

An Application of Condensation Polymerization in Solid Phase

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A series of model filaments showing successively increasing molecular weights were prepared by hydrolytic polymerization of ϵ -caprolactam (in some cases with hexamethylenediammoniumdiadipate as a co-reactant) according to an easily reproducible schedule. The molten polymer was extruded as monofilament, quenched in cold water, washed, cold drawn and subjected to a hot stretching at 190°C. A change in tenacity and viscosity number was observed at prolonged heating in an inert atmosphere. Favourable conditions for reaching a high mechanical strength were found already at a *medium* molecular weight of the treated specimen (viscosity number 1.0—1.2 in formic acid). A further increase of molecular weight did not improve the tensile properties, probably due to unfavourable flow conditions in the spinnerette at high melt viscosities, or an increased degree of entanglement at high degrees of polymerization. This limitation can be avoided by extruding the primary polymer at a stage of medium molecular weight and subjecting the hot stretched filament to a continued polymerization in solid phase. The said operation causes a significant increase of the tensile strength if carried out in an inert atmosphere at a high permanent stress. The time of reaction should not exceed two hours at 190°C.

As repeatedly emphasized by Carothers¹, orientability and fibreforming properties in high polymeric systems are distinctive features of the linear molecules, intimately connected with their average absolute size. This means, among other things, that the average chain length should exceed a certain minimum (approximately 800 Å in the case of linear polyamides and polyesters). As a consequence, in polymer homologous series, the degree of polymerization has a marked influence on solubility and mechanical properties. Thus in 66 nylon² the tensile strength is known to increase in relation to the molecular weight, the increments being large in the region representing low and medium molecular weights but fairly low at higher ones. This saturation phenomenon is found in most linear macromolecular systems, for instance in fibres of polyethylene, polyvinyl chloride, polyacrylonitrile, polyamides, polyesters and cellulose acetate, but its physical significance is difficult to elucidate.

Table 1. Tenacity and viscosity number of cold drawn filaments, obtained from a polymerizing system of caprolactam, water and coreactant. (The hydrolytic reaction step is not included in the schedule but found in the experimental part below.)

Sample index	Time of reaction, min.	Viscosity number (in formic acid) * of polymer **				Tenacity, g/denier (aver. denier ~500)			
		I	II	III	IV	I	II	III	IV
1	0	part. sol.	0.48	0.50	0.48	{NOT FIBRE- FORMING			
2	15	0.48	0.53	0.56	0.50				
3	30	0.62	0.61	0.68	0.63				
4	45	0.88	0.94	0.98	0.77				
5	60	1.00	1.07	1.07	0.95	4.5	4.5	4.8	4.0
6	75	1.08	1.15	1.17	1.19	5.2	5.7	4.8	4.3
7	90	1.18	1.26	1.21	1.31	6.4	5.8	5.3	5.1
8	105	1.26	1.31	1.28	1.34	5.6	5.5	5.4	5.3
9	120	1.28	1.38	1.32	1.41	4.8	5.7	5.6	4.9
10	135	1.30	1.40	1.42	1.49	4.2	5.1	5.0	4.9
11	150	1.32	1.47	1.46	1.47	4.6	4.6	4.5	4.6

* Conc. of acid: 85 %

Conc. of polymer: 1.00 %

** Polymer I: pure poly ϵ -caproamide

II: 2 % coreactant

III: 5 % coreactant

IV: 7.5 % coreactant

The present paper deals with the tensile properties of homologous polymer series of ϵ -caprolactam and some copolymers with hexamethylenediammoniumdiadipate. Model filaments of the different polymers have been obtained by melt extrusion into cold water, followed by a "cold" stretching at room temperature. The latter operation is generally considered to develop a high mechanical strength in the direction of the fibre axis due to an increased orientation with subsequent formation of crystalline regions between adjacent molecules. It seems apparent, however, that a saturation effect enters at medium molecular weights, as shown in Table 1. As the possibility *a priori* must be precluded that the strength of oriented molecules rises to a maximum and then falls off, it appears reasonable to seek for an explanation of the actual discrepancy in some imperfections of the fibre, inherently connected with the molecular weight.

