end-to-end distance and radius of gyration.

To find the relationship between the simulation data studied here and macroscopic experimental observation of the melting rate, one must assume that the melting process occurs one layer after the other and also that any one extended chain molecule is totally molten as soon as its end-to-end distance (or radius of gyration) reaches the random coil value in the three-dimensional melt. The melting rate observed experimentally can thus be connected with the rate constant λ_{eed} or λ_g. Based on eq 6 therefore, the melting process simulated here could be called "nucleation-controlled". However, in our computer simulation only one extended chain, rather than a layer of extended chains, was taken into account. The price of such a simplification is thus paid by a decrease of interactions between the selected chain and its neighbors (as given by eq 4). Therefore, the melting rate in our simulated data should be considerably speeded up.

Assuming that the rate of the melting process could be described by the simulated data here, typical experiments are 4–5 orders of magnitude slower. By use of data on the melting kinetics of extended chain PE crystals, melting rates of 0.1–1 μm/s have been detected.[10]

Three reasons may account for this discrepancy. The first one has already been detailed above; i.e., our simulated data are for one extended chain only, not for one layer, and even less for observable macroscopic crystal thicknesses. The second may be that the coefficients of the interaction in eq 1–4 were not properly chosen. They may cause too few or too small an interaction between the chain and the simulated crystal surface. This is reflected also in the fact that melting as simulated occurs even at temperatures lower than the equilibrium melting temperatures ($T_m^\circ = 414.3(N - 1.5)/(N + 5.0)$, where N is the number of CH_2 groups).[1] The third reason may be that there is a pause after completion of the melting of the first layer until the second layer is molten; i.e., one may assume one must first produce "molten nuclei" on each layer. Overall, the first two reasons are very likely; the third is more speculative.

Further work is thus necessary in two directions: first, to search for the relationship between λ and crystal melting rates, and second, to extend our simulation to multiple chain systems and introduce defects on the crystal surface in order to fully understand polymer crystal melting in a molecular level.

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Kinetic Model for Tensile Deformation of Polymers. 3. Effects of Deformation Rate and Temperature

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ABSTRACT: This paper describes a theoretical and experimental study of the effect of temperature and deformation rate on the drawability of melt-crystallized flexible polymers of monodisperse molecular weight. The theoretical part of this study employs the kinetic model described in parts 1 and 2. Application to monodisperse polyethylene shows that, for each molecular weight, there exists a very narrow temperature or elongation rate window within which maximum drawability occurs. These theoretical predictions are compared against experimental results reported in the literature and those obtained in a study of the temperature and elongation rate dependence of the maximum draw ratio of melt-crystallized near-monodisperse linear polyethylene ($M_w = 125000$). The theoretical results are found to be in semiquantitative agreement with experimental observations.

Introduction

In preceding papers, we introduced a kinetic model for tensile deformation of polymer solids.[1,2] In this model, the polymer solid is represented by a loose network of entangled chains that are tied together through numerous weak (van der Waals) bonds. Upon tensile deformation, these bonds are broken, and the chains are deformed and are allowed to slip through entanglements with the help of a Monte Carlo process based on the Eyring chemical activation rate theory. This model was developed as a first attempt to quantitatively predict the stress/strain behavior of solid polymer materials, including effects of molecular weight distribution, temperature, and deformation rate, and to forecast the complex morphological and orientational phenomena that occur during deformation.

In the current series, this model is applied to the tensile drawing behavior of semicrystalline linear polyethylene. Part 1[1] describes a brief study of the influence of chain length of melt-crystallized solids; part 2[2] deals with the effect of the entanglement spacing (varied through, for example, solution-crystallization techniques[3]) on the deformation behavior of high molecular weight polyethylene.

