

A Semiempiric Model for Establishing the Drawability of Solution-Spun Linear Polyamides and Other Flexible Chain Polymers

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Synopsis

A series of high molecular weight, linear polyamide samples have been subjected to various solution spinning techniques, such as gel, wet, and dry spinning, in an attempt to produce high-tenacity filaments. The spinning experiments involved polyamide 6, polyamide 12, and copolymers thereof, with a molecular weight M_w in the range of 10^5 – 10^6 kg/kmol. Filaments with a tenacity of 100 cN/tex have been obtained. Their draw ratio never surpassed a value of six, which may also be reached after conventional melt spinning. Apparently, the drawability of polyamides cannot be improved via solution spinning techniques, although a favorable molecular topology for accomplishing high draw ratios has most likely been realized. This behavior is in sharp contrast with the highly increased drawability after solution spinning of less polar polymers, such as polyethylene or polyvinyl alcohol. A semiempirical equation is now proposed that relates the maximum drawability of flexible chain polymers with their polarity, being expressed in terms of cohesive energy. A pre-assumption underlying this equation is that drawability is not limited by a high entanglement density as is, e.g., the case after melt processing.

INTRODUCTION

The salient work on the gel spinning of polyethylene at the end of the seventies^{1–3} has led to a definite breakthrough in the preparation of high-strength, high-modulus fibers from flexible chain polymers. In the past decade this spinning method has been successfully applied to other more polar polymers as well, such as polyacrylonitrile,^{4–7} polyvinyl alcohol,^{8–10} and poly-L-lactic acid.¹¹

The essential part of the gel spinning method¹² lies in the possibility of drawing a polymeric material comprising a very dilute entanglement network to extremely high draw ratios. This procedure promotes a strong alignment and extension of the molecules in the draw direction and thereby accounts for the impressive mechanical properties that may be realized. A low entanglement density is accomplished by dissolving high molecular weight polymer at a low concentration in a suitable solvent. In subsequent spinning of the solution this low entanglement density is preserved through gelation crystallization behind the spinneret, followed by removal of the solvent from the gel fiber. The highly porous filaments thus obtained may then be superdrawn at temperatures close to the melting temperature.

The proper choice of a solvent can play a crucial role as was recently demonstrated by Leenslag et al. for PLLA.¹¹ In this case the production of high-

tenacity filaments appeared to be possible only after spinning from a specific solvent mixture.

In principle, however, the gel spinning method seems to be successfully applicable to all flexible chain polymers, provided that high molecular weight material is available, the material is able to crystallize in a well-organized manner (preferably with a zigzag chain conformation), and last but not least a suitable solvent in which thermoreversible gelation takes place, can be found.

For polyamide 6 these criteria also seem to be within reach and, therefore this article describes several gel—or more generally speaking—solution spinning attempts to produce high-tenacity filaments from this material. Such fibers would be of particular interest since they may be expected to exhibit a better temperature and creep resistance than, e.g., gel-spun polyethylene.

It will be shown, however, that in spite of applying the gel spinning procedure under appropriate conditions, the drawability of polyamide 6, as well as of polyamide 12 and copolymers thereof, is not increased. For this reason a model will be introduced that relates the maximum drawability of flexible chain polymers with their polarity, thereby assuming that a sufficiently reduced entanglement concentration is already present.

EXPERIMENTAL

Samples

Ultra high molecular weight polyamide 6, polyamide 12, as well as copolymers thereof have been synthesized via anionic polymerization of caprolactam and lauro lactam, respectively, in Carius tubes at a polymerization temperature of 160°C.^{13,14} Extreme care was taken to free the reaction mixture from oxygen and moisture before the polymerization was started. The molecular weight M_w of the samples ranged between 10^5 and 10^6 kg/kmol as determined from viscosity measurements in *m*-cresol. The linearity of the samples was explicitly checked and confirmed by correlating light scattering data with viscosity measurements.¹⁵

Spinning Experiments

Spinning experiments have been performed on a small-scale piston-driven spinning machine equipped with a single-hole spinning capillary ($D = 200 \mu\text{m}$, $L/D = 50$).

