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Modelling Rheology and Free Energy of Entangled Polymers. State of the Art

Giuseppe Marrucci, Giovanni Ianniruberto*

Chemical Engineering, University Federico II, Piazzale Tecchio 80, 80125 Napoli, Italy

Summary: Significant progress made in recent times on the basic molecular theory of Doi and Edwards for entangled polymers is briefly reviewed. In particular we present a recent version of the theory that is entirely described by a set of differential equations, and is therefore especially useful for simulations of complex flows as encountered in polymer processing. The model also provides an expression for the excess free energy that can be of use to predict the onset of flow-induced crystallisation.

Introduction

The tube model of Doi and Edwards for entangled polymers[1] is now well known and widely accepted. The idea that long polymers in concentrated solutions and melts can only move longitudinally along themselves (a motion called reptation by de Gennes[2]) is indeed intuitively appealing. Moreover, the theory has helped interpreting, qualitatively and even semi-quantitatively, many results of linear viscoelasticity, especially after the basic relaxation mechanism, that of reptation, has been later augmented with other important effects, like chain-end fluctuations and constraint release due to motion of surrounding chains (see Watanabe[3] for a recent review). In fact, the latter effects become dominant in branched polymers.[4]

In the nonlinear range, i.e., in fast flows (as often encountered in processing operations), the success of Doi-Edwards theory has been hampered by the fact that the theory predicted an excessive shear thinning; in fact so strong an effect as to generate an instability that prevented using the model in numerical codes for complex flow simulation. Because of that shortcoming, the theory has long been kept on the side in engineering circles. Recently, however, it has again attracted much attention, after the introduction of the relaxation mechanism known as convective constraint release (CCR).[5,6] Indeed, CCR effectively suppresses the excessive shear thinning predicted by the original model, as it makes the shear stress to approach a plateau at high shear rates (in the absence of chain stretch). Still in the absence of chain stretch, further refinements

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of the CCR theory were recently proposed,[7,8] which predict a fully monotonic flow curve.

As regards chain stretch, it should be recalled that chain stretch per se (i.e., in the absence of CCR) does not modify the excessive shear thinning of the basic model. This feature of theory was shown long ago,[9] together with the fact that, conversely, a strong stretch effect is predicted in elongational flow. Recently, however, progress has been made in accounting for both CCR and chain stretch.[10-14] With all ingredients put together, it so appears that comparison of theory with data in fast flows is encouraging,[14-16] and that a theoretically sound constitutive equation is finally in sight. In the following, we will present the state of the art on such a matter. We will also derive an expression for the free energy to be used in flow-induced crystallisation.

Single Mode Model

It is well known that polymers, even when monodisperse, typically exhibit a spectrum of relaxation times. It is nevertheless useful to start presenting the complex behaviour of entangled polymers by first considering the monodisperse situation, and, furthermore, by following for such a case a single-mode approach, i.e., by assuming that all polymer segments behave in the same way, irrespective of their position along the chain.

For such a simplified schematic situation, the internal variables describing the rheological state of the system are only two, namely an orientation tensor **S**, and a stretch ratio λ. Indeed, if **u** is the unit vector along the segments connecting consecutive entanglements, $\mathbf{S} = \langle \mathbf{uu} \rangle$ describes the average orientation of those segments. (Of course, under isotropic conditions such as at equilibrium, **S** reduces to 1/3 **I**, where **I** is the unit tensor.) The length ratio λ describes chain stretching, $\lambda = 1$ corresponding to the relaxed situation, while $\lambda = \lambda_{max}$ (a material parameter) is attained in the fully stretched chain.

It is important to remark immediately that λ will increase above unity only in very fast flows, faster than the reciprocal Rouse time. Indeed, since the sliding motion of the chain along its own contour ignores the entanglements, and only involves the basic frictional resistance with the surrounding medium, the relaxation time for chain stretch is the basic Rouse time of the chain (scaling with M^2), indicated as τ_R in the following. On the other hand, anisotropy is induced much more easily in entangled systems, because entangled chains cannot reorient without accounting for the topological obstacles formed by the surrounding chains (a non-frictional effect). The topological obstacles must be removed one way or the other, and this takes a much longer time, certainly longer than τ_R. Hence, significant departures from isotropy of tensor **S** will occur already in moderately fast flows, i.e., in flows faster than the reciprocal of some other characteristic time, somehow related to the process of disengagement from entanglements.