The present study focuses on the important effects of temperature and elongation rate on the drawing behavior, particularly on the maximum draw ratio, of melt-crystallized, monodisperse polyethylene. The latter quantity is of obvious interest, since it has been shown to be the primary factor controlling the orientation, and therewith the mechanical properties, of flexible polymers. Already in the early studies by Peterlin and co-workers[4,5] on plastic deformation of polyethylene, it was recognized that the temperature and rate of deformation strongly affect, among other properties, the maximum draw ratio. These authors discovered that, for their relatively low molecular weight polyethylene (M_n = 5000 and M_w = 80 000), there appeared to be a temperature range from 50 to 70 °C where maximum draw was obtained. At temperatures both below and above this range, failure occurred at lower draw ratios. These observations were confirmed by Ward and coworkers (e.g., ref 6 and 7) and extended to melt-crystallized polyethylenes of a wide range of molecular weights. In addition, the latter authors established the important experimental fact that, for their (polydisperse) polyethylenes, the temperature for maximum draw increased with increasing molecular weight. These results seemed to indicate that, for each molecular weight, there may exist an optimum draw temperature and most likely—because of time/temperature superposition principles—draw rate. As a matter of fact, Kanamoto et al.[8] recently reported such a rate effect in a careful study of experimental conditions on the maximum draw ratio of solution-crystallized ultrahigh molecular weight polyethylene. Careful examination of the results obtained in earlier experimental studies[9] suggests that polydispersity might obscure such time/temperature windows for maximum draw. In view of the rare availability of polyethylene of narrow molecular weight distribution, the search for these optimal drawing conditions was considered to be a problem exceptionally well-suited for exploration with our kinetic model for polymer deformation.

Indeed, application of the model to monodisperse polyethylene shows that, for each molecular weight, there exists an optimum temperature or elongation rate window within which maximum drawability occurs. Experimental results for (near) monodisperse polyethylene with M_w = 125 000 are found to be in qualitative agreement with the theoretical predictions.

Theoretical Section

For a detailed description of the kinetic model and values of its parameters, the reader is referred to parts 1 and 2.[1,2] In the present work, we neglect the temperature and/or strain rate dependence of the values of the moduli, activation energies, and volumes used in the model. In other words, the model describes the effects of testing conditions only on the van der Waals bond breakage and chain slippage processes. In addition, the effect of initial crystallinity on the drawing behavior is not considered explicitly (see ref 1). All simulations are for (near) *monodisperse* (see ref 2) polyethylenes of molecular weights in the range 6800 < M < 256 500.

