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The onset of tube-like constraining effects in polydisperse polymer melts

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Summary

This paper describes the onset of the influence of entanglement effects on the mobility of polymer chains in a polydisperse melt. Extending a scaling relation between the critical molecular mass of homodisperse melts and segment number density yields in the case of polydisperse melts a functional equation for the critical chain length. The case of the normal distribution will be solved and discussed.

Introduction

The change in the molecular mass M dependence of viscosity η of monodisperse polymer melts occurs over a relatively narrow range of molecular masses around the critical molecular mass M_c. The M_c value is obtained from the intersection of straight lines drawn through the two branches of the log η - - log M curve. For $M < M_c$ the relation $\eta \sim M$ reflects the Rouse chain behaviour, whereas for $M \geq M_c$ the power dependence $\eta \sim M^{3.4}$ reflects features attributed to entanglement constraints which act effectively as an open-ended tube which surrounds any given macromolecule along its average contour. The chain moves inside the tube by local reptation (1). Otherwise, in the case of polydisperse polymer melts it exists still the unsettled question concerning the role of short chains and their contributions to the formation of the tube field. Further, it would be of interest to examine a relation between the critical molecular mass of the polydisperse sample and characteristics of the molecular mass distribution (number-average molecular mass, etc.).
We will show that this question can be attacked by applying a scaling relation between the critical molecular mass of homodisperse melts and segment number density (4) to the case of polydisperse melts if in the latter case the shorter chains are expected to behave like solvent.

Theory

The lateral tube dimension of a homodisperse sample, d_o, may be calculated by means of a microscopic theory of the topological constraints in melts or concentrated solutions (2). The model is based on the screening concept of the global topology

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effects and takes into account the conservation of the local topology. It yields the relation

$$d_o = 8.5\ (n_s l^3)^{-1/2}\ l \qquad (1)$$

with n_s the segment number density and l the statistical segment length. Combining Eq. (1) with the expression for the plateau modulus G_N^o of the melt according to the Doi/Edwards theory (3) yield an universal power law for G_N^o deduced by Graessley and Edwards (4). Combination of Eq. (1) with a phenomenologically deduced expression for the critical molecular mass in bulk polymers (4),

$$M_c^{-1} = \frac{K_2}{M_s}\ (n_s l^3) \quad , \quad K_2 = 0.0049 \ , \qquad (2)$$

(M_s is the molecular mass of a statistical segment)

gives for the r.m.s. end-to-end distance R_c of a chain with the critical molecular mass M_c the following relation:

$$R_c \approx 1.7\ d_o \qquad (3)$$

Eq. (3) means that already for $R_c/d_o \gtrsim 1$ the mobility of any chain in lateral direction is effectively confined by the collective effect of all neighbouring chains. This behaviour may hardly be caused only by the action of single entanglements.

This shortly sketched picture will now be used for studying the polydisperse case.

In the case of a polydisperse polymer melt we assume that the collective constraining effect due to a molecule with the molecular mass $M \geq M_c(p)$ is caused by the topological constraints of all neighbouring chains with $M \geq M_c(p)$. The determination of the critical molecular mass of the polydisperse melt, $M_c(p)$, will be our aim. All the chains with $M < M_c(p)$ exhibit Rouse behaviour and do not contribute to the forming of tubes according to Eq. (1). Therefore, we have to replace the local segment number density n_s by its reduced value (n_s') of the non-Rouse part of the melt (Fig. 1):

$$n_s' = \sum_{N=N_c(p)}^{Z} n_s\ w(N) \qquad (4)$$

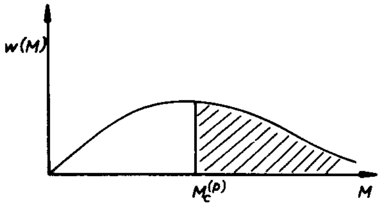

Figure 1

All chains with $M < M_c(p)$ exhibit Rouse behaviour. Otherwise, all chains with $M \geq M_c(p)$ contribute to the forming of tube-like configurational constraints.

$N_c^{(p)} \equiv [M_c^{(p)}/M_s]$ denotes the number of segments of a macromolecule with the critical molecular mass $M_c^{(p)}$ ($[\ldots]$ is the largest integer which is smaller than the ratio within the brackets). Z is the total segment number and w(N) characterizes the molecular size distribution of the dispersed molecular mass system. It is normalized according to Eq. (5).

$$\sum_{N=1}^{Z} w(N) = 1 \tag{5}$$

Eqn. (4) and (5), in combination with Eq. (2), yield the following equation for the critical molecular mass $M_c^{(p)}$:

$$m_c \, \phi(m_c, \{w(N)\}) = 1 \tag{6}$$

In Eq. (6)

$$\phi(m_c, \{w(N)\}) = \sum_{N \geq N_c^{(p)}} w(N) \tag{7}$$

and $m_c \equiv M_c^{(p)}/M_c$ is the ratio of the critical molecular mass of the polydisperse to the monodisperse melt. The general solution of Eq. (6) is

$$m_c = m_c(\{w(N)\}) = m_c(\bar{M}_n, \bar{M}_w, \bar{M}_i) \tag{8}$$

where $\bar{M}_n$ is the number-average and $\bar{M}_w$ the weight-average molecular mass, and $\bar{M}_i$ represents the higher molecular averages. The case of the most probable (or the random) distribution gives

$$w(N) = N \alpha^{N-1} (1-\alpha)^2 \tag{9}$$

where the number-average of structural units, $\bar{N}_n = \bar{M}_n/M_s$, is equal to $1/(1-\alpha)$. The corresponding weight-average is $\bar{N}_w = (1+\alpha)/(1-\alpha)$. Inserting of Eq. (9) into Eq. (7) gives

$$\phi(m_c) = ((1-\alpha) m_c N_c + \alpha) \alpha^{(m_c N_c - 1)} \tag{10}$$

where $N_c \equiv [M_c/M_s]$ denotes the critical number of segments in the monodisperse case.