In the original Doi-Edwards theory, the only disengagement mechanism accounted for was reptation within fixed obstacles. The characteristic time for such a process (scaling with M^3) is indicated as τ_d in the following. Later it was recognised that the reptative motion of the surrounding chains also speeds up disengagement, a notion called constraint release. In particular, if one assumes that entanglements are essentially binary interactions, the entanglement will vanish (and the stress carried by it disappear) when a chain end of either one of the two chains will reach the entanglement, an assumption known as 'double reptation', [17,18] which is particularly important for the polydisperse case. However, for the single-mode situation considered in this section, the enhancement of relaxation due to double reptation merely reduces to the fact that the disengagement time becomes $\tau_d/2$.

It was recognised only recently[5] that a very important further enhancement of orientational relaxation could occur during flow, as a result of the relative motion between entangled chains. Such an effect, called convective constraint release (CCR), generates a renewal frequency given by $|\mathbf{k}:\mathbf{S}|$, where **k** is the velocity gradient of the flow. The term $|\mathbf{k}:\mathbf{S}|$ speeds up orientational relaxation in moderately fast flows, i.e., as soon as the magnitude of **k** exceeds $1/\tau_d$. However, by further increasing **k**, we eventually reach a situation whereby entanglements are removed so quickly that they are no longer important in constraining the chain. In that limit, also the orientational relaxation becomes controlled by the basic friction, i.e., the orientational relaxation time reduces to the Rouse time τ_R.

By putting all these aspects together, we have recently proposed[13] that the orientational relaxation time, called τ, could be obtained through the simple equation

$$\tau = \frac{1}{2\left(\dfrac{1}{\tau_d} + |\mathbf{k}:\mathbf{S}|\right)} + \tau_R \qquad (1)$$

where the factor of 2 in the denominator accounts both for double reptation and for CCR2, an additional convective mechanism refining CCR.[7] Notice that, for very large values of $|\mathbf{k}:\mathbf{S}|$, τ reduces to τ_R, as discussed above. On the other hand, in the linear limit, i.e. for **k** approaching zero, Eq. (1) gives $\tau = \tau_d/2 + \tau_R \approx \tau_d/2$, where the approximate equality holds true because, at high M, τ_R is much smaller than τ_d. However, if the linear limit needs to be recovered exactly, Eq. (1) can be modified as:

$$\tau = \frac{1}{2\left(\dfrac{1}{\tau_d} + |\mathbf{k}:\mathbf{S}|\right)} + \frac{3}{2}\left(\mathbf{S} - \frac{1}{3}\mathbf{I}\right) : \left(\mathbf{S} - \frac{1}{3}\mathbf{I}\right)\tau_R \qquad (1')$$

Indeed, in the linear limit **S** becomes isotropic, and the scalar product added in Eq. (1') vanishes in such a limit. On the other hand, in very fast flows the chains fully orient, and the added factor approaches unity.

The orientation dynamics, i.e. the rate of change of tensor **S**, can be described through the following differential equation[13]

$$\overset{\nabla}{\mathbf{S}^2} + 2\mathbf{S}^2(\mathbf{k}:\mathbf{S}) + \frac{2}{\tau}\mathbf{S}\cdot\left(\mathbf{S} - \frac{1}{3}\mathbf{I}\right) = \mathbf{0} \qquad (2)$$

where τ is given by Eq. (1) or (1'), and the triangular hat symbol on $\mathbf{S}^2$ indicates the usual upper-convected time derivative ($\overset{\nabla}{\mathbf{A}} = \dot{\mathbf{A}} - \mathbf{k}\cdot\mathbf{A} - \mathbf{A}\cdot\mathbf{k}^T$). Eq. (2) is the differential version of an integral equation containing the **Q** tensor of the Doi-Edwards theory.[11] Eq. (2) contains the time derivative of $\mathbf{S}^2$ (rather than that of **S**) because the **Q** tensor can be effectively approximated by an expression involving the square root of the Finger tensor,[19] which then allows one to transform the integral equation into the differential form.[20] Needless to say, a differential form is more easily handled in complex flow simulations.