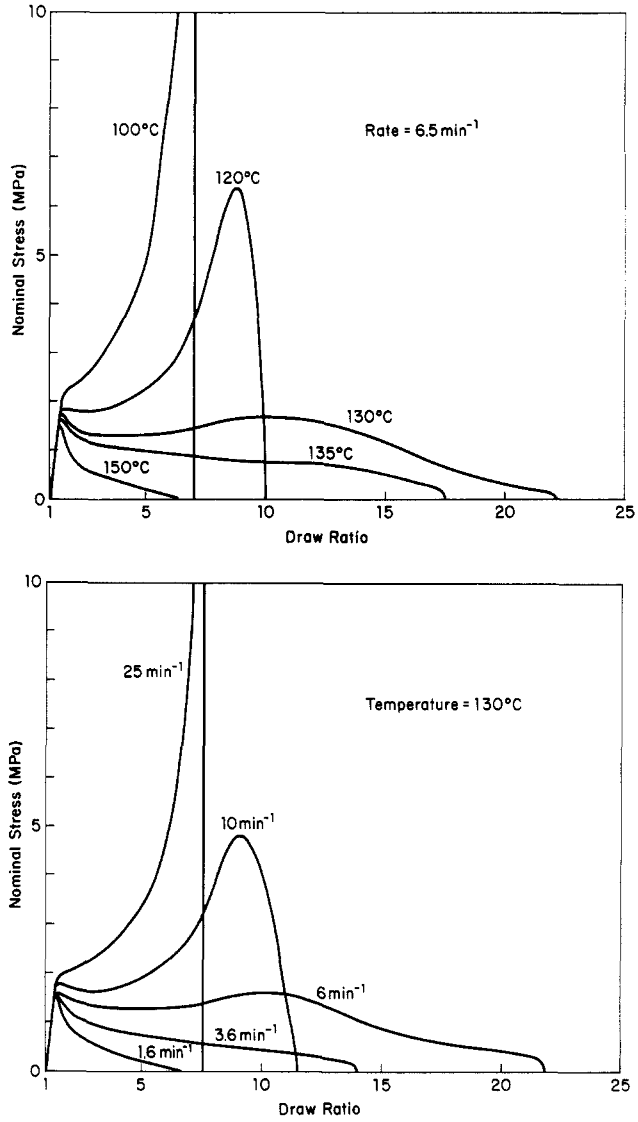

Figure 1. Calculated nominal stress/draw ratio curves for (close to) monodisperse linear polyethylene with M = 143 000. (a, top) Effect of temperature of deformation, at an elongation rate of 6.5/min. (b, bottom) Effect of rate of deformation at 130 °C.

Experimental Section

Material. The experimental part of this study was performed employing NBS SRM 1484 linear polyethylene. According to the supplier, this polymer has a (close to) monodisperse molecular weight distribution with M_n = 111 000 and M_w = 125 000.

Techniques. Polyethylene films having a thickness of about 100 μm were prepared by compression molding at 175 °C and subsequent quenching, from the melt, to room temperature. Dumbell-shaped specimens of 1 mm width and 6 mm gauge length were cut from these films. The tensile deformation behavior of these specimens was investigated over a wide range of rates of elongation and temperatures by using an Instron tensile tester (Model 1122) that was equipped with a temperature-controlled environmental chamber.

Results

Figure 1a shows a series of nominal stress/draw ratio curves for monodisperse polyethylene (M = 143 000) calculated at different temperatures of deformation. The elongation rate, referring to the rate of extension/*initial* specimen length, was kept constant at 6.5/min. At low temperatures (T < 100 °C), the computer results show an important strain-hardening effect immediately after the

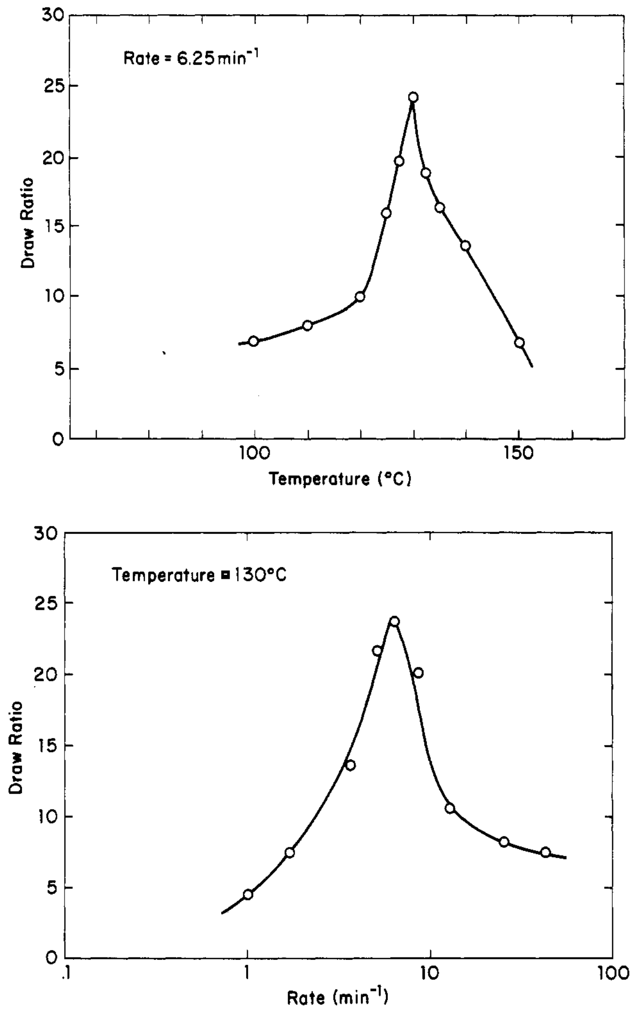

Figure 2. Calculated dependence of the maximum draw ratio on testing conditions for polyethylene with M = 143 000. (a, top) Dependence on temperature at constant elongation rate (6.5/min). (b, bottom) Dependence on elongation rate at constant temperature (130 °C).