Discussion

Qualitatively, it can be shown that a solution of Eqn. (6), (7) and (10) exists only in the case of distributions with number-average molecular weights $\bar{M}_n \geq \bar{M}_n^*$. The quantity $\bar{M}_n^*$

characterizes such a distribution where the onset of a solution m_c according to Eq. (6) starts (bifurcation), and the relation $\overline{M}_n^* > M_c$ holds. In the case $\overline{M}_n > \overline{M}_n^*$, Eqn. (6), (7) and (10) exhibit two solutions m_c but only the smaller solution has the physical meaning. With increasing $\overline{M}_n$ (i.e. decreasing part of Rouse chains in the distribution), m_c tends to unity (Fig. 2) whereas the second (unphysical) solution goes to infinity.
As an example, Fig. 2 illustrates a melt characterized by N_c = 100 in the monodisperse case and distributed according to Eq. (9) in the polydisperse case. The onset of collective constraints according to the criteria of Eq. (2) or (3) and to Eq. (6) starts at a random distribution characterized by the number-average $\overline{N}_n^* (\equiv \overline{M}_n^*/M_s) = 118$ and with the solution $m_c^* \equiv m_c(\overline{M}_n = \overline{M}_n^*) = 1.92$. That means, that all chains with a number of structural units smaller than $N_c^{(p)} = 192$ exhibit Rouse behaviour and do not contribute to the forming of tubes. The corresponding weight-average of structural units is $\overline{N}_w = 235$. With increasing number-average $\overline{N}_n$ the ratio m_c approaches to unity. In this case, the number of Rouse chains goes to zero.

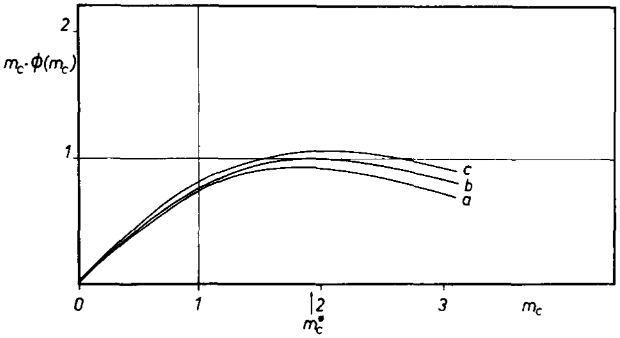

Figure 2

Illustration of the onset (curve b) of a solution of the $M_c^{(p)}$ determining equation (N_c = 100, w(N) = Eq. (9)):

a no solution, $\overline{N}_n = 111$ ($\alpha = 0.9910$)

b $m_c = m_c^* = 1.92$, $\overline{N}_n = \overline{N}_n^* = 118$ ($\alpha = 0.9915$)

c physical solution:
$m_c = 1.60$, $\overline{N}_n = 125$ ($\alpha = 0.9920$)

Summarize

We derived a criterion for the onset of non-Rouse behaviour in the dynamics of polydisperse melts. We used the picture that the large scale motions of individual chains longer than the critical chain length are restricted by the presence of (enough) neighbouring chain contours (exceeding the critical length), and that these tube-like restrictions are topological

in origin, having to do with the uncrossability of the chain contours. Eqn. (1) - (4) reflect this idea.
Further, Eq. (4) contains the idea that the communal topological interactions (entanglements) between large ($N \geq N_c^{(p)}$) or small ($N < N_c^{(p)}$) chains are not equally effective as obstacles for the motion of the interacting pair and only the molecules with $N \geq N_c^{(p)}$ act as tube-forming units.
It could be shown that the onset of tube-like topological constraints (in dependence of the degree of polydispersity) corresponds to the bifurcation of the solution of the $M_c^{(p)}$ determining equation.
Non-Rouse behaviour of the melt is predicted for distributions with $\bar{M}_n > M_c$ and one gets the relation $\bar{M}_n < M_c^{(p)} < \bar{M}_w$. The difference between $M_c^{(p)}$ and M_c increases with increasing degree of polydispersity.
The onset of a solution $M_c^{(p)}$ according to Eq. (6) can be described in a similar way using a more general molecular size distribution, but the mathematics will become more complicated.
The presented concept, including the case of random distribution, has been successfully applied in the explanation of the experimentally observed onset of non-Rouse dynamics (5) in melts of hydrogen-bonded poly(oxypropylene) chains.
The assumption that the short chains do not cooperate with the long chains for supporting the tube wall has been recently used (6) to derive a mole-basis blending law for the relaxation spectrum. It gives a better prediction of the terminal viscoelastic properties of polymer blends in the entangled state than does the weight-basis blending law.

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