The dynamics of chain stretching, i.e. the rate of change of the λ ratio, is described through the simple differential equation:[13]

$$\frac{d\lambda}{dt} = \lambda \mathbf{k} : \mathbf{S} - \frac{\lambda_{\max}}{\tau_R} \frac{\lambda - 1}{\lambda_{\max} - \lambda} \tag{3}$$

Here, the last term describes stretch relaxation, which, as long as λ remains much smaller than $\lambda_{\max}$, coincides with the linear expression $(\lambda - 1)/\tau_R$. On the other hand, for λ approaching $\lambda_{\max}$, the vanishing denominator prevents that $\lambda_{\max}$ is ever exceeded. The forcing term in Eq. (3) (driving λ away from unity) is $\lambda\mathbf{k}:\mathbf{S}$, which arises from the convective motion of the chain relative to its surroundings along the chain contour itself. Because of the orientation dependence of this term, Eq. (3) must be integrated in time together with (or after) Eq. (2) that provides **S**.

Once **S** and λ are obtained from Eqs. (2) and (3), respectively, the stress tensor **T** and the refractive index tensor **n** are given by

$$\frac{\mathbf{T}}{G} = \mathbf{S}\,\lambda^2 \frac{\lambda_{\max} - 1}{\lambda_{\max} - \lambda} \quad ; \quad \frac{\mathbf{n}}{K} = \mathbf{S}\,\lambda^2 \tag{4}$$

where G is the shear modulus, and K is the equivalent optical quantity. Notice that, while **S** describes the orientation of *tube* segments (a quantity that cannot be measured), the product $\mathbf{S}\,\lambda^2$ gives the orientation of *monomers* (more precisely, of Kuhn segments), which is experimentally accessible through birefringence. Notice also that, if λ is much smaller than $\lambda_{\max}$, the deviatoric parts of **T** and **n** are proportional to one another, which constitutes the well known stress-optical law. Conversely, when λ approaches $\lambda_{\max}$, **n** saturates (that is, monomers become fully oriented) while **T** diverges because of the nonlinearity of the force in the chain near full extension.

The constitutive parameters in Eqs. (1–4) are four, namely the shear modulus G (or the equivalent optical quantity K), the relaxation times τ_d and τ_R, and the maximum possible stretch $\lambda_{\max}$, all of which can (in principle) be determined from linear viscoelasticity, either directly (G, τ_d, τ_R) or indirectly ($\lambda_{\max}$). The latter can in fact be obtained as $\lambda_{\max} = \sqrt{n}$, where n is the number of Kuhn segments between consecutive entanglements at equilibrium, itself deducible from the plateau modulus.

Although the predictions of Eqs. (1-4) compare well with data in a qualitative sense, quantitative comparison requires that the model be extended to a multi-mode situation. Indeed, even in the monodisperse case, chain segments close to chain ends relax much sooner than internal ones, mostly because of tube length fluctuations. Hence, not all chain segments can be treated in the same way. Fluctuations, which are perforce neglected in the single-mode model, are so important as to be responsible for the famous 3.4 power law M-dependence of the zero-shear viscosity. Indeed, both reptation and double reptation predict a M^3 scaling law, while fluctuations constitute the fundamental ingredient to explain the observed deviation from the third power.[21,22]

The Multi-Mode Extension

Extensions to the full spectrum of relaxation times have been considered recently.[14,15] In the following we describe that based on Eqs. (1-4) discussed in the previous section.[14] Let us assume that chain segments can be classified in N categories. For example, in the monodisperse case, segments can be distinguished according to their distance from the closest chain end. In the polydisperse situation, we need to distinguish also among the different values of M in the sample.