The spinning speed invariably amounted to approximately 2 m/min. Several spinning methods have been applied, such as gel spinning (quenching filament below spinneret in cold air promoting gelation crystallization), dry spinning (evaporating solvent below the spinneret with hot air), and wet spinning (using water for the coagulation bath). For further details of the spinning techniques we refer to the literature.¹⁶

Subsequently, the filament was freed from remaining solvent and hot drawn close to the melting temperature. Drawing took place through a hot tube flushed with nitrogen. The draw ratio was adjusted via the speed of the feeding and takeup roll. The drawing temperature was between 230 and 240°C, while the

drawing speed was approx 1 m/min. The draw ratio was calculated from the filament count before and after drawing.

Tensile Testing

Mechanical properties have been tested on single filaments at a clamping length of 10 cm and a tensile speed of 10 cm/min. The filaments have been conditioned at 20°C and 65% relative humidity. All the data are the average of 10 measurements.

DSC Measurements

DSC measurements have been performed on a Du Pont 990 thermal analyzer at a scan speed of 20°C/min. Sample sizes were between 1 and 2 mg. The melting temperatures quoted in this article are peak melting temperatures. Thermograms of the PA6 filaments were recorded under so-called constrained conditions. It means that a piece of a filament about 1 m in length has been tightly wrapped around a small aluminum frame with dimensions 4 × 4 mm. The frames were provided with a hole in their center to allow the fiber ends to be knotted onto the frame. Loose fiber ends were cut off. The reference pan was also filled with an aluminum frame.

RESULTS AND DISCUSSION

Spinning and Drawing of PA6, PA12 and Their Copolymers

Table I is a compilation of some spinning results obtained with PA6 samples having M_w of approximately 5×10^5 kg/kmol. In each case the polymer was dissolved at a concentration of ca. 10 wt %. The presented mechanical properties reflect the best values registered with the various spinning systems. The two solvent mixtures, i.e., *m*-cresol/glycol (60/40) and formic acid/1.4 butanediol (65/35) represent compositions in which PA6 can be brought to thermoreversible gelation at temperatures of 85 and 50°C, respectively. It should be noted

TABLE I
Survey of Various Spinning Attempts with PA6

Solvent	Solvent type ^a	Spinning technique	Max. draw ratio	Tenacity (cN/tex)	Modulus (cN/tex)	Elongation at break (%)
<i>m</i> -Cresol/Glycol (60/40)	I	Gel	5.5	68	940	9.0
Formic acid/1.4-butanediol (65/35)	I	Gel	4.0	78	1270	10.1
Formic acid	II	Dry + wet	5.9	84	870	17.3
Sulfuric acid (96–100%)	II	Wet	2.0	6	100	14.7
Ethanol/LiCl ^b	III	Dry	—	—	—	—
Formic acid/LiCl	III	Wet	4.2	57	660	9.3

^a I = solvent causing thermoreversible gelation, II = good solvent, III = solvent based on complex formation.

^b Filaments obtained from ethanol/LiCl were too brittle to determine mechanical properties.

that the examples in Table I represent only a minor excerpt of the various spinning systems that have been tried. Spinning from glycol and glycerol, for instance, required high spinning temperatures between 150 and 200°C, which caused severe degradation of the PA6. Also chemical modification of the PA6 with trifluoroacetic anhydride in dichloromethane to eliminate the possibility of hydrogen bond formation owing to acylation of the amide bond has been attempted. The resulting filaments proved to be fully amorphous and could not be collected.

The maximum draw ratio of all the fibers mentioned in Table I does not exceed that of an ordinary melt-spun yarn, which may usually be drawn to a ratio of six. The same holds for their mechanical properties, which are at best similar to those of a melt-spun yarn. From the viewpoint of handling and polymer stability (no degradation) the most attractive way of solution spinning PA6 appeared to be dry spinning of solutions of PA6 in a mixture of formic acid and dichloromethane.¹⁷ Such mixtures have an exceptionally low boiling point in a broad composition range, as can be seen in Figure 1. The optimum ratio of HCOOH/CH₂Cl₂, amounts to 40/60 w/w %, i.e., giving the best tenacity results, as shown in Figure 2, as well as easiest handling during spinning. These solutions were spun at room temperature into a drying shaft maintained at 100°C. The filaments appeared to be dry enough for collection, without sticking on the takeup roll positioned 1.5 m below the spinneret, the takeup speed being 2 m/min. Such dry-spinning experiments have been performed with PA6 samples of different molecular weights, each of the samples being spun at the appropriate concentration (Fig. 3). The mechanical properties of the filaments have been plotted as a function of draw ratio in Figures 4 and 5. It can be seen that at a fixed draw ratio both the tenacity and the modulus increase with

