

Theoretical study of the ultimate mechanical properties of poly(*p*-phenylene-terephthalamide) fibres

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(Received 11 March 1986)*

A stochastic model for failure of perfectly ordered and oriented polymer filaments, previously introduced, is used for a theoretical study of the factors limiting the ultimate mechanical properties of poly(*p*-phenylene terephthalamide) (PPTA) filaments. The approach is entirely microscopic and the inhomogeneous distribution of the external stress among atomic bonds near chain ends is explicitly taken into account. Both primary and secondary bonds are assumed to break during fracture of the filament. Stress-strain curves have been calculated for filaments of various (monodisperse) molecular weights at different temperatures. The predicted tensile strengths have been compared with related experimental values. The mode of failure and the lifetime under fixed strain conditions of PPTA filaments are also investigated and compared with those for polyethylene. Finally, the sensitivity of our results to the choice of values of the model's parameters is discussed and illustrated in a few special cases.

(Keywords: poly(*p*-phenylene terephthalamide); ultimate mechanical properties; stress-strain curves)

INTRODUCTION

A theoretical study of the mechanical properties of semi-crystalline polymers is extremely complex due to the many structural parameters that need to be considered, such as crystallinity, amorphous defects, trapped entanglements, chain ends and misalignments. For that reason, existing theories of the strength of polymeric materials are based on many simplifying assumptions with regard to both the structure of the solid and the failure mechanism. For example, Giffith-type approaches¹ assume that the solid is totally homogeneous except for the presence of relatively large cracks. These treatments fail to take into account molecular aspects such as the local distribution of stresses near chain ends and ignore all together the semi-crystalline nature of the polymer solid. On the other hand, kinetic theories of fracture commonly focus on only one mode of failure, i.e. merely primary bond breakage^{2,3}, or solely secondary bond breakage (i.e. pure slippage)^{4,5}, while both mechanisms are known to operate during fracture of polymer fibres⁶.

We have recently⁷ proposed a new approach for the theoretical treatment of the strength of polymer fibres, which takes both primary and secondary bond failure into account. The approach has been restricted to the case of ideal fibres made of a perfectly ordered array of fully extended macromolecules, with no defects other than chain ends resulting from finite molecular weight. This simplification of the macromolecular structure was made not only to avoid the complexity of a general treatment of the strength of polymer solids, but particularly to address the important issue of the so-called 'ultimate' mechanical properties of polymer fibres.

In our approach⁷, the fibre is modelled as a three-dimensional array of bonds which are viewed as coupled oscillators in a state of constant thermal vibration. The basic events are controlled by thermally activated bond breakages which are simulated with the help of a Monte-Carlo process that is based on the kinetic theory of fracture⁶.

This treatment has been successfully employed to study the ultimate mechanical properties of polyethylene⁷. In the present paper, it is applied to filaments comprised of perfectly ordered and oriented poly(*p*-phenylene terephthalamide) (PPTA) molecules; the macromolecules that constitute Du Pont's aramid fibre Kevlar[®]. The effects of molecular weight and temperature on the strength of the filaments are studied in detail and the results are compared with related experimental data. The mode of failure of PPTA fibres and their lifetime under fixed strain conditions are also investigated, and compared with those for polyethylene⁷. The sensitivity of the calculated results to the choice of values of the model's parameters is discussed and illustrated in a few special cases.

STOCHASTIC MODEL

The repeating unit of the PPTA molecule is represented in *Figure 1a*. The chain axis is oriented in the *y*-direction. In the lateral direction, each unit has 4 hydrogen bonds. For the purpose of simplicity of the model, these 4 bonds are evenly distributed in both the *x*- and *z*-directions⁸. A schematic representation of the PTA unit in the model is given in *Figure 1b* in which K_2 is the elastic constant for a hydrogen bond (so-called 'secondary' bond), whereas K_1 is for the PTA bond ('primary' bond). These units are arranged on a 3-dimensional simple cubic array of up to $8 \times 8 \times 500$ nodes, each node representing *m* chain units aligned in series along the *y*-axis. The elastic constant

