cold crystallization comprises a fast primary and a slower secondary process. In quenched, nearly amorphous, polyamide-6, -7, -8 and -9 primary and secondary cold crystallization are observed, while in quenched semi-crystalline polyamide-11, -12 and -15 only the secondary cold crystallization is found. The lack of primary cold crystallization for the higher polyamides is attributed to their relatively low glass transition temperature, which prevents the most effective quenching.

INTRODUCTION

It is well established that the non-ordered (amorphous) regions of semicrystalline polymers exhibit a glass transition at T_g, whose strength decreases with increasing crystallinity. The hole-equilibrium and the segmental mobility are frozen in when a polymer is colled through the glass transition region, giving rise to the well known changes in many physical properties (thermal expansion, specific heat, dynamic modulus).

In a recent paper it was concluded by Lord[1] from differential scanning calorimetry (d.s.c.) that no glass transition exists in quenched samples of 'odd' ω-amino acid polyamides (nylon-5, -7 and -11). For 'even' polyamides (nylon-4, -6, -8 and -12) the glass transition has been detected[1] by the same experimental technique.

If a crystallizable polymer is quenched quickly from the melt to a temperature below T_g it is eventually transformed into an amorphous or nearly amorphous state. The completeness of this undercooling depends on the cooling (quenching) rate relative to the rate of nucleation and crystallization. Upon heating the quenched samples from the glassy state, cold crystallization will start at a temperature $T_c \overset{=}{>} T_g$. For a given heating rate $(T_c - T_g)$ depends on the number of nuclei that were either present in the melt or have been formed during the quenching process or during storing or drawing the sample not too far below T_g. Well-known examples for cold crystallization are quenched samples of isotactic polystyrene, polyamide-6, polyamide-6,6 and poly(ethylene terephthalate).

Surprisingly, the d.s.c. curves in ref 1 showed an exothermal cold-crystallization peak for the quenched 'even' polyamides only, but not for the 'odd' ones. The absence of both the glass transition and the cold crystallization peak for the 'odd' polyamides has been explained in ref 1 by complete hydrogen bonding leading to a much faster crystallization, while in the 'even' members the existence of unbonded –NH groups was postulated.

The absence of a glass transition in 'odd' polyamides contradicts other published physical experiments. The dynamic mechanical measurements of Kawaguchi[2] clearly show that in semicrystalline samples of nylon-7, -9 and -11 the loss peak, which is associated with the glass transition, is present at 83°–90°C for frequencies of 60–70 Hz.

Furthermore, the assumption of non-bonded –NH groups in polyamide-6 is not in agreement with infra-red measurements which have been performed in our laboratory[3]. Even under conditions of complete absence of humidity during quenching, mounting the sample into the apparatus and measurement, no indication of free –NH groups is found in the infra-red spectrum of the amorphous sample.

Because of these discrepancies, the thermal behaviour of quenched polyamide-7, -9, -11 and -15 has been examined by the d.s.c. technique. The results will be compared with that for polyamide-6, -8 and -12.

EXPERIMENTAL

Films with a thickness of 200 μm were obtained from dried pellets by compression moulding. The compression moulding was performed with the polyamide pellets between two aluminium foils, thickness 20 μm, which stick very strongly on both surfaces of the film. The aluminium foils prevent the penetration of humidity into the samples. The sandwiched samples were melted in a Woods metal bath at a temperature 50°C above the polyamide melting point and then quenched as quickly as possible. Liquid nitrogen and ice–water mixture were chosen as quenching baths.

The quenched sandwich sample was rapidly transferred into the d.s.c. calorimetric cell of a Du Pont Thermal Analyzer 990, which was precooled to a temperature of –60°C. After further cooling to –100°C the measurement was started with a heating rate of 20°C/min and a sensitivity of 0.5 mcal/sec/in. The sample weight was about 7 mg (excluding aluminium foils).