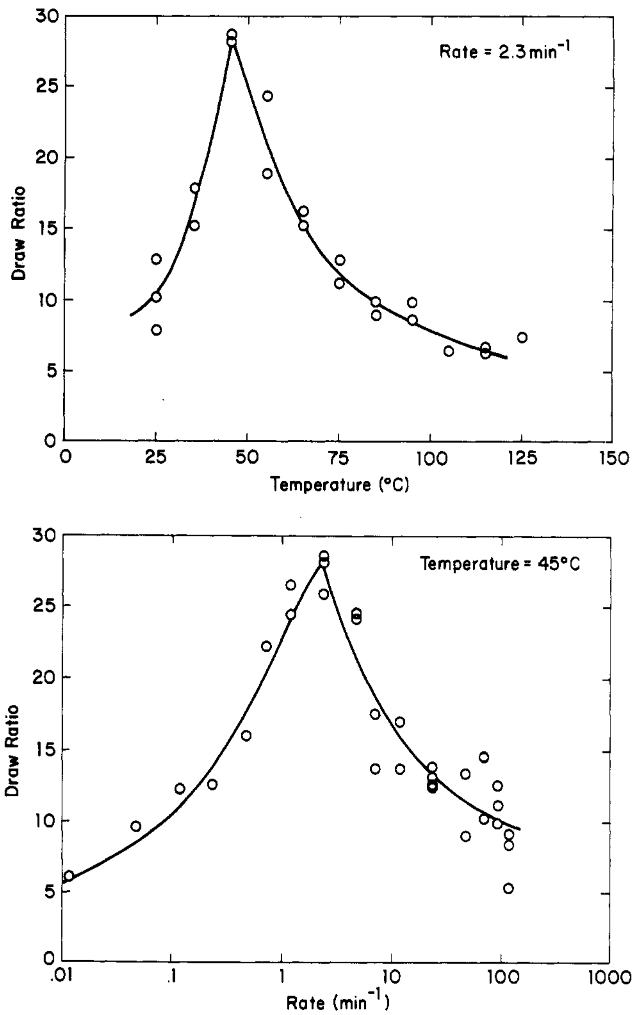

Figure 3. Experimental data of the dependence on testing conditions of the maximum draw ratio of polyethylene (NBS SRM 1484 M_n = 111 000; M_w = 125 000). (a, top) Dependence on temperature at constant elongation rate (2.3/min). (b, bottom) Dependence on elongation rate at constant temperature (45 °C).

yield point. This effect is due to a straining of the molecular chain strands between entanglements which break at their maximum draw ratio. For the network, this maximum draw ratio is given by the relation

$$\lambda_{\max} = n^{1/2}\, 3^{1/2} \tag{1}$$

In eq 1, n denotes the number of statistical segments between entanglement points, whereas $3^{1/2}$ is due to geometric considerations.[10] For melt-crystallized polyethylene, $n = 14^3$ so that, at 100 °C, catastrophic failure of the specimen is expected to occur at a draw ratio $\lambda_{\max} = 6.5$, as is found in the calculation (Figure 1a). When the temperature is increased (T = 120–130 °C), a smoothening of the strain-hardening effect is observed. Inspection of the computer results shows that this smoothening is a result of slippage of chains through entanglement points: a process that is exacerbated at elevated temperatures. Chain slippage leads to an effective increase in the number (n) of statistical segments between entanglements and, therefore (see eq 1), to an increase in the draw ratio at break. Simulations carried out at temperatures exceeding 130 °C show that chain slippage becomes substantially faster than the elongation rate. This causes a continuous decrease of the stress past the yield point and a lowering in the largest attainable draw ratio. These results point to the existence of an optimum temperature for the achievement of maximum draw. For monodisperse polyethylene of M = 143 000 elongated at a rate of 6.5/min, this temperature is predicted to be around T = 130 °C (see Figure 1a).

Figure 1b, also for M = 143 000, shows the effect on the stress/draw ratio curve of varying the elongation rate at constant draw temperature (T = 130 °C). Inspection of these results reveals that decreasing the elongation rate has an influence similar to increasing the temperature (cf. Figure 1a). This is, of course, not a surprising finding since it is obtained with a model which employs a thermal activation rate approach to deformation.