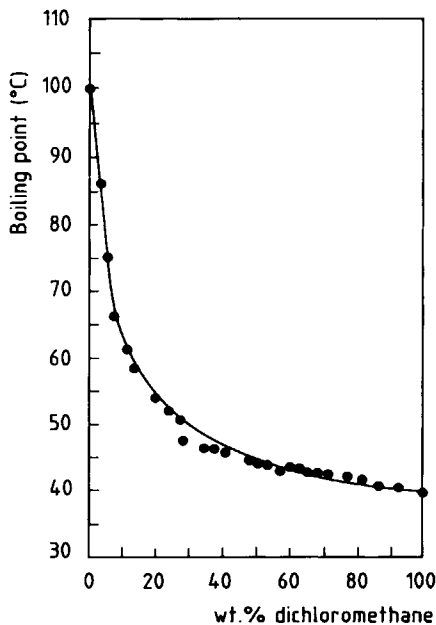


Fig. 1. Boiling point of CH₂Cl₂/HCOOH mixtures.

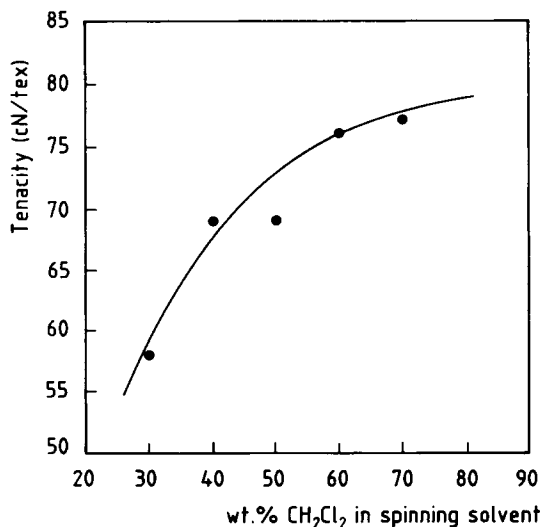


Fig. 2. Dependence of tenacity of PA6 filaments on the amount of CH_2Cl_2 in the spinning solvent ($\text{HCOOH}/\text{CH}_2\text{Cl}_2$) ($M_w = 5.5 \times 10^5$ kg/kmol).

molecular weight. On the other hand, the maximum draw ratio slightly decreases with increasing molecular weight. However, also with this spinning system, the tenacity never surpassed the standard tenacity level for a melt-spun PA6 yarn of approximately 80 cN/tex. Moreover the draw ratio always remained below a value of six.³²

For this reason some dry-spinning experiments were also performed with copolyamides derived from PA6 and PA12, again applying a mixture of 40/60 w/w % $\text{HCOOH}/\text{CH}_2\text{Cl}_2$ as the solvent. It was hoped that by reducing the crystallinity of the filaments the drawability could be increased. With the same objective a small amount of lubricant (Cetamoll 13, supplied by BASF) was included in the spinning solution. The results in Table II indicate a slight increase in tenacity to 100 cN/tex for a filament composed of PA6/PA12 (80/

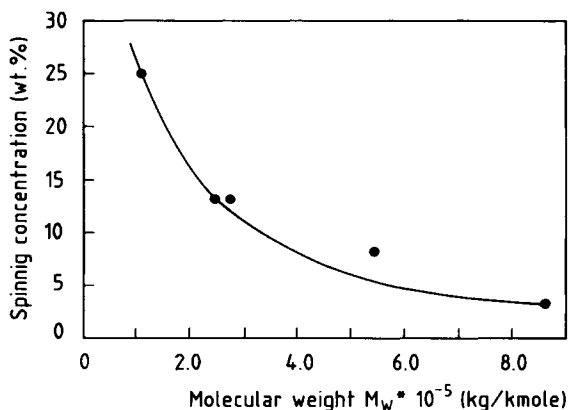


Fig. 3. Minimum spinning concentrations vs. molecular weight.

