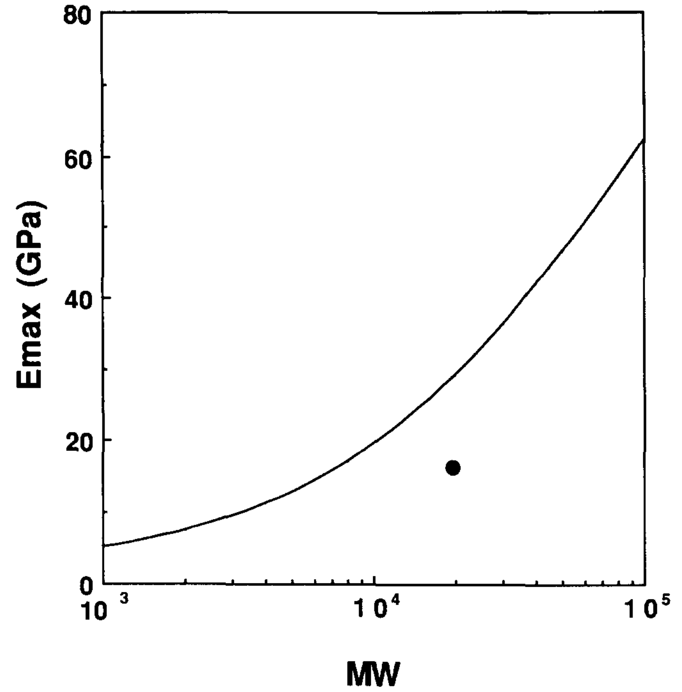

Figure 2 Maximum axial Young's modulus achievable through tensile drawing as function of molecular weight, calculated for poly(ethylene terephthalate) with equations (1) and (3). Experimental data point was taken from Hofmann *et al.*[1]

that the initial crystallinity (0–50%) (ref. 9) as well as the drawing procedure[8] of the samples barely affected the development of the Young's modulus with draw ratio. This finding, of course, justifies one of the prime assumptions in the development of the presently employed theory[2].

From the intercept of a plot of E^{-1} *versus* $\lambda^{-3/2}$, the value of the theoretical modulus, E_h, of 125 GPa was obtained and from the slope of the curve $E_u = 2.6$ GPa was calculated. Despite the expected scatter of the data at the relatively low draw ratios, the calculated axial modulus shows gratifying accord with the theoretical modulus determined by many other authors[10–17]. The development of the axial Young's modulus with draw ratio calculated according to equation (1), with $E_h = 125$ GPa and $E_u = 2.6$ GPa, is represented by the solid line in *Figure 1*. The results in this graph illustrate that equation (1) accurately describes the experimental data.

The molecular weight dependence of the maximum modulus, achievable through tensile drawing, calculated with equations (1) and (3), is presented in *Figure 2*. In this figure we also plotted the maximum Young's modulus obtained by Hofmann *et al*[1]. The graph clearly shows that their highest modulus is within 60% of the upper limit that is expected for a PET sample of molecular weight (M_w) of 20000.

Conclusion

The results presented in this paper clearly demonstrate that the molecular weight sets a theoretical upper limit to the maximum draw ratio of flexible polymers, and, therewith, also to the maximum axial modulus that can be achieved *through tensile drawing*. This limit can be surpassed only if processes other than tensile drawing are applied, that lead to superior uniaxial order, such as in-situ growth of extended chain polymer whiskers (e.g. ref. 18). As yet, such processes have not been developed for PET.