Parts a and b of Figure 2 summarize the results of, respectively, the temperature and rate dependence of the draw ratio at break for the monodisperse polyethylene of M = 143 000. These plots unveil the existence of a very narrow temperature (at constant rate) and rate (at constant T) window within which maximum draw occurs. Under these optimum conditions, a maximum draw ratio of 23 is found.

Parts a and b of Figure 3 show experimental data of the maximum draw ratio—at various temperatures and elongation rates—of the NBS polyethylene sample with M_w = 125 000. These data are in good qualitative agreement with the theoretical results (Figure 2), which were obtained for monodisperse polyethylene of approximately the same molecular weight. Quantitative agreement is found between the theoretically predicted and experimentally observed values of the maximum draw ratio of, respectively,

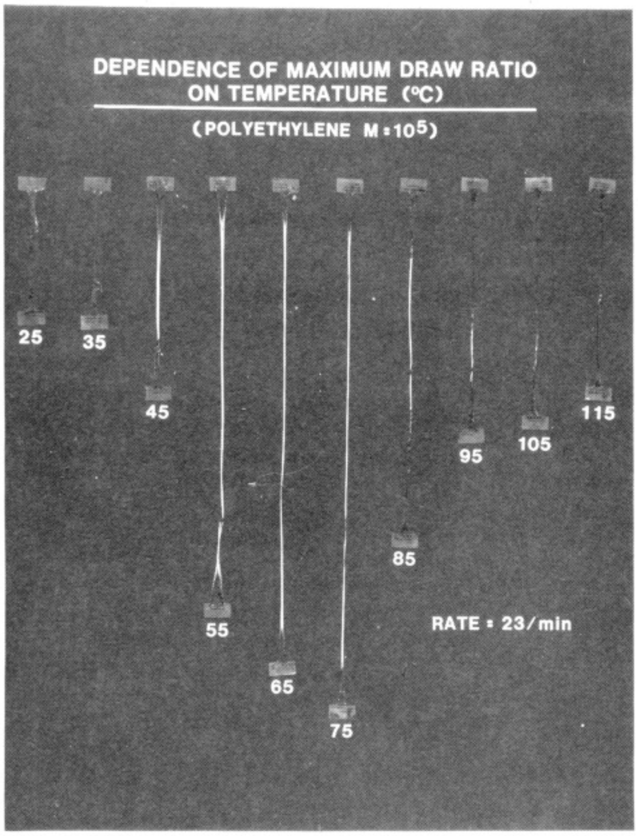

Figure 4. Actual NBS SRM 1484 polyethylene samples drawn to break at different temperatures. The elongation rate was 23/min.

~23 and ~28. Note, also, the striking asymmetry in the experimental curves of Figure 3 for the dependence of the draw ratio on temperature and elongation rate. The curves exhibit a plateau at too low temperatures (too high rates), whereas a continuous decrease in draw ratio is observed as temperature is increased (or rate is decreased) past its optimum value. That behavior is very similar to that observed in the simulations (Figure 2). This agreement leads to further support for the interpretation of the above phenomena in terms of thermal activated slippage of chains through entanglements.

Unlike the values for the maximum draw ratio, the predicted and observed optimum temperature or rate windows differ significantly (Figures 2 and 3). Good quantitative agreement between theory and experiment can be obtained by adjusting in the model the value for the activation energy (or volume) for chain slippage. This is, however, beyond the scope of the persent work, and no parameter fitting has been attempted in the calculations of Figure 2.

Figure 4 displays some of the NBS polyethylene samples drawn to their breaking point at different values of the deformation temperature and at a constant elongation rate of 23/min. It is self-evident that, for this particular rate, the optimum drawing temperature is around 75 °C.

