The Melting Temperatures of 66/6 Copolyamides

SVEN SÖNNERSKOG

A-B Svenskt Konstsilke, Borås, Sweden

A series of 66/6 copolyamides have been prepared by hydrolytic condensation polymerization. Methods of purification and identification of macroscopic melting points are described. Factors, influencing the numerical value of the melting temperature, are discussed. Measurements, carried out on isotropic samples, show appreciable discrepancies from reference values in some cases.

The existence of sharply measurable melting temperatures of polyamides, polyesters and polyurethans is a notable exception from the general behaviour of high polymers. In most cases the melting points of these substances can be observed in the same way and with the same degree of accuracy as on corresponding monomers. This should be compared with the general case, where fusion without decomposition is a rare phenomenon, and, in the best cases, occurs over a range of temperatures. In terms of molecular structure, the temperature of melting is depending on the equilibrium degree of crystallinity. From thermodynamical point of view it is thus convenient to consider the melting as a first order transition where crystallinity completely disappears, and the melting temperature as the highest one, where traces of crystallinity can be detected [1].

Even if this idea is a sound basis for theoretical considerations, experimental difficulties limit the application. The precision of the measurements should be largely depending on the sensitivity of the method employed to detect traces of crystallinity, a circumstance giving preference to combined dilatometric and optical methods. The dilatometric method implies observation of the phase transition in the presence of a diluent. But in the case of polyamides inert, high boiling diluents are uncommon, and, moreover, the 6 polymer releases its equilibrium amount of monomer (caprolactam) at elevated temperature, which interferes with the solvent action of the diluent. It does not seem likely that a dilatometric measurement would give a higher degree of accuracy than a direct observation of the melting process, provided that proper directions are observed to obtain a reproducible structure of the samples. The more important details will be shortly discussed here.

Polyamides and polyesters may show very divergent degrees of crystallinity, even in the isotropic state, but before all in oriented specimens, such as extruded, quenched filaments and cold drawn or annealed fibres. The macroscopic melting point is depending on the difference in crystallinity. This dependence of the prehistory of the polymer has been observed to be valid for many macromolecular substances, but it is especially clearly expressed in a recent investigation on polyester fibres [2], where a gradual increase in melting point of 3° C is observed by a penetrometer technique, when the degree of crystallinity is increased from 38 to 65 %. The simplest way to avoid the influence of the crystallinity is, of course, to prepare all samples in an identical equipment and allow the molten polymers to solidify at rest by rapid cooling. Equivalent result would be obtained by dispersing the polyamide in a good solvent, such as formic acid, and gradually adding a non-solvent (acetone or water) until incipient precipitation occurs. At this stage a large amount of the nonsolvent is added, sufficient to cause a complete separation of the polymer.

An even more important source of error, however, is the inherent sensitivity of polyamides to oxydation in air, even before melting. Chips of 66 nylon melt sharply at 264° C in the absence of air, but as low as 248—256° on a melting block Maquenne [3,4]. Unfortunately 66 nylon shows the highest melting point and the least thermal stability of all the actual polyamides [6]. Pure 6 nylon, poly-(ε-caproamide), melts at 214° C in equilibrium with its monomer, which partly prevents an oxidation on the phase boundary. But the application of an inert atmosphere is necessary even here on prolonged heating.

It seems difficult to find a satisfactory explanation for the large difference in melting temperatures between 6 and 66 nylon. If we start from the general formulation of melting point as a ratio between latent molar heat of fusion and entropy of fusion of the repeating unit, a fairly small difference would be expected, as seen from the following formula of the building sequences:

$$—(CH_2)_4—CO—NH—(CH_2)_6—NH—CO— \qquad —NH—(CH_2)_5—CO—$$

Repeating unit of 66 nylon   Repeating unit of 6 nylon
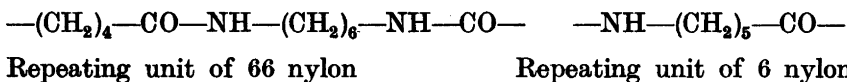
The two units show identical ratios between polar and non-polar groups. If any difference exists in the entropy change on fusion, the largest change would occur in the case of 66 nylon with asymmetric distribution of methylene groups.

The question has recently [5] been discussed from other points of view. In short, it seems clear that the "odd-even" effect, known from other homologous series of organic compounds, is of primary importance. At the ends of an odd methylene sequence, the bonds to the amide groups are inclined at an angle of 112°, when the ends of an even sequence are parallell. The analogy with energetic differences, arising from *cis* and *trans* isomerism, is apparent. Even if an exhaustive explanation is still remote, it is sufficient here to establish that steric differences between the structural units makes a mutual space unit cell impossible (isomorphous replacement). Condensation polymerization of caprolactam with increasing amounts of hexamethylenediammonium adipate would thus lead to a decrease in the melting point of the copolymer until a

Table 1. *Hydrolytic copolymerization of caprolactam and hexamethylenediammonium adipate.*

Comp. of reaction mixture. Per cent, (b. w.) of Nylon Lactam — salt	Lactam content after reaction, % b. w.	Content of 6-unit in *polymer,* as (mole ratio) × 100	Melting points, °C, uncorr.	Viscosity number, at 1 %, conc. in formic acid. Temp. 20.0° C
100 — 0	12.4	100	214	1.1
90 — 10	5.3	95	204	1.1
80 — 20	6.0	91	190	1.2
70 — 30	5.1	83.5	176	1.2
60 — 40	4.0	77	159	1.1
50 — 50	5.1	69	175	1.1
40 — 60	5.0	59.5	188	1.1
30 — 70	4.9	48.5	197	1.2
20 — 80	6.0	35.3	205	0.9
10 — 90	5.1	19.6	234	0.9
66 nylon chips (com. grade)			264	0.9

minimum is reached. At still higher contents of 66 salt, a gradual increase in melting point is expected up to the limit (264° C) found only for the pure 66 polymer.