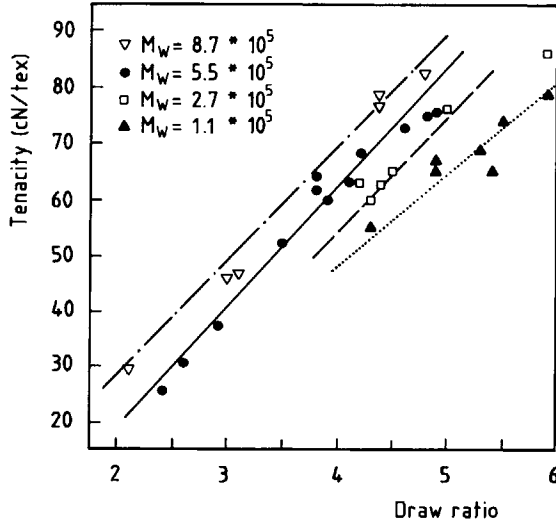


Fig. 4. Plot of tenacity vs. draw ratio for PA6 filaments spun from $\text{HCOOH}/\text{CH}_2\text{Cl}_2$ (40/60 w/w).

20) but no significant increase in drawability. All these attempts illustrate that the drawability of polyamide 6 cannot simply be increased by applying solution spinning techniques, irrespective of the use of high molecular weight samples and low spinning concentration. In this respect its drawing behavior strongly deviates from less polar polymers, such as polyethylene, polyacrylonitrile, polyvinyl alcohol, polypropylene, and poly-1-lactic acid for which superdrawing to high draw ratios has indeed been established.

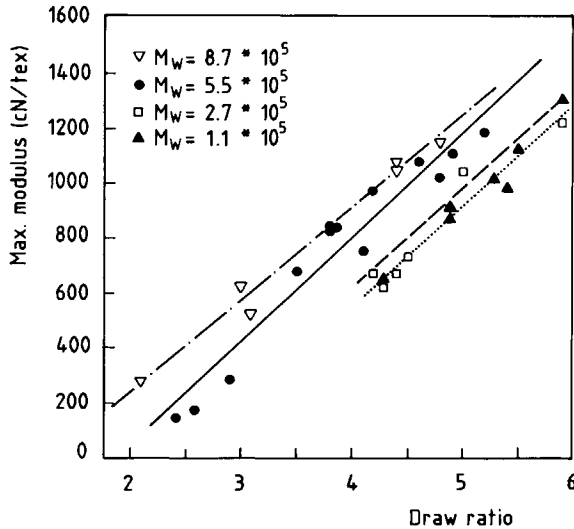


Fig. 5. Plot of maximum modulus vs. draw ratio for PA6 filaments spun from $\text{HCOOH}/\text{CH}_2\text{Cl}_2$ (40/60 w/w).

TABLE II
Mechanical Properties of Various Copolyamides Spun from HCOOH/CH₂Cl₂ (40/60 w/w)

Sample	Composition (mol %)	$M_w \times 10^{-5}$ (kg/kmol)	Draw ratio	Tenacity (cN/tex) ^a	Modulus (cN/tex)	Elongation at break (%)
PA12	100	3.1	5.5	49	500	11.0
PA6-12	20/80	5.5	6.0	55	680	10.9
PA6-12	50/50	5.5	5.5	68	800	17.0
PA6-12	80/20	5.5	5.3	100	1300	14.7
PA6	100	5.5	4.8	75	1120	10.8

^a 1 GPa = 88 cN/tex for PA6.