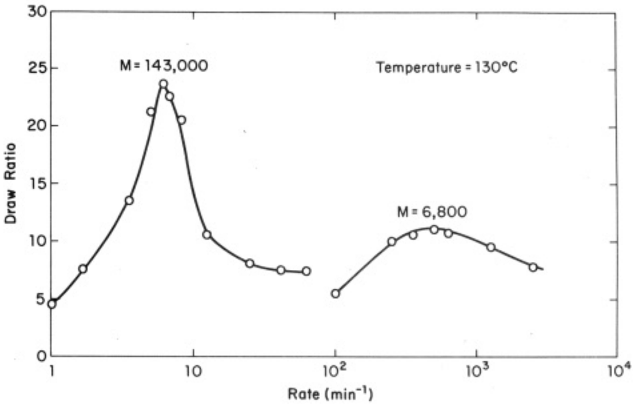

Figure 5. Calculated dependence of the maximum draw ratio on elongation rate for $M = 143\,000$ and 6800. The drawing temperature was set equal to 130 °C.

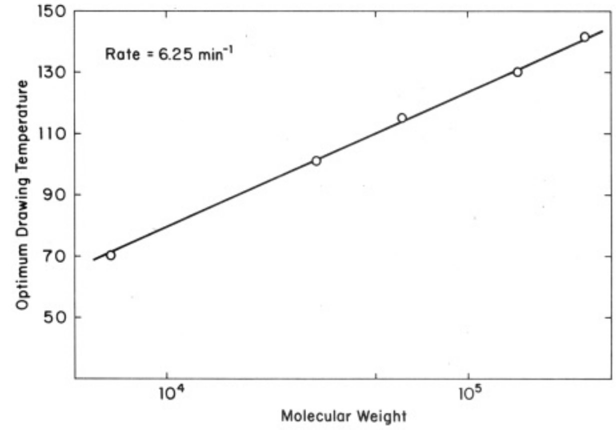

Figure 6. Plot of calculated optimum drawing temperatures versus log molecular weight of (near) monodisperse polyethylene. Elongation rate equals 6.25/min.

In subsequent simulations, we explored the molecular weight dependence of these "optimum drawing windows" of the deformation temperature and rate. Figure 5 shows a plot of the maximum draw ratio versus rate of elongation at a constant temperature of 130 °C for two monodisperse polyethylenes having widely different molecular weights. This figure shows that increasing the molecular weight from 6800 to 140 000 leads to a drastic reduction of the optimum deformation rate (from, respectively, 50 to 6 min^{-1}) and of the width of the "rate window". Figure 5 also reveals that the maximum attainable draw ratio increases at increasing molecular weight: from ~11[11] to ~23 for, respectively, $M = 6800$ and $M = 143\,000$. This is due to the fact that the latter quantity ultimately is determined by the largest number of statistical segments between entanglements that can be reached through slippage before disentanglement occurs.

Simulations carried out at constant elongation rate and varying temperature of deformation showed that increasing molecular weight leads to higher temperatures for optimum deformation, which is in accordance with experimental observation (see, e.g., ref 6). This effect is presented quantitatively in the graph of Figure 6 which shows the dependence of the calculated optimum drawing temperature versus (log) molecular weight for several (near) monodisperse polyethylenes. The dependence is found to be almost linear over the range studied.

Further investigation also indicated that, for a given molecular weight, the optimum drawing temperature shifts toward higher values with an increase in the elongation rate and vice versa. These temperature shifts are recorded in Figure 7 for two widely different molecular weights ($M_w = 32\,900$ (○) and $M_w = 143\,000$ (△)). Inspection of the figure shows that the two sets of data fall on the same, virtually linear, line. Thus, although the optimum temperature is strongly dependent on the molecular weight (see Figure 6), its *shift* with the rate of deformation is much more "universal": a 10-fold increase in the rate of deformation of any monodisperse polyethylene is predicted to shift its optimum temperature toward a 25–30 °C higher value. Also represented in Figure 7 is an experimental