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Reply to comments

In their comment on our paper[1] Postema and Smith discuss the maximum attainable longitudinal modulus of tensile drawn PET samples as a function of the weight average molecular weight $\bar{M}_W$. But the model used by these authors is limited to affine drawing. Crystallization processes in particular are neglected. That means that this treatment is suited mainly for our cold and slow drawn PET strips 1 and 8 (see Table 1 in ref. 1). For the hot zone drawn samples, however, a semicrystalline structure is present (i.e. the molecular chains are fixed segmentwise in crystalline regions). These materials can be assumed to be composed of microfibrils with each microfibril being an arrangement of structural unit elements. The elements have an average length L and contain in each case one crystallite with one longitudinally adjoining non-crystalline region (see Figure 6 in ref. 1). The cross-sectional area A of a structural unit element can be obtained roughly from $A = L_{100}L_{010}$ with L_{100} and L_{010} being lateral crystallite dimensions as obtained from WAXS (see Table 2 in ref. 1). Then $A/0.25$ nm^2 gives the number n of molecular chain segments leaving the crystalline part of a structural unit element. (Note that 0.25 nm^2 is the average cross-sectional area per PET chain in the crystalline lattice.). L, A and n are given in *Table 1*.

Since there are also chain ends and entanglements in the non-crystalline regions, the number of intrafibrillar tie molecules is smaller than n. The relative fraction e of chain ends in the non-crystalline part of a structural unit element can be calculated from:

$$e \approx 2L/L_0 \qquad (1)$$

(see refs 2 and 3) with $L_0 = 84$ nm being the average length of a

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Table 1 Some parameters of the structural unit element for PET samples investigated (see also ref. 1)[a]

Sample	L (nm)	A (nm^2)	L_c/L	n	e	β
2	14.5	11.9	0.26	48	0.35	0.093
3	14.7	13.3	0.27	53	0.35	0.103
4	15.7	13.3	0.33	53	0.37	0.108
5	14.7	12.1	0.28	48	0.35	0.097
9	12.7	11.0	0.39	44	0.30	0.070

[a] See text for notation

PET molecule for the given number average molecular weight $\bar{M}_n = 15\,000$ ($L_0 = (M_n{:}192)1.075$ nm). As shown in *Table 1*, e is about 0.35 and thus much greater than for ultra-high modulus PE fibres[2–4]. Neglecting chain entanglements (i.e. considering only $\bar{M}_n$) there could be achieved a maximum relative content of taut tie molecules $\beta_{max} = 0.65$ by drawing. On the other hand the maximum attainable linear degree of order (L_c/L_{max}) seems to be about 0.4 for our material (note that L_c is the average length of the crystalline portion of the structural unit element with $L_c \approx L_{105}$; see ref. 1 and *Table 1*). Using $\beta = 0.65$ and $(L_c/L) = 0.4$ the maximum attainable longitudinal modulus of our PET samples ($\bar{M}_w \approx 20\,000$, $\bar{M}_n = 15\,000$) can be calculated using[1,5]:

$$E \approx E_c\beta/(1-(L_c/L)(1-\beta)) \qquad (2)$$

to $E_{max} = 83$ GPa. This value is considerably greater than the maximum value of about 28 GPa calculated by Postema and Smith for drawn PET of $\bar{M}_w = 20\,000$. That means that for semicrystalline (i.e. hot zone drawn or fast cold drawn) PET samples the finite chain length of the molecules is not of the same importance for the maximum attainable longitudinal modulus as in the case of slow and cold drawn PET where the assumptions of Postema and Smith are fully valid.

In our paper[1] we assumed that the total relative fraction of tie molecules is nearly equal to the maximum obtained relative content of taut tie molecules β in a non-crystalline region which was about 0.11 (see ref. 1 and *Table 1*). That means 89% of molecular sections in such a region have to be chain ends or to be included in chain entanglements. Since there are about 35% chain ends (see *Table 1*), 54% of the molecular sections are assumed to take part in entanglements. Then the average number i of entanglements per molecule is $i = (0.54L_0)/L$ (see refs 2 and 3). Using a typical L value of 14.5 nm, $i = 3.2$ is obtained.

Conclusion

The results presented in this reply show that for semicrystalline PET samples the maximum attainable longitudinal modulus does not only depend on the molecular weight (i.e. on the chain-end density) but also on the degree of crystallinity and the density of chain entanglements in the sample. The model of Postema and Smith, however, is especially suited for the discussion of cold and slow drawn PET fibres.