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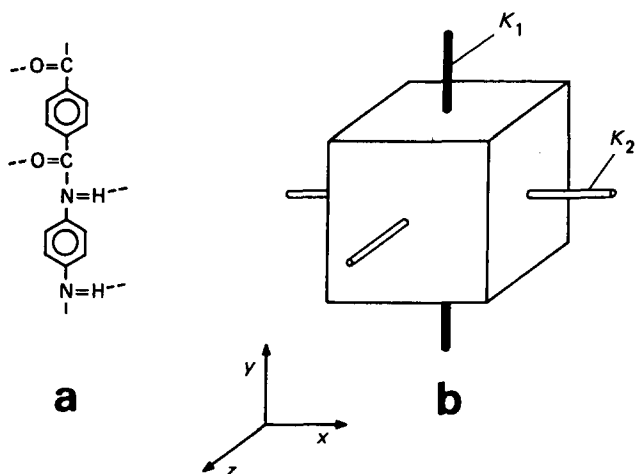


Figure 1 (a) The PTA repeating unit. (b) Schematic representation in the model with the four hydrogen bonds distributed evenly in the x - and z -directions. K_2 is the elastic constant of a single hydrogen bond, whereas K_1 is that of the PTA bond

between neighbour nodes in the transverse x - and z -directions equals $m \times K_2$, whereas that in the y -direction is K_1 . The array of nodes is strained at a constant speed; bonds are broken at a rate

$$v = \tau \exp[-(U - \beta\sigma)/kT] \quad (1)$$

with the help of the stochastic process described in ref. 7. In equation (1), τ is the thermal vibration frequency, T is the (absolute) temperature, β is an activation volume and σ is the local stress

$$\sigma = K\varepsilon \quad (2)$$

Here, K and ε are the elastic constant and the local strain, respectively. The bond breaking process and the subsequent relaxation of the nodes towards local mechanical equilibrium with their neighbours⁷, lead to motions of the nodes along the three coordinate axes. For simplicity, we assume that the motions along the x -, y - and z -axes are mutually independent and we focus on displacements in the y -direction, along which the filament is strained. Thus, the strain values ε (equation (2)) are for elongations along the y -axis and they represent either an axial tensile strain (for primary bonds) or a shear strain (for secondary bonds), K_2 being a shear modulus.

Approximate values of the parameters in equations (1)–(2) for PPTA, are as follows. The thermal vibration frequency τ is set to 10^{12} s^{-1} ⁷ and we choose $T = 296 \text{ K}$.

Primary bonds

The axial tensile modulus K_1 equals 200 GPa .⁹ Values of 40 – 45 kcal mol^{-1} have been recently reported¹⁰ for the activation energy, U , and we take $U = 45 \text{ kcal mol}^{-1}$ for the PTA bond. Values for the activation volume are difficult to determine experimentally. However, covalent bonds are known to break at $\varepsilon = 8$ – 10% strain which, by using equations (1)–(2), leads to taking $\beta = (2.37 \text{ \AA})^3$.

Secondary bonds

The shear modulus K_2 is set equal to the transverse modulus $K_T = 4.08 \text{ GPa}$.¹¹ For a single hydrogen bond, $U = 5 \text{ kcal mol}^{-1}$ ¹² and we choose $\beta = (2.5 \text{ \AA})^3$.⁷ Because there are m hydrogen bonds between two

neighbouring nodes in the transverse directions, we choose to break these bonds in groups of 7 units, at a rate given by equations (1)–(2) with $U = 7 \times 5 \text{ kcal mol}^{-1}$. $K_2 = 7 \times 4.08 \text{ GPa}$, τ and β having the same value as for a single bond. Note that the latter value $U = 35 \text{ kcal mol}^{-1}$ ensures that the hydrogen bonds in our model readily break, in the absence of stress, at temperatures above 250 – 300°C , which is the range of melting temperatures of hydrogen-bonded flexible polymers, such as nylon-6.

RESULTS AND DISCUSSION

Effect of the molecular weight on strength

Figure 2 shows a series of stress–strain curves calculated for PPTA filaments of various (monodisperse) molecular weights ranging from $M = 10\,000$ to $100\,000$. The molecular weight of a single PTA unit is quite large (238) so that the corresponding number of monomer units per macromolecule is low (42 to 420). Thus for $M = 10\,000$, there are at most 42 secondary bonds available for transferring the external load across chain ends. Since $K_1/K_2 = 50$, that number is insufficient to ensure total transfer of the tensile load. As a result, the filament is tested mainly in shear and the calculated modulus is relatively low and strongly dependent on M (see Figure 2 in which the theoretical modulus for infinite M is given by the slope of the broken line). That behaviour is unlike that previously observed⁷ for polyethylene ($K_1/K_2 = 100$). In polyethylene of, for example, molecular weight 10000, as many as 714 secondary bonds are available for the load transfer and the calculated modulus already equals that for infinite M .⁷

Finally, note that the elongation at failure for PPTA is of the order of a few per cent, corresponding to a time to fracture of $\sim 3 \text{ s}$, at a strain rate of $1/\text{min}$, which is in good agreement with experimental data⁵.