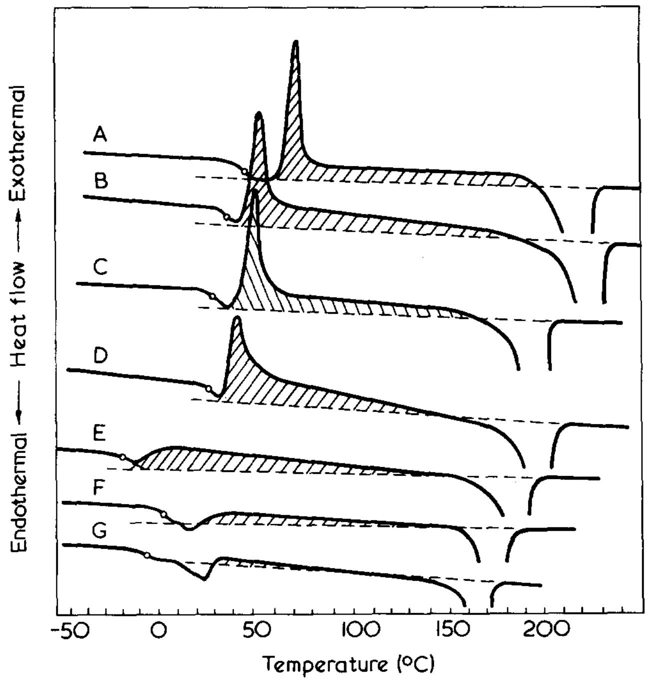

Figure 1 D.s.c. thermograms of quenched polyamides. Polyamide-6, -7, -8 and -9 quenched into ice–water mixture. Polyamide-11, -12 and -15 quenched into liquid nitrogen. Heating rate 20°C/min. Sample weight ~7 mg. A, PA-6, T_g = 47°C; B, PA-7, T_g = 37°C; C, PA-8, T_g = 30°C; D, PA-9, T_g = 27°C; E, PA-11, T_g = 20°C; F, PA-12, T_g = 0°C; G, PA-15, T_g = –7°C

RESULTS AND DISCUSSION

The d.s.c. measurements in *Figure 1* clearly demonstrate the occurrence of cold crystallization (shaded areas) after ice–water quenching for 'even' as well as 'odd' polyamides. Above the glass transition the cold crystallization starts and extends over a very broad temperature range. The cold crystallization consists of two components: a fast cold crystallization giving rise to the sharp exothermal peak just above T_g, followed by a slower continuous exothermal process, which extends up to the beginning of the endothermal melting peak. The two crystallization processes are attributed to primary and secondary cold crystallization. They are the counterpart of the two corresponding processes which occur during dynamic crystallization from the melt[4]. The behaviour of polyamide-7, -8 and -9 agrees with the results already published for polyamide-6 and -6,6,[4–6]. Thus it is not justified to differentiate between the cold crystallization behaviour of 'even' and 'odd' polyamides.

The d.s.c. curves shown in *Figure 1* for the higher polyamides (-11, -12 and -15) have been obtained with samples which were quenched into liquid nitrogen. The main difference, as compared with the lower members, is that polyamide-11, -12 and -15 show only the secondary cold crystallization; the primary cold crystallization is missing. The same result is found for ice–water quenched samples of polyamide-11, -12 and -15. Neither types of quenching is very effective for the higher members. In liquid nitrogen the quenched sample is immediately surrounded by isolating nitrogen vapour, while the temperature of ice–water is not low enough, compared with the relatively low T_g values.

Even for polyamide-9 the liquid nitrogen quenching is incomplete. This is shown in *Figure 2*, which compares the curves of samples quenched into ice–water and liquid nitrogen, respectively. The sample quenched into liquid nitrogen has a strongly reduced primary cold crystallization peak, while the secondary cold crystallization is not changed.

From the d.s.c. curves in *Figure 1* the experimental values of heat fusion ΔH_m and heat of cold crystallization ΔH_c may be calculated by integration of the endothermal and exothermal peak areas. The difference ($\Delta H_m - \Delta H_c$) is roughly proportional to the crystalline fraction within the sample at the start of the d.s.c. thermogram. For the ice–water quenched samples of polyamide-6, -7, -8 and -9, ($\Delta H_m - \Delta H_c$) is found to be very small or even zero, while for the higher polyamides there is a considerable increase of ($\Delta H_m - \Delta H_c$) with increasing length of the CH_2 segment in the monomer unit. This means that, in the higher polyamides, present quenching procedures are unable to prevent primary crystallization during the cooling process.