Clearly, the limited drawability of the polyamide 6 samples cannot be accounted for in terms of a high entanglement density, since the spinning concentrations applied were low enough to ensure the presence of a reduced entanglement concentration. One could argue that some reentangling may have occurred, especially in the course of dry spinning. However, it seems highly unlikely that the equilibrium entanglement topology as present in the melt can be restored on a time scale of seconds in the course of drying. So, one would at least expect some effect on drawability if entanglement density were the decisive factor. Moreover, the linearity of the PA6 samples has been checked, implying also that the possibility of chain branching hampering the drawing process can be excluded.¹⁵ Furthermore, the experiments with the copolyamides rule out the option of crystallites formed in the course of drawing, limiting further alignment.

Taken these considerations into account, it is most conceivable that the drawing of the polyamides is restricted by the presence of strong hydrogen bonds between amide bonds of neighboring chains. In the course of the alignment process, when the chains get straightened out, a number of strong hydrogen bonds is probably formed in a series of consecutive amide bonds.

For further alignment these hydrogen bonds will have to be broken and restored again. However, the energy required to disconnect approximately 5–10 H bonds will approach the amount needed to break a covalent bond.^{18,31} Apparently, this situation is reached at a draw ratio of six, and further drawing is accompanied by the cleavage of an increasing number of covalent bonds, ultimately leading to failure of the filament. In this respect it may be noted that the formation of radicals has frequently been observed for the drawing of polyamide 6.¹⁹

A point that needs some consideration is why a similar phenomenon does not take place in the drawing of PVA, since this material is also capable of hydrogen bonding. PVA is, however, a somewhat exceptional polymer in the sense that it is atactic but capable of crystallizing.²⁰ Owing to the irregular distribution of the hydroxyl groups along the chain, the formation of hydrogen bonds will be significantly disturbed. Moreover, the strength of H bonds between hydroxyl groups is³⁰ less than that of H bonds between amide groups. In the next section attempts will be made to account for these polarity effects on the relation between drawability and significant molecular parameters.

Drawability of Flexible Chain Polymers

As already stated, gel spinning followed by superdrawing has been attempted with several flexible chain polymers. Table III summarizes maximum draw ratio values attained for a list of polymers, showing clearly a decreasing value of λ_{\max} with increasing polarity of the corresponding polymer. Invariably the polymers were gel spun from relatively low-concentration solutions, which implies that reduction of the entanglement density in the as-spun fibers is not the only decisive factor for reaching high draw ratios. On the other hand the intrinsic maximum draw ratio of the various polymers may be predicted from the extensibility of isolated chains. According to Smith et al.²¹ λ_{int} may be estimated from

$$\lambda_{\text{int}} = (n \cdot l_p / c_\infty \cdot l)^{0.5} \quad (1)$$

where n is the number of bonds, l_p is the projection of bond length in chain direction, l is the bond length, and c_∞ is the characteristic ratio, a measure of chain flexibility.

Values for λ_{int} have been included in Table III as well, and they significantly deviate from the experimentally observed ones, with the exception of polyethylene. Obviously, a discrepancy may arise from the fact that actual drawing proceeds via a molecular network, i.e., the presence of junction points will limit the drawability. Moreover, some additional fluctuation may be expected due to effects of solvent quality,^{22,23} which can affect the nature of the entanglement distribution, i.e., a poor solvent quality promotes the formation of intramolecular entanglements, as well as the severity of the knots between molecules. However, the deviation of λ_{\max} from λ_{int} is widely different for the various polymers and seems to be growing with increasing polarity.

Having established this, we attempted to correlate the drawability of the polymers in various ways with their polarity, assuming that with increasing polarity more and more energy would be required to overcome the chain interaction in the alignment process. For this reason we tested the idea of maximum draw ratios being expressed in terms of a thermally activated process.

$$\lambda_{\max} = \lambda_0 \exp(-E/RT_d)^\alpha \quad (2)$$

in which E is an activation energy, R is the gas constant, and T_d the drawing temperature and λ_0 and α are adjustable parameters.

In a primary attempt it was tried to correlate λ_{\max} values with the heat of fusion ΔH_F or more correctly $C_p \cdot \Delta T + \Delta H_F$ as the activation energy. As can be seen from the data in Table III, however, there is virtually no correlation between λ_{\max} and these two quantities.