Let us indicate with w_i ($i = 1,..,N$) the mass fraction of the segments of the i-th kind, and with $\mathbf{S}_i$ and λ_i their mean orientation and stretch, respectively. Since $\lambda_{\max}$ is the same for all segments, Eq. (4) immediately becomes

$$\frac{\mathbf{T}}{G} = \sum_{i=1}^{N} w_i \mathbf{S}_i \lambda_i^2 \frac{\lambda_{\max} - 1}{\lambda_{\max} - \lambda_i} \qquad \frac{\mathbf{n}}{K} = \sum_{i=1}^{N} w_i \mathbf{S}_i \lambda_i^2 \tag{5}$$

Also Eq. (3) for the evolution of chain stretch is readily extended. We need only consider that each λ_i will have its own Rouse time τ_{Ri}. Indeed, segments which are well inside the chain relax the stretch with the Rouse time of the whole chain, whereas segments close to chain ends relax the stretch much sooner. We shall mention later how to assign values to these times. Similarly to Eq. (3), the time evolution of λ_i is then written as:

$$\frac{\mathrm{d}\lambda_i}{\mathrm{d}t} = \lambda_i \mathbf{k} : \mathbf{S}_i - \frac{\lambda_{\max}}{\tau_{Ri}} \frac{\lambda_i - 1}{\lambda_{\max} - \lambda_i} \tag{6}$$

The orientational situation is more complicated because binary interactions are involved, and the possible different binary combinations between segments of N kinds are as many as N^2. Hence we need to introduce a new set of orientational tensors $\mathbf{S}_{ij}$ representing the mean orientation of the i-th type segments coupled (or entangled) with segments of the j-th kind. Then $\mathbf{S}_i$ appearing in Eqs. (5) and (6) is given by

$$\mathbf{S}_i = \sum_{j=1}^{N} w_j \mathbf{S}_{ij} \tag{7}$$

representing the orientation of the segments of the i-th type, averaged over all possible interactions.

On the other hand, the evolution of the orientation must be written for each $\mathbf{S}_{ij}$ because it is sensitive to the specific interaction. Hence, similarly to Eq. (2), we write

$$\overset{\nabla}{\mathbf{S}}{}^2_{ij} + 2\mathbf{S}^2_{ij}\left(\mathbf{k}:\mathbf{S}_{ij}\right) + \frac{2}{\tau_{ij}}\mathbf{S}_{ij}\cdot\left(\mathbf{S}_{ij} - \frac{1}{3}\mathbf{I}\right) = \mathbf{0} \tag{8}$$

with an orientational relaxation time τ_{ij} given by

$$\tau_{ij} = \frac{1}{\dfrac{1}{\tau_{\mathrm{d}i}} + \dfrac{1}{\tau_{\mathrm{d}j}} + \left|\mathbf{k}:\mathbf{S}_i\right| + \left|\mathbf{k}:\mathbf{S}_j\right|} + \frac{3}{2}\left(\mathbf{S}_i - \frac{1}{3}\mathbf{I}\right):\left(\mathbf{S}_i - \frac{1}{3}\mathbf{I}\right)\tau_{\mathrm{R}i} \tag{9}$$

which is the extension of Eq. (1’), with $\tau_{\mathrm{d}i}$ and $\tau_{\mathrm{d}j}$ the disengagement times (within fixed obstacles) of i and j segments, respectively. Notice that in this case double reptation is more important in slow flows, as the smallest between $\tau_{\mathrm{d}i}$ and $\tau_{\mathrm{d}j}$ will dominate for both i and j segments. The terms $\left|\mathbf{k}:\mathbf{S}_j\right|$ and $\left|\mathbf{k}:\mathbf{S}_i\right|$ account for CCR and CCR2, respectively. Of course Eq. (9) reduces to Eq. (1’) for $i = j$.

