

Aubouy, Manghi, and Raphaël Reply: A controversy is raised by Kumar and Jones in their Comment [1]. The issue is the dependence of the surface tension, γ , of polymer melts on molecular weight (MW), M_n . Our recent theory, which is essentially an improvement upon de Gennes's idea [2], proposes that [3]

$$\Delta\gamma \propto \ln(M_n/M_n^*)/M_n^{1/2}, \quad (1)$$

where M_n^* is a constant. The two points raised by Kumar and Jones are as follows: (i) Many experiments and theories point to the law

$$\Delta\gamma \propto 1/M_n, \quad (2)$$

and (ii) the variations $\gamma(M_n)$ as given by Eq. (1) are non-monotonic, which is in contradiction with the experimental observations.

Concerning the first argument.—It is instructive to fit the experimental data mentioned by Kumar and Jones with Eq. (2) (Fig. 1). As a first approximation, a simple power law is fair. However, we observe a departure from this law for low and intermediate MW samples, which we think is significant. Convincingly enough, a simple power law does not account for all the data, and whether Eq. (2) is correct in the limit $M_n \rightarrow \infty$ is questionable since only a very small subset of the data is fitted. On the contrary, Eq. (1) happens to fit the whole set of data with a very high accuracy, as shown in [3].

Concerning the second argument.—The function γ defined by Eq. (1) first increases with N , the index of polymerization (when $N < eN^*$) until it reaches γ_{\max} and then decreases (when $N > eN^*$) to reach its asymptotic value, γ_∞ . However, for large values of N^* (we find $N^* \sim 50$), the difference $\gamma_{\max} - \gamma_\infty \sim \frac{1}{eN^{*1/2}}$ vanishes. Accordingly, from a physical point of view, γ is *essentially* an increasing function of the MW. This is what we observe once reasonable values of N^* are implemented in the fits (Figs. 1 and 2 of [3]).

Reference [6] is an interesting contribution to this debate, although we do not find that the results described therein provide a decisive answer. First, these are rather indirect evidences: (a) a blend of chemically different polymers is considered (a situation conceptually more delicate); (b) the observable is not the surface tension (the amount of segregation is monitored). Second, the experimental window of observation ($11 < N < 162$) is small. Since we expect $eN^* \sim 150$, it is not quite obvious that our theory predicts a nonmonotonic variation within this window. Finally, the uncertainty (much larger than in the direct experiments discussed in detail before) does not substantiate the conclusion suggested by Kumar and Jones. A plateau at high MW is not ruled out by these experiments.

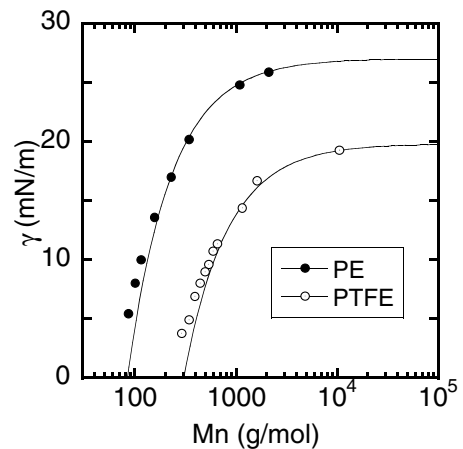


FIG. 1. $\gamma(M_n)$ for two different polymers: Poly-ethylene (PE) (data from [4]) and Poly-tetrafluoroethylene (PTFE) (data from [5]). Full line represents fits with Eq. (2). Error bars (0.2 mN/m) are smaller than the size of the dots.

In summary, we are not convinced that the arguments presented by Kumar and Jones provide any strong evidence against our theory. Presumably, it is fair to say that the set of experimental data available is not yet able to resolve the controversy. We fully agree that more experimental data are needed.

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