In the case of polyamides and polyesters it has generally been stated³ that molecular weight and melt viscosity are unambiguously dependent according to the formula:

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

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 expression emphasizes that the viscosity of the molten polymer rapidly increases at increasing degrees of polymerization. Its numerical value may well be above 10^6 cps

Table 2. A comparison, showing the ultimate strength and elongation at break for two types of fibres after rapid hot stretching at 190°C. (Fibres I:7—IV:7 are labeled as *medium* viscosity polymers, I:11—IV:11 as *high* viscosity polymers, in accordance with the preceding table.)

Fibre	Denier after stretching	Breaking load, kg (Scott tester)	Tenacity, g/denier	Ultimate elongation, %
I:7	420	2.75	6.6	11.8
II:7	442	3.02	6.8	12.7
III:7	469	3.21	6.8	12.0
IV:7	386	2.43	6.3	13.1
I:11	483	2.60	5.4	12.1
II:11	445	2.58	5.8	11.6
III:11	415	2.27	5.5	12.9
IV:11	501	2.81	5.6	13.7

at equilibrium in a polymerizing system. Such a dope shows a rheology similar to glass. On extrusion through a cylindrical orifice, especially at a low shear stress, all essential features of the liquid polymer will remain in the subcooled state, obtained by quenching in cold water. The behavior of this specimen at subsequent cold stretching will largely depend upon the internal friction. This magnitude has the same characteristics as viscosity and can also be estimated according to the cited formula. It leaves no doubt that a low temperature and a high degree of polymerization can cooperate in such a manner, that rupture occurs before cold flow ("necking") sets in.

Such a filament can be subjected to stretching at elevated temperature, even in the vicinity of its melting point ("hot stretching"), but experience shows that such an operation alone is insufficient to develop a high mechanical strength. Due to an increased molecular mobility above the second order transition temperature a hot stretching enhances the effect of cold drawing, as seen from Table 2, but is inefficient to impart a high degree of orientation upon the chain molecules directly from the isotropic state.

Another influence of molecular weight arises from the change in shape of the weight distribution function of the polymer at increasing extent of reaction. In the case of most probable distribution the weight fraction w_n showing a degree of polymerization n at an extent of reaction p is given by⁴

$$w_n = n \cdot p^{n-1} \cdot (1-p)^2$$

This function shows a distinct maximum already at $p = 0.9$, corresponding to an average degree of polymerization $n = 1/(1-p) = 10$, but is very broad at $p = 0.98$ ($n = 50$). The internal friction between single chain molecules can hardly be independent of this change of distribution, as it predicts the presence of an increasing number of *very* long molecules at high extents of reaction. This would increase the probability of chain rupture at cold drawing. In fact such a degradation has frequently been observed to judge from a slight but significant change of viscosity number.

Table 3. Tenacity and viscosity number of polyamide fibres on prolonged heating in an inert atmosphere at 190°C under stress (2 g/denier). Polymer I: homopolymer of caprolactam, polymer IV: copolymer (cf. Table 1).

Time of heating, min.	Type of fibre							
	Homopolymer				Copolymer			
	I : 7		I : 11		IV : 7		IV : 11	
	Tenacity g/denier	Visc. number	Tenacity g/denier	Visc. number	Tenacity g/denier	Visc. number	Tenacity g/denier	Visc. number
0	5.6	1.18	4.6	1.32	5.3	1.31	4.6	1.47
15	5.9	1.22	5.4	1.34	6.4	1.33	5.8	1.47
30	6.4	1.22	6.5	1.36	7.4	1.34	7.1	1.49
45	7.1	1.25	6.7	1.36	7.8	1.36	7.6	1.49
60	7.1	1.24	6.8	1.36	8.3	1.38	7.9	1.50
75	8.2	1.26	6.8	1.36	8.6	1.38	7.9	1.50
90	8.3	1.31	6.9	1.37	8.8	1.41	7.8	1.49
120	8.1	1.30	6.8	1.34	8.9	1.42	7.8	1.51
150	8.3	1.32	—	—	8.7	1.40	7.7	1.48
180	8.1	1.26	6.6	1.34	8.3	1.34	7.4	1.49
240	8.1	1.26	6.3	1.34	8.1	1.34	7.3	1.48