At first sight, it might seem that the multi-mode version cannot be used in practice, as it contains too many parameters. Indeed, together with the modulus G and maximum stretch $\lambda_{\max}$ (related to G), there appear N values of disengagement time $\tau_{\mathrm{d}i}$ plus N values for the Rouse times $\tau_{\mathrm{R}i}$ plus their respective fractional weights w_i. However, in the next section we will discuss how all these parameters are in fact linked to one another.

Parameter Determination

Parameter determination always refers to linear viscoelasticity. Initially we will refer in particular to the zero-shear viscosity η_0 which, with the language of the model discussed here, is given by:

$$\eta_0 = \frac{G}{6}\sum_{i=1}^{N}\sum_{j=1}^{N} w_i w_j \tau_{ij} \quad ; \quad \frac{1}{\tau_{ij}} = \frac{1}{\tau_{\mathrm{d}i}} + \frac{1}{\tau_{\mathrm{d}j}} \tag{10}$$

We will first discuss the monodisperse situation, to show how the introduction of fluctuations can generate the 3.4 power law. For the monodisperse case, we have successfully made[14] the economic choice of $N = 2$, only distinguishing between internal segments (index 1) and segments close to chain ends (index 2). The weight w_2 of the chain end segments is taken consistently with the Doi suggestion[21]

$$w_2 = \frac{1.5}{\sqrt{\mathrm{M}/\mathrm{M}_\mathrm{e}}} \quad ; \quad w_1 = 1 - w_2 \tag{11}$$

where M_e is the molecular weight between consecutive entanglements (deducible from the plateau modulus $G_N^0 = G/6$). Concerning the two disengagement times $\tau_{\mathrm{d}1}$ and $\tau_{\mathrm{d}2}$, we take

$$\tau_{\mathrm{d}2} = \tau_\mathrm{R} = \tau_\mathrm{e}\left(\frac{\mathrm{M}}{\mathrm{M}_\mathrm{e}}\right)^2 \quad ; \quad \tau_{\mathrm{d}1} = \tau_\mathrm{d} w_1^2 = 3\alpha\,\tau_\mathrm{e}\left(\frac{\mathrm{M}}{\mathrm{M}_\mathrm{e}}\right)^3 w_1^2 \tag{12}$$

where τ_e is the Rouse time of the M_e chain, and α is a nondimensional parameter accounting for a cooperative effect of the entangled network, which accelerates disengagement ($\alpha < 1$).[23] Equating $\tau_{\mathrm{d}2}$ to the Rouse time of the chain is in line with the detailed study of fluctuations reported by Milner and McLeish.[22] The equation for $\tau_{\mathrm{d}1}$, except for α, is the classical result of reptation theory,[1] reduced by the factor w_1^2 to account for the fact that the length to cover by reptative diffusion is shortened by w_1. Equations (10-12) automatically generate the 3.4 power law over a wide range of M values (up to ca. 100M_e). The parameter α is set by the condition that the transition from Rouse-like to entangled behaviour occurs at the critical molecular weight M_c.

With the above explained strategy, the only free parameters (for whatever linear polymer of assigned molecular weight M_w and molecular weight distribution) are: the basic time τ_e and the modulus G (both of which independent of M_w and of the distribution of M), and maybe α itself (possibly dependent on M-distribution). These few parameters are easily determined against linear viscoelastic data, e.g., of G′ and G″. For the use of the constitutive equation in the nonlinear range, there remains to specify values for the Rouse times τ_{R1} and τ_{R2}. For each M, we will obviously take $\tau_{R1} = \tau_R$, while for τ_{R2} we need to scale with the square length from the chain end, i.e., we take $\tau_{R2} = \tau_R (w_2)^2$. No other specifications are required (except for the already mentioned λ_{max} to be obtained from G) and no other degrees of freedom are available.

With such a strategy, extensive comparison with rheological data on various polymers is currently being made, with encouraging results[16,23]. In the following, we will concentrate on an aspect of the theory that is specially relevant for flow-induced crystallisation.

Free Energy

A good understanding of the rheology of entangled polymers is a pre-requisite for dealing with flow-induced crystallisation. Indeed, the molecular orientation brought about by flow, corresponding to an increase in free energy, appears to be the cause for the accelerated crystallisation.