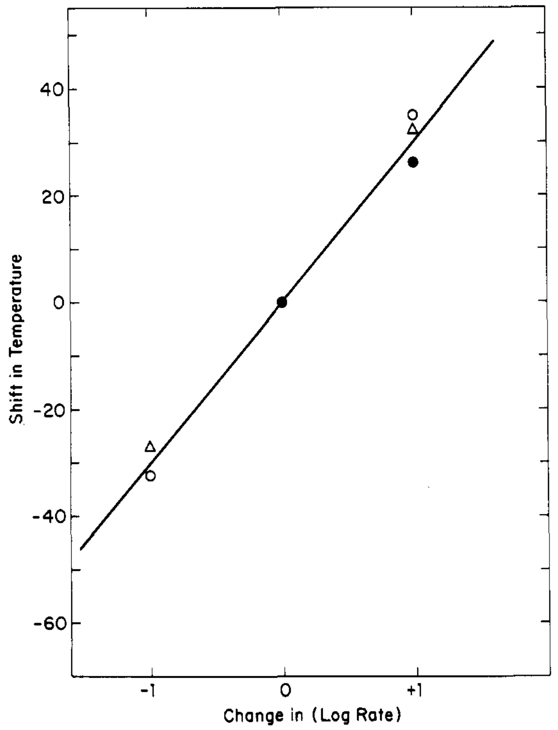

Figure 7. Shift in optimum drawing temperature versus change in (log) elongation rate for different (near monodisperse) molecular weights. Calculated values are denoted by open symbols; experimental values for the NBS sample are represented by filled symbols. Notation is as follows: (○) $M = 143000$ ($T = 130$ °C, rate = 6.5/min); (△) $M = 32900$ ($T = 102$ °C, rate = 6.5/min); (●) $M_w = 125000$ ($T = 45$ °C, rate = 2.3/min). Numbers in parentheses denote the reference values for temperature and elongation rate.

point (symbol ●) derived from the data of Figure 3 and 4 for the NBS sample. This experimental data point agrees surprisingly well with the calculated value. The interdependence between optimum temperature and rate is correctly predicted, despite the fact that agreement between calculated and experimental (absolute) values of these variables is absent.

The results of Figures 1–7, obtained for monodisperse polyethylenes, clearly demonstrate that each molecular weight exhibits a different temperature or elongation window within which optimum drawing occurs. The model reveals that, within those windows, the rate of slippage of chains through entanglements reaches its optimum value. These observations strongly point to the need for very accurate control of the temperature and rate of deformation for optimum drawing, particularly for high molecular weight polymers.

It should be pointed out that the present work is concerned only with the maximum attainable draw ratio, with no attention being paid to the resulting mechanical properties. It is well-known[7] that the modulus shows a linear increase with draw ratio, but only at temperatures well below the melting range. Thus, we expect that the high optimum temperatures required for polyethylenes of commercial interest ($M_n > 10^6$), see, e.g., Figure 6, will lead to disappointing mechanical properties. For that reason, the ideas developed in the present work should be of practical interest only for low molecular weight materials.

As was mentioned in the Introduction, the existence of optimum conditions for deformation of a given polymer has been noticed in several previous experimental studies (see, e.g., ref 4–9). However, until recently,[8] relatively little attention has been paid to this phenomenon, presumably because the observed optimum windows were rather broad and did not lead to a dramatic increase in the attainable draw ratio.[9] In view of the remarks made above concerning the molecular weight dependence of such temperature and rate windows, this might be expected because of the large polydispersities (e.g., $M_w/M_n = 16$ in ref 9) of the experimental samples used. This complex issue will be addressed in a forthcoming part 4.

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(11) Note the relatively high value of the maximum draw ratio obtained for the low molecular weight ($M = 6800$) sample. The number of statistical segments *per macromolecule* of $M = 6800$ is estimated to be $6800/140 = 48$; 140 equals the molecular weight per segment: Flory, P. J. *Statistical Mechanics of Chain Molecules*; Interscience: New York, 1969; p 12. Assuming a minimum of two entanglements per macromolecule before complete disentanglement occurs, the maximum number of segments per strand is $n = 48/2 = 24$. This leads to an *upper limit* of $\lambda_{max} = n^{1/2} 3^{1/2} = 8.5$ for the maximum draw ratio, a value lower than observed in Figure 5. The computer simulations reveal, however, that, at these very low molecular weights, a large part of the drawability arises from unfolding of the (almost linear) network of connected chains supporting the external load.