The computer results show that, for all the molecular weights studied, fracture of the fibre is a catastrophic process which is initiated through the breaking of a small number of primary bonds. These bond breakings occur near 6% local strain, at which point a high concentration of stress rapidly builds up due to the high concentration of

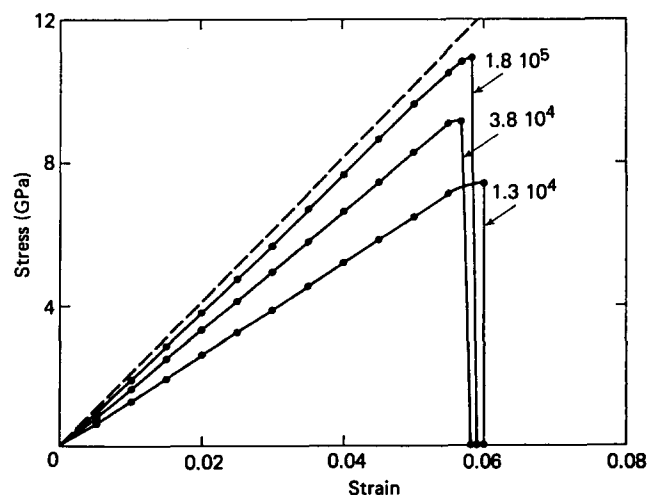


Figure 2 Stress–strain curves calculated for several PPTA fibres of various (monodisperse) molecular weights. The strain rate is $1/\text{min}$. The broken line indicates a slope equal to the theoretical modulus ($= 200 \text{ GPa}$)

chain ends. As a result, catastrophic failure occurs and the specimen rapidly breaks above 6% strain.

Figure 3 shows the calculated dependence of the tensile strength (maximum of the curves in Figure 2) on the molecular weight. Symbols indicate different values, used in the simulations, for the number m of PTA units per node. The tenacity/molecular weight curve in Figure 3 displays no simple power-law dependency. The lack of a simple relation is clearly due to the molecular weight dependence of the modulus at low M ($M < 10\,000$). At high M ($M > 100\,000$), the tensile strength asymptotically approaches the ultimate tensile strength, estimated to be about 15 GPa. In the range $10\,000 < M < 100\,000$, the tenacity varies with M approximately as $M^{0.4}$, as was observed both theoretically and experimentally for polyethylene^{7,13}. For $M = 20\,000$, our model predicts a strength of ~ 7.5 GPa. Experimental data of currently produced PPTA fibres (Kevlar[®] 29) of molecular weight $\bar{M}_n \sim 2 \times 10^4$, are a tenacity ~ 3.4 GPa and a modulus $E = 75$ GPa. Assuming, to a first approximation, that the tensile strength varies linearly with the modulus, these data would correspond, at our theoretical modulus $E \sim 150$ GPa (for $M = 20\,000$, see Figure 2), to a strength of around 6.8 GPa, in good agreement with our predicted value.

We have also investigated the effect of the choice of values for the model's parameters on the tenacity/molecular weight dependence. Thus, we tested the model using, for the activation energy of the PTA bond, the same value ($U = 25 \text{ kcal mol}^{-1}$) as that used for the primary bonds in polyethylene⁷. In order to ensure that the latter new value still leads to breaking of the PTA bonds at $\varepsilon = 8\text{--}10\%$ strain, we took $\beta = (1.40 \text{ \AA})^3$ for the activation volume of those bonds. Results obtained with the new set of values, with all other parameter values constant, are represented by the dashed line in Figure 3. These results reveal no change in the functional dependence of the strength σ on the molecular weight M . The effect of the new choice of parameter values is a shift of the σ vs. M curve towards lower values of the molecular weight.