Chain rupture at cold stretching might also occur by a high degree of molecular entanglement (irreversible looping). Recent calculations⁵ on simplified models indicate that in polymerhomologous series this phenomenon increases in relation to the degree of polymerization. It is obviously also connected with the internal friction. Its influence on physical properties is wellknown from the theory of rubber elasticity and needs no discussion here. The absence of a network structure in the actual polymers does not principally prevent a qualitative comparison. At rapid plastic deformation (400—450 % elongation) of a polyamide fibre the internal friction acts in a similar manner as crosslinks in a network. In other words the time available for a long molecule to extricate itself from entanglements with adjacent ones is too short, resulting in chain rupture.

To sum up, the observed maximum of tenacity at medium molecular weights, observed in Table 1, appears to be a superposed effect due to gradually increasing imperfections of the fibre. Most of these can be avoided by selective choice of molecular weight and stretching temperature(s).

When the second stretching was carried out at 190° C on unstabilized polymer, an increase of viscosity number was observed on prolonged heating (Table 3), indicating that a continued polymerization in solid phase takes place. This statement is also valid for copolymers. Under carefully controlled conditions it gives a considerable increase of tenacity (Table 3) provided it is carried out at high stress (2 g/denier) in an inert atmosphere. This reactivity of polyamides below their melting point is known from previous investigations⁶ and considered to be a consequence of the accumulation of end groups in the amorphous phase, where chain mobility is high. A number of important appli-

cations of this effect seem to have been overlooked, before all its usefulness of eliminating imperfections in the weakest, most disordered regions of the polymer structure.

EXPERIMENTAL

Model filaments were prepared by hydrolytic condensation polymerization of ϵ -caprolactam and water. In some cases 66 nylon salt was added as a coreactant to increase the plasticity of the polymer on stretching (reducing the melting point and the second order transition temperature). The reaction was carried out in the absence of a chain stopper.

Apparatus: An autoclave of stainless steel, volume approximately 1 000 ml, fitted with a surrounding jacket (a cylinder of aluminium) serving as heat transfer medium from an electrically heated plate. Samples of the molten polymer were extruded during the reaction through a horizontally directed needle valve and a cylindrical orifice. As a mantle for heat control in the valve served an aluminium block, electrically heated by a copper-bolt, placed in a bore. This arrangement for extrusion proved to work very satisfactory by applying different pressures (carbon dioxide or water vapour) in the autoclave. At the beginning, *e. g.* when the melt is mobile and non-filogenic, great care must be exercised to avoid sprinkling of the hot liquid.

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

Nylon salt. The commercial grade was purified by dissolving in distilled water to give a 40 % (by wt.) aqueous solution, filtered and precipitated in a large excess of methanol, analytical grade. The alcohol was removed in a current of dry carbon dioxide at room temperature.

Schedule of reaction: The autoclave was charged with 750 ml aqueous solution of monomer(s). A first, hydrolytic reaction step was carried out at 260°C during 120 min. After release of pressure to 4 atm, polymerization was continued for another 2 h, when samples were drawn every 15 min from the heated bottom valve.

Purification: Rapid cooling of the model filaments in a water bath between extrusion nozzle and bobbin, followed by washing in water for 15 min and cold stretching to a draw ratio of 4.5. After a further extraction with water at room temperature the fibre was subjected to hot stretching at 190°C. Part of the cold drawn fibres were used also for measurements of primary tensile strength.

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