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We thank Professor S. J. Fakirov (Sofia) for the determination of $\bar{M}_n$ for the precursors and the drawn materials. These results also revealed that there is no significant chain breaking during all drawing procedures applied by us.

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Corrigendum

'Kinetic theory of directional isomerism in polymer chains: 1. Polymer microstructure'
Deyue Yan and Xiaodong Hu
Polymer 1988, **29**, 1858–1866
Equations (17) to (21) should read as follows:

$$x = \int_0^t [\mathrm{HT}]\,\mathrm{d}t \qquad (17)$$

$$\sum_{n=1}^{\infty} P_n^* = I_0 k_{\mathrm{ht}}\left(\frac{c}{K_1} + \alpha_1\,\mathrm{e}^{-K_1x} + \frac{\beta}{K_1-K_3}\mathrm{e}^{-K_3x} - \frac{c+\beta}{K_1-K_4}\mathrm{e}^{-K_4x}\right) \qquad (18)$$

$$\sum_{n=1}^{\infty} Q_n^* = I_0 k_{\mathrm{th}}\left(\frac{1-c}{K_2} + \alpha_2\,\mathrm{e}^{-K_2x} - \frac{\beta}{K_2-K_3}\mathrm{e}^{-K_3x} - \frac{1-c-\beta}{K_2-K_4}\mathrm{e}^{-K_4x}\right) \qquad (19)$$

$$B^* = I_0 k_{\mathrm{tt}}\left[\frac{1-c}{K_1} + \left(\frac{K_4}{K_1(K_1-K_4)} - \alpha_1\right)\mathrm{e}^{-K_1x} - \frac{\beta}{K_1-K_3}\mathrm{e}^{-K_3x} - \frac{1-c-\beta}{K_1-K_4}\mathrm{e}^{-K_4x}\right] \qquad (20)$$

$$D^* = I_0 k_{\mathrm{hh}}\left[\frac{c}{K_2} + \left(\frac{K_4}{K_2(K_2-K_4)} - \alpha_2\right)\mathrm{e}^{-K_2x} + \frac{\beta}{K_2-K_3}\mathrm{e}^{-K_3x} - \frac{c+\beta}{K_2-K_4}\mathrm{e}^{-K_4x}\right] \qquad (21)$$

Equations (44) and (45) should read as follows:

$$\begin{aligned} f(\text{H-H}) &= \frac{D}{B+D+\sum_{n=1}^{\infty} n(P_n+Q_n)} \\ &= k_{\mathrm{hh}}[cK_3K_4x - K_4\beta(\mathrm{e}^{-K_3x}-1) \\ &\quad + K_3(c+\beta)(\mathrm{e}^{-K_4x}-1)]/ \\ &\quad \{[K_2+(K_1-K_2)c]K_3K_4x + K_4\beta(K_2-K_1) \\ &\quad \times(\mathrm{e}^{-K_3x}-1) \\ &\quad + [K_2+(K_1-K_2)(c+\beta)]K_3(\mathrm{e}^{-K_4x}-1)\} \end{aligned} \qquad (44)$$

$$\begin{aligned} f(\text{T-T}) &= \frac{B}{B+D+\sum_{n=1}^{\infty} n(P_n+Q_n)} \\ &= k_{\mathrm{tt}}[(1-c)K_3K_4x + K_4\beta(\mathrm{e}^{-K_3x}-1) \\ &\quad + K_3(1-c-\beta)(\mathrm{e}^{-K_4x}-1)]/ \\ &\quad \{[K_2+(K_1-K_2)c]K_3K_4x + K_4\beta(K_2-K_1) \\ &\quad \times(\mathrm{e}^{-K_3x}-1) \\ &\quad + [K_2+(K_1-K_2)(c+\beta)]K_3(\mathrm{e}^{-K_4x}-1)\} \end{aligned} \qquad (45)$$