Effect of the temperature on the strength

It is important to stress that this study deals exclusively with the effect of temperature on the fracture phenomena

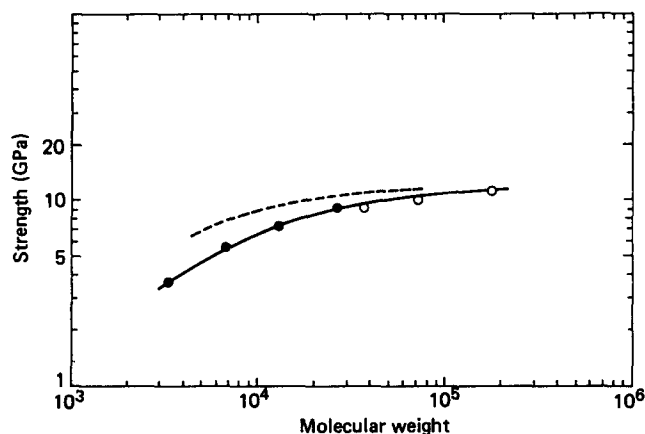


Figure 3 Dependence of the strength (maxima of the curves in Figure 2) on the molecular weight. The symbols are for different values for the number m of PTA groups per node (\bullet : $m = 7$; \circ : $m = 21$), taking $U = 45 \text{ kcal mol}^{-1}$ and $\beta = (2.37 \text{ \AA})^3$ for the PTA bond. The dashed line is for $U = 25 \text{ kcal mol}^{-1}$ and $\beta = (1.4 \text{ \AA})^3$ for the PTA bond

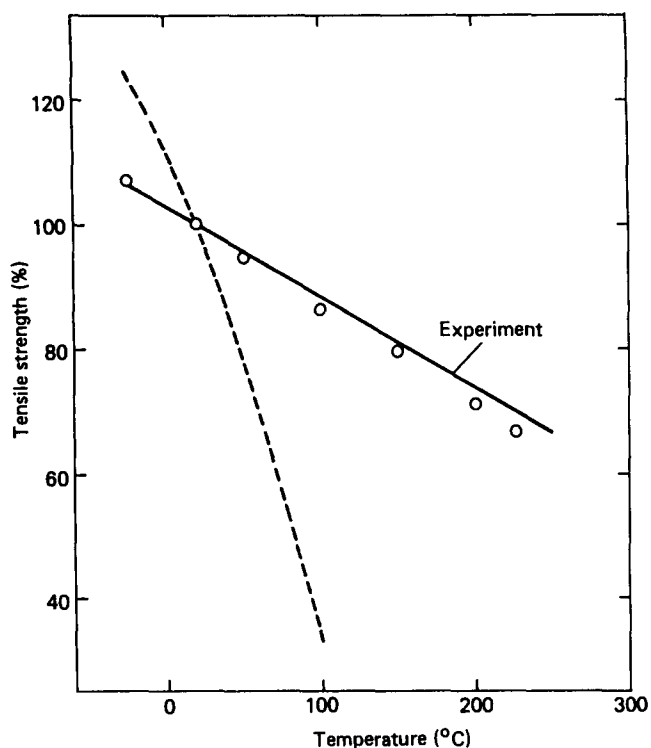


Figure 4 Dependence of the maximum tensile strength on temperature for PPTA. The strength is expressed as a percentage of its value at room temperature. The symbols (\circ) are for our model (with $U = 45 \text{ kcal mol}^{-1}$ and $\beta = (2.37 \text{ \AA})^3$) and a molecular weight $M = 40\,000$. The straight line indicates experimental data reported in ref. 5. The broken line is for $U = 25 \text{ kcal mol}^{-1}$ and $\beta = (1.4 \text{ \AA})^3$ for the PTA bond

initiated by the external stress (see equation (1)). In other words, we do not consider temperature effects on internal degrees of freedom, such as rotation and translation modes, so that the approach is incapable of describing the melting transition as well as the dependence of the moduli on temperature¹⁴. The present explorative study is nevertheless an instructive exercise that allows us to investigate the influence of temperature on the bond breakage process itself, and its limiting effect on the maximum tensile strength.