Actually, this need not be surprising. Generally, drawing of polymers to as high a ratio as possible is performed at temperatures close to the melting point. In fact the drawing temperature is frequently above the melting temperature of the as-spun material. Under such conditions the majority of the originally present poor crystallites will melt in the early stages of the drawing process,²⁴ while those that remain, presumably have a high pliability. This point may be illustrated with the DSC thermograms of as-spun and drawn PA6 filaments in

TABLE III
Correlation of Maximum Draw Ratio with Various Physical Parameters of Flexible Chain Polymers

Polymer	λ_{\max} (experimental)	T_{draw} (K)	$M_w \times 10^{-6}$ (kg/kmol)	Spinning concentration (%)	λ_{int}^a [from eq. (1)]	ΔH_f (kJ/kmol)	$C_p \cdot \Delta T + \Delta H_f$ (kJ/kmol)	E_{coh}^c (kJ/kmol)	$(E_{\text{coh}}/RT_d)^{0.5}$
Polyethylene ²⁶	100	423	1.5	5	94.0	7900	11,200	7120	1.42
Polypropylene ²⁷	47.5	413	3.4	1.5	77.4	9900	18,550	13,300	1.96
Polyvinylalcohol ⁸⁻¹⁰	30	493	0.4	9	67.1	6900	19,900	21,700	2.30
Polyacrylonitrile ⁴⁻⁶	28	473	1.3	5	56.3	5030	17,000	27,800	2.65
Poly-L-lactic acid ¹¹	20	477	0.9	4	—	—	—	21,100	2.30
Polyethylene- terephthalate ²⁸	10	513	—	40	78.8	23,500	92,750	54,600	3.58
Polyamide 6	4.8	503	0.87	4	90.7	22,600	59,640	79,800	4.37
	5.8	473	0.1	100					

^a Values based on a molecular weight M_w of 10^6 kg/kmol, taken as a first approximation since explicit data concerning M_w or MWD were lacking.

^b Values taking into account $\Delta T = T_{\text{draw}} - 298$.

^c Values corrected for drawing temperature, according to $E_{\text{coh}} = E_{\text{coh}_{298}} - R(T_{\text{draw}} - 298)$.

Figure 6. The applied drawing temperature $T_d = 235^\circ\text{C}$ is clearly above the melting temperature $T_m = 216^\circ\text{C}$ of the as-spun fiber. On the other hand the melting temperature of the drawn filaments, measured under constrained conditions—as is the case during drawing—is well above the drawing temperature.

Consequently, the mobility of the chains during drawing near T_m is primarily governed by interaction forces (van der Waals, dipole, and hydrogen bonds) in the liquid state. In the course of this process junction points (entanglements) will prevent the molecules from recoiling. Once the molecules have been