In ref 1 only the *primary* cold crystallization was taken into account. However, an inspection of the published d.s.c. curves indicates that secondary cold crystallization is also present in ref 1, but has been overlooked. The main problem in quantitative discussion of d.s.c. thermograms is the baseline, especially if crystallization and melting extend over such a broad temperature range (about 200°C). In the present experiments the linearity of the baseline has been proved by measuring an amorphous polymer, thermally crosslinked polybutadiene, for which a linearly increasing specific heat has been measured within the temperature range under discussion. The absence of primary cold crystallization for polyamide-5 and -7 in ref 1 is most probably the consequence of insufficient quenching.

The d.s.c. thermograms in *Figure 1* show clearly that the quenched 'odd' polyamides undergo glass transitions, which has been denied by Lord[1]. The glass transition of the quenched samples is shifted to lower temperatures with increasing length of the CH_2 segment in the monomer unit. Except for polyamide-6, the cold crystallization process starts immediately at, or even below, the upper end of the glass transition range. This makes the T_g values, as well as the slope of the baselines in *Figure 1*, somewhat uncertain. Surprisingly, the glass transition of polyamide-11 occurs at a lower temperature than that of polyamide-12 and -15. A possible reason for this may be a higher monomer content of the polyamide-11 sample, which is known to have a strong influence upon T_g.

The glass transition has also been measured for samples

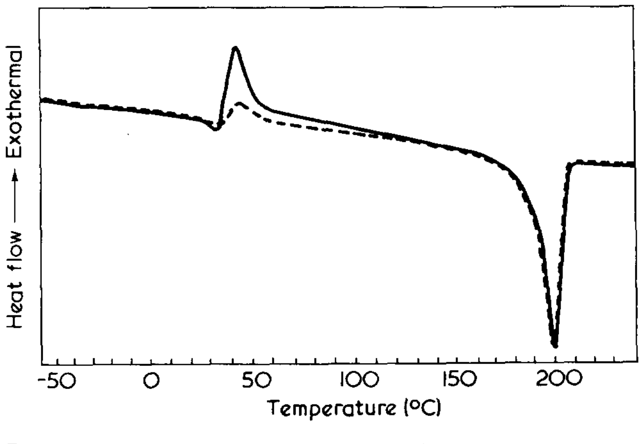

Figure 2 D.s.c. thermograms of polyamide-9: ———, quenched into ice–water mixture; – – – –, quenched into liquid nitrogen. Heating rate 20°C/min. Sample weight ~7 mg

Table 1 Glass transition temperature* of quenched polyamides after cycling to different upper temperatures. Heating and cooling rate 20° C/min

Upper temperature (° C)		Glass transition temperature (° C)					
		−6	−7	−8	−9	−11	−12
As quenched		47	35	30	27	~−20	~0
25	Increasing crystallinity	47	35	30	27	25	35
60		48	47	42	50	44	45
100		57	62	46	65	48	46
140		59	64	48	65	46	46
$>T_m$		57	60	47	65	45	42

* T_g is defined as the temperature where half of the sigmoidal c_p change has occurred

which, after quenching, have been cycled between −100° C and different upper temperatures, using heating and cooling rates of 20° C/min. With increasing upper temperature an increasing amount of cold crystallization develops, resulting in samples of increasing crystallinity. It is clear from *Table 1* that, with increasing crystallinity, T_g is shifted to higher temperature and this becomes more pronounced with increasing length of the CH_2 sequence. The first stage of cold crystallization has the strongest effect upon T_g. The glass transition temperature of the as-quenched samples decreases continuously with increasing CH_2-sequence length. In the semicrystalline state (upper temperature ⩾60° C) there is an alternation of T_g between 'even' and 'odd' polyamides, which is also known for their melting points[7].

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