The step from the stress tensor to the corresponding excess free energy is generally not easy to make. However, if we limit attention to situations where the flow strength never exceeds the reciprocal Rouse time, i.e., to the case of unstretched chains, then some progress can be made. Already some years ago, the free energy was computed for the original Doi-Edwards model with the independent alignment approximation.[24] That result has recently been used with success by Coppola et al.[25] to obtain quantitative predictions of flow-induced crystallisation rate.

Still within the assumption that chain stretch is absent, which is probably the case most frequently encountered during flow-induced crystallisation, we can derive an alternative expression for the free energy in terms of the orientation tensor **S**, which is consistent with the model described in the previous sections. The starting point is the general relationship between free energy and stress tensor, which is

$$\delta A = \mathbf{T} : \delta \varepsilon \tag{13}$$

where A is free energy per unit volume, and ε is an arbitrary (volume preserving) step deformation, performed at constant temperature.

By assuming that the stress is purely orientational, i.e., $\mathbf{T} = G\mathbf{S}$, we may rewrite Eq. (13) as

$$\delta A = G\left(s_1 \delta\varepsilon_1 + s_2 \delta\varepsilon_2 + s_3 \delta\varepsilon_3\right) \tag{14}$$

where s_1, s_2, s_3 are the eigenvalues of **S**, and $\delta\varepsilon_1$, $\delta\varepsilon_2$, $\delta\varepsilon_3$ are virtual deformations along the eigendirections of **S**, obeying $\delta\varepsilon_1 + \delta\varepsilon_2 + \delta\varepsilon_3 = 0$, because of incompressibility.

Let us now temporarily restrict to the case where the anisotropy has been obtained through a single step deformation of eigenvalues λ_1, λ_2, λ_3. Consistently with the model previously described, **S** coincides with $\mathbf{C}^{-1/2}/\mathrm{tr}(\mathbf{C}^{-1/2})$, where $\mathbf{C}^{-1/2}$ is the square root of the Finger tensor.[19] Hence, the eigenvalues of **S** are given by:

$$s_1 = \frac{\lambda_1}{\lambda_1 + \lambda_2 + \lambda_3} \qquad s_2 = \frac{\lambda_2}{\lambda_1 + \lambda_2 + \lambda_3} \qquad s_3 = \frac{\lambda_3}{\lambda_1 + \lambda_2 + \lambda_3} \tag{15}$$

Since $\lambda_1\lambda_2\lambda_3 = 1$, if the virtual deformation steps $\delta\varepsilon_i$ are expressed as $\delta\lambda_i/\lambda_i$, they automatically satisfy the volume-preserving condition. Equation (14) then becomes

$$\delta A = \frac{G}{\lambda_1 + \lambda_2 + \lambda_3}\delta\left(\lambda_1 + \lambda_2 + \lambda_3\right) \tag{16}$$

which readily integrates to:

$$A = G \ln \frac{1}{3}\left(\lambda_1 + \lambda_2 + \lambda_3\right) \tag{17}$$

Here, the constant of integration has been chosen so that A represents the excess free energy with respect to the undeformed state $\lambda_i = 1$.

In order to generalise Eq. (17) to an arbitrary deformation history, we invert Eqs. (15) (accounting for the condition $\lambda_1\lambda_2\lambda_3 = 1$) so as to express the λ_i's in terms of the s_i's. Equation (17) then becomes:

$$\frac{A}{G} = ln\frac{1}{3}\left[\left(\frac{s_1^2}{s_2 s_3}\right)^{\frac{1}{3}} + \left(\frac{s_2^2}{s_3 s_1}\right)^{\frac{1}{3}} + \left(\frac{s_3^2}{s_1 s_2}\right)^{\frac{1}{3}}\right] \tag{18}$$

Although Eq. (18) has been derived for a step deformation, it is of general validity for the single-mode model (in the absence of chain stretch). Indeed, without chain stretch the state of the material is fully specified by the single variable **S**. Hence, the material cannot distinguish whether a given orientational state has been reached through a step deformation or otherwise.