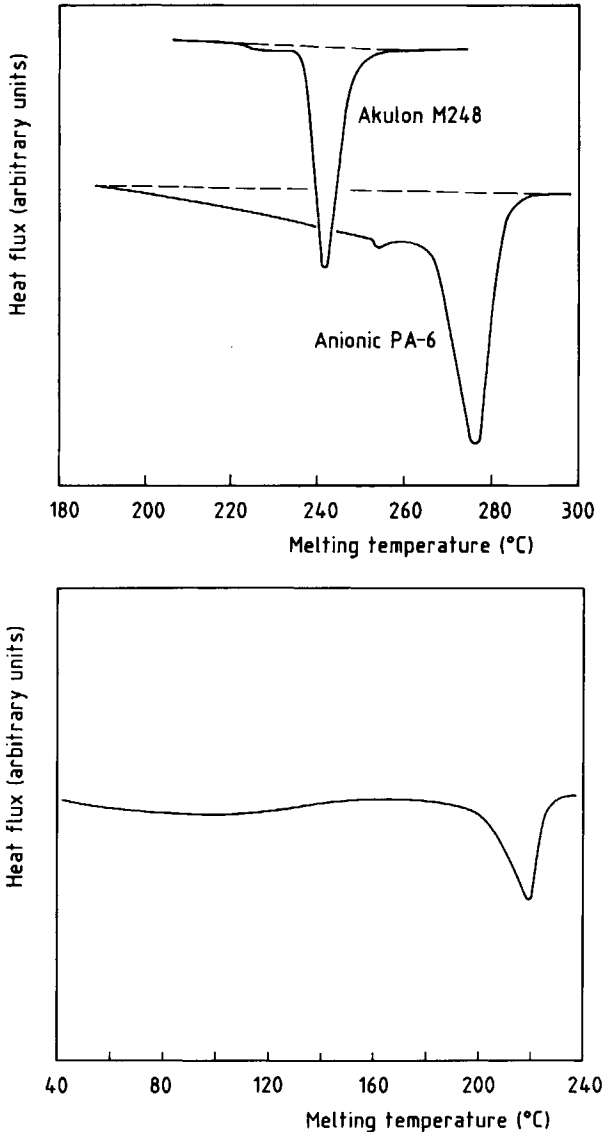


Fig. 6. Constrained melting endotherms of dry-spun PA6 filaments. Upper figure: as-spun filament from PA6 with $M_w = 5.5 \times 10^5$. Lower figure: drawn filaments from PA6 with $M_w = 1.1 \times 10^5$ (Akulon 248) and $M_w = 5.5 \times 10^5$.

straightened, however, recrystallization will take place, leading to the formation of a more perfect crystalline texture with a higher melting temperature (Fig. 6) after drawing. This mechanism leads us to believe that drawability may be correlated with the cohesion energy E_{coh} , which is the energy required to break all the intermolecular contacts in a liquid, and as such it may be connected with the activation step during drawing.

From the salient work of van Krevelen²⁵ it follows that E_{coh} may be considered as an additive property composed of contributions arising from the various interaction forces between the chains. In this way values for E_{coh} have been estimated for the polymers in Table III, taking into account the contribution for various structural units.

No value is listed for PA12 in Table III (and Ref. 25). However, for aliphatic polyamides E_{coh} is determined mainly by the contribution of the amide bonds, and therefore a value for PA12 will closely resemble the PA6 value. The values of E_{coh} have been adjusted to the drawing temperature.

A surprisingly good linear correlation is found between λ_{max} and $(E_{\text{coh}}/RT_d)^{0.5}$ as demonstrated in Figure 7. This value of 0.5 for the exponent may seem somewhat unexpected. However, $E_{\text{coh}}^{0.5}$ has been widely recognized as being proportional to molecular attraction forces, e.g., in the determination of solubility parameters.^{29,30}

In conclusion, the drawing behavior of several high molecular weight, scarcely entangled flexible chain polymers can properly be described by the following simple relation:

$$\ln \lambda_{\text{max}} = 360 \exp(-E_{\text{coh}}/RT_d)^{0.5} \quad (3)$$

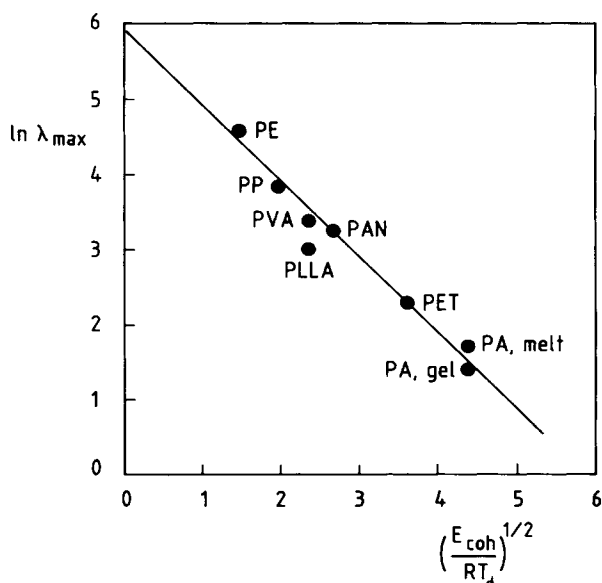


Fig. 7. Plot of maximum draw ratio λ_{max} vs. cohesive energy contribution for a series of flexible chain polymers.

Clearly, still much work has to be done to give the outcome of Eq. (3) a more solid physical background, especially with respect to the physical meaning of the preexponential. Nevertheless, using it in its present semiempirical state may be justified since it may serve as a first approximation of the maximum draw ratio to be expected after gel spinning and hot drawing of any flexible chain polymer.

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