Copolymers are somewhat rubbery in character before melting, a factor making the temperature of phase transition more difficult to observe. Slow heating is essential. The melt viscosity also appears to be higher than for pure
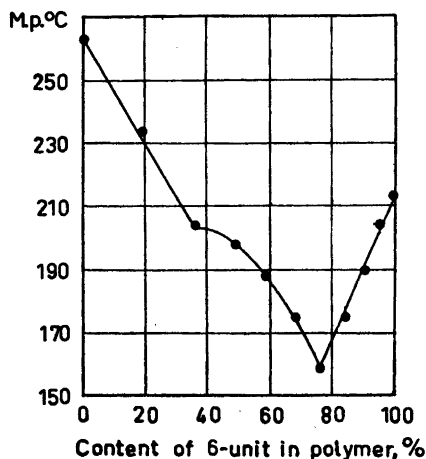

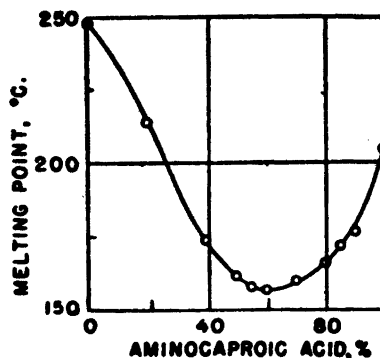Fig. 1. *The melting point of 6/66 copolyamides, according to the present investigation.*

·Fig. 2. *The melting point of 6/66 copolyamides according to Reynolds*[3] *and Catlin et al.*[4] *Reproduced by permission from the Journal of Polymer Science.*

polymers in the same range of molecular weight. This is most clearly expressed in the relation, found by Flory [7]:

$$\ln \eta = A + B \, M_w^{1/2} + E/RT$$

where η indicates the melt viscosity in arbitrary units, A and B constants, M_w the weight average molecular weight, E the activation energy of flow, R the gas constant and T the temperature in Kelvin units.

The discussion above has the purpose of searching out the main difficulties in carrying out melting point determinations on polyamides and copolymers. In the experimental part, the preparation and purification of a number of 66/6 copolyamides are described. On determination of their melting points, fairly large deviations are found from the figures in earlier references [3,4]. (Table 1, Figs. 1 and 2). The discussion above may be a guide to find an explanation for this discrepancy.

EXPERIMENTAL

Synthesis of 66/6 copolyamides, including pure 6 polymer.

Apparatus: Tubes of stainless steel, fitted with a cover and a needle valve as an in- or outlet for inert gases and water vapour. The steel tubes are shaped to contain a standard Pyrex test tube with an approximative volume of 50 ml.

Heating device: A cylindrical block of aluminium on an electrically heated plate. The metal cylinder contains six bores for the steel tubes at equidistant positions from the centre, where automatic control of temperature is applied.

Chemicals: *Caprolactam*, recrystallized from ethyl acetate and dried in a slow current of carbon dioxide at room temperature. Added to the reaction mixture as a saturated (80 % b. w.) aqueous solution.

Hexamethylenediammonium adipate. The commercial grade ("nylon salt") was dissolved in distilled water to give a 40 % aqueous solution. After filtering through a Pyrex C glass filter the solution was poured into a large excess of methanol. The transparent, large crystals appeared fairly slow, and only a main fraction was collected and dried in the same manner as the 6 monomer.

Schedule of reaction: Temperature range: 260 — 265° C. Time of hydrolytic polymerization step: 120 min. Gradual release of pressure and removal of water at atmospheric pressure: 120 min. Cooling to room temperature: 240 min.

Note: The water, removed from the reaction mixture, contains a noticeable amount of caprolactam. It was collected for determination of caprolactam, together with the water used in the subsequent purification of crude polymer.

Purification: The solid polymers are easily knocked free from the test tubes, especially if these earlier had been coated with a thin layer of a silicone oil. The rods were cut into pieces by sawing. The "sawdust" was collected and extracted in hot water for 24 hours together with the residue. After filtering the powder was dried, sieved and used for melting point determination. As a parallel test the large parts were dissolved in formic acid, precipitated with methanol, washed and dried. No difference in melting temperature was detectable even by the mixing of the two fractions. — The mother liquor was evaporated on a waterbath at reduced pressure. The residue was extracted with cold water. This fraction showed the melting point of caprolactam (70 °C) after recrystallization in ethyl acetate. The smaller, insoluble fraction was not studied further in this connection, but according to earlier work [8,9] its main components should be lower cyclic and linear oligomers. The amount of ε-aminocaproic acid formed during the reaction is known to be very low at high degrees of polymerization [8]. In fact, no change in solid content could be observed, when the water soluble fraction was passed over an anion exchanger of the strongly alkaline type. This seems to be in agreement with earlier work [9].

The precipitated polymers were also used for the determination of viscosity number (1 % solutions in 85.0 % formic acid at 20.0° C in an Ubbelohde viscometer).

Melting point determinations: A thin semimicro test tube was placed at the centre of a 50 ml Pyrex tube, containing a light silicone oil. The specimen in the inner tube was observed with a large pocket lens. Heating was carried out by an infrared furnace with a reflecting mirror as a bottom. The rate of heating was less than one degree min^{-1} above 150° C. A calibrated thermometer was selected with such a diameter as would just fill up the remaining volume of the inner test tube. Air was removed by flushing with dry carbon dioxide.

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