Figure 4 shows the temperature dependence of the maximum tensile strength for a molecular weight $M = 40\,000$. The tensile strength is a percentage of that measured at room temperature. Our results indicate that, up to 200°C , the failure of PPTA filaments is initiated through rupture of the macromolecules themselves, without any hydrogen bond failure (except at the point of catastrophic failure). Inspection of Figure 4 shows that our results for the strength are in quite good agreement with experimental data reported by Schaeffgen *et al.*⁵ This, in turn, confirms the good mechanical resistance of the hydrogen bonds at temperatures up to 200°C . Indeed, any hydrogen bond breaking in that temperature range, would have increased our calculated temperature dependence of the strength, thus leading to discrepancy with experimental data. Also represented in Figure 4 (broken line) are calculated results for the alternate choice $U = 25 \text{ kcal mol}^{-1}$ and $\beta = (1.4 \text{ \AA})^3$ for the PTA bond (see previous section above). These parameter values lead to an unrealistically strong dependence of the tenacity on temperature, which is not observed experimentally. This provides confidence in the initial choice of values for the PTA bond.

A different study of the effect of elevated temperatures on the tensile strength of PPTA filaments is presented in Figure 5. Here, the fibres were 'exposed' for various periods of time at temperatures ranging from 230°C to 270°C. Subsequently, their room temperature mechanical properties were calculated. The tensile strength of these 'heated' filaments is presented as a percentage of that of the unexposed fibres. The calculated data (solid lines) show that the tenacity of PPTA filaments starts to decrease significantly for long exposures at temperatures above 230°C. Further investigation reveals that this loss is due to a thermal degradation process of the PPTA macromolecules. Exposure for 1 day at 270°C, for example, was found to decrease the average molecular weight by a factor of about 2.7. The calculated tenacity values in Figure 5 have also been compared with experimental data¹⁵ obtained at slightly lower temperatures (200°C and 250°C, respectively). In view of the wide scatter in the experimental data and the many simplifying assumptions made in the model, the agreement is judged to be quite satisfactory. That agreement is a direct consequence of taking, from ref. 10, $U = 45 \text{ kcal mol}^{-1}$ for the activation energy of the PPTA bond¹⁶. Indeed, a choice $U = 25 \text{ kcal mol}^{-1}$ leads to important thermal degradation already above 100°C, whereas a higher value $U = 55 \text{ kcal mol}^{-1}$ leads to no degradation below 340°C, both these results are in disagreement with the experimental observations.

Comparison of the lifetimes of PPTA and polyethylene under fixed strain

In this work, we restrict ourselves to the molecular weights typical for the two types of high strength filaments, i.e. $M = 40\,000$ for PPTA and $M = 356\,000$ for polyethylene. Recalling our previous results: the 1 s breaking strain of perfectly ordered and oriented polyethylene at room temperature equals 3.3%⁷; that of defect-free PPTA equals 5.5%. Figure 6 shows the calculated (symbol ○) dependence of the log time to break on the external strain expressed as fraction of the 1 s breaking strain for the two polymers. The results show that polyethylene, despite its excellent short-time properties, exhibits poor long-term endurance.

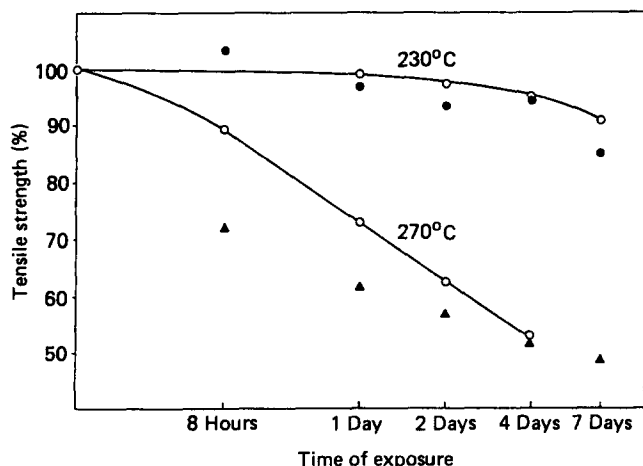


Figure 5 Maximum tensile strength for PPTA fibres exposed at high temperature and tested at room temperature. The strength is given as a percentage of its value for an unexposed fibre. The curves (—○—) are calculated for exposure at the temperatures shown. The other symbols are experimental data¹⁵ for exposure at 200°C (●) and 250°C (▲)

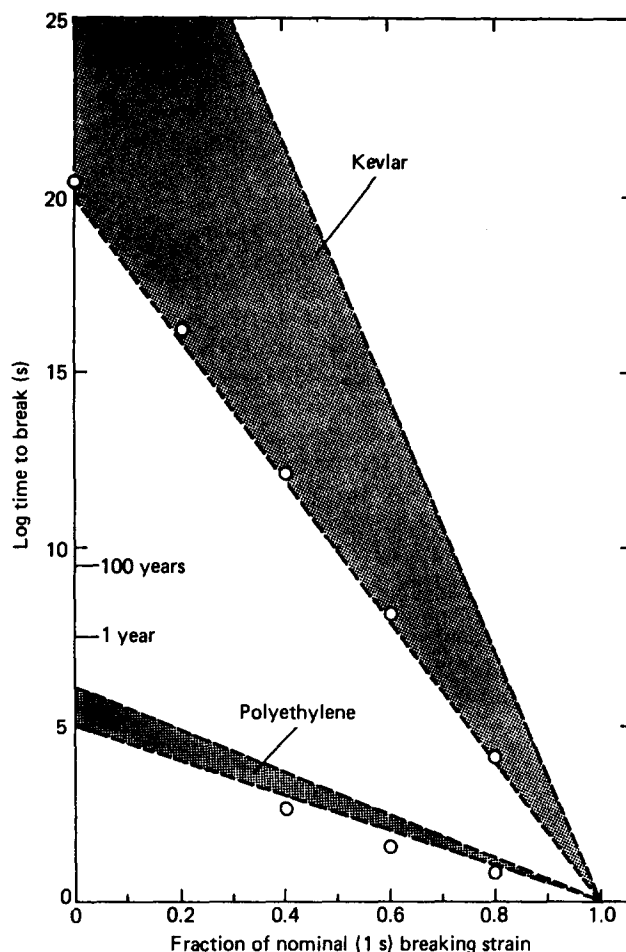


Figure 6 Dependence of the log time to break on the external strain expressed as fraction of the 1 s breaking strain. The figure is for testing at room temperature. The symbols (○) are calculated using a molecular weight $M = 356\,000$ for polyethylene and $M = 40\,000$ for PPTA. The shaded area shows the range of variability normally encountered experimentally, as reported in ref. 5

Polyethylene fibres, for example, fail in less than 2.5 min when strained to half their 1 s breaking strain. PPTA, on the other hand, is observed to exhibit an excellent creep rupture behaviour with a lifetime around 100 years at half its 1 s breaking strain. Figure 6 also shows the range of variability (shaded area) normally encountered in experimental values for the lifetimes of polyethylene and of PPTA⁵. Although these values are for a fixed load, they should also quite well describe the behaviour of the fibres under fixed strain conditions. Inspection of Figure 6 shows a good agreement between experimental and calculated values.

The modes of failure of PPTA and of polyethylene under fixed-strain conditions deserve some discussion. Fracture initiation is the same for both polymers and it proceeds through the breaking of a small number of primary bonds. As already discussed in the section above dealing with the 'effect of molecular weight on strength', fracture propagation is, however, different. For PPTA, a high concentration of stress rapidly starts to build up due to the high concentration of chain ends resulting from the small number of PTA units per macromolecule. As a result, catastrophic failure occurs and the specimen breaks in a brittle fashion. In polyethylene, on the other hand, the concentration of chain ends is much lower and the local stress concentrations arising from the few initial

primary bond breakings are distributed among the numerous neighbouring Van der Waals bonds. However, as these primary bond fractures increase in number, the stress concentration in the Van der Waals bonds also increases and secondary bond fracture occurs. As a result, failure of the specimen is accompanied by a creep-like mode of deformation.

Since fracture of both PPTA and polyethylene filaments is initiated through primary bond breaking, the good agreement between model and experiment in *Figure 6* is a direct consequence of the values used for the activation energies U for primary bond breakage, those for the activation volumes being of secondary importance. Using, for example, $U = 35 \text{ kcal mol}^{-1}$ (instead of 25 kcal mol^{-1}) for polyethylene yields a lifetime of about 1 month (instead of 2.5 min) at half the 1 s breaking strain, in disagreement with experimental observations. Our calculations demonstrate that higher values of U lead to longer lifetimes. Since high activation energies U for primary bond breakage also lead to high thermal resistance (see previous section), our model clearly indicates that long-term endurance is an intrinsic property of high melting polymers.

In summary, we have presented a theoretical study of the factors limiting the ultimate mechanical properties of PPTA filaments. Our results are in good agreement with available experimental data and they provide strong support to the usefulness of the model and to the choice of its parameter values.

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