Conversely, for the multi-mode situation where the orientational variables are the numerous $\mathbf{S}_{ij}$, Eq. (18) only applies to the step deformation, where all $\mathbf{S}_{ij}$ are the same. However, in the general case we can sum the free energy over the modes. Hence, for the multi-mode model, Eq. (18) becomes

$$\frac{A}{G} = \sum_{i=1}^{N}\sum_{j=1}^{N} w_i w_j ln\frac{1}{3}\left[\left(\frac{s_1^2}{s_2 s_3}\right)^{\frac{1}{3}} + \left(\frac{s_2^2}{s_3 s_1}\right)^{\frac{1}{3}} + \left(\frac{s_3^2}{s_1 s_2}\right)^{\frac{1}{3}}\right]_{ij} \tag{19}$$

where the indices i and j on the square bracket indicate that the eigenvalues within the bracket refer to the tensor $\mathbf{S}_{ij}$. We look forward to comparing predictions of these formulas with data of flow-induced crystallisation.

Before concluding it is worth emphasising the expected limitations of the theory so far developed. We wish to point out that the double reptation concept used in the model certainly fails for very broad polydispersities. Indeed, the longest chains under those conditions do not relax by double reptation with the short ones (which would be too fast a process), but rather by a mechanism known as Rouse-like tube relaxation.[26] The modifications required by the model for such extreme situations are not simple, however. On the other hand, the longest chains can influence crystallisation significantly.

The other fundamental limitation refers to coupling effects between rheology and crystallisation. More specifically, we certainly expect that, once crystallisation has started, the rheology of the system is strongly influenced by the crystallites, which somehow act like crosslinks among amorphous chains. The basic model described above does not account for such effects, and therefore can only be applied to predict the onset of flow-induced crystallisation rather than its subsequent evolution.

[1] M. Doi, S. F. Edwards, "*The Theory of Polymer Dynamics*", Clarendon, Oxford 1986.
[2] P. G. de Gennes, *J. Chem. Phys.* **1971**, *55*, 572.
[3] H. Watanabe, *Prog. Polym. Sci.* **1999**, *24*, 1253.
[4] T. C. B. McLeish, S. T. Milner, *Adv. Polym. Sci.* **1999**, *143*, 195.
[5] G. Marrucci, *J. Non-Newtonian Fluid Mech.* **1996**, *62*, 279.
[6] G. Ianniruberto, G. Marrucci, *J. Non-Newtonian Fluid Mech.* **1996**, *65*, 241.
[7] G. Ianniruberto, G. Marrucci, *J. Non-Newtonian Fluid Mech.* **2000**, *95*, 363.
[8] S. T. Milner, T. C. B. McLeish, A. E. Likhtman, *J. Rheol.* **2001**, *45*, 539.
[9] G. Marrucci, N. Grizzuti, *Gazz. Chim. It.*, **1988**, *118*, 179.
[10] G. Marrucci, G. Ianniruberto, *Macromol. Symp.* **1997**, *117*, 233.
[11] D. W. Mead, R. G. Larson, M. Doi, *Macromolecules* **1998**, *31*, 7895.
[12] J. Fang, M. Kröger, H. C. Öttinger, *J. Rheol.* **2000**, *44*, 1293.
[13] G. Ianniruberto, G. Marrucci, *J. Rheol.* **2001**, *45*, 1305.
[14] G. Ianniruberto, G. Marrucci, *J. Non-Newtonian Fluid Mech.* **2002**, *00*, 00.
[15] C. Pattamaprom, R. G. Larson, *Macromolecules* **2001**, *34*, 5229.
[16] G. Marrucci, G. Ianniruberto, in "*ICAPP 2001 Yonezawa Proc.*", K. Iwakura, Ed.
[17] C. Tsenoglou, *ACS Polym. Prepr.* **1987**, *28*, 185.
[18] J. des Cloizeaux, *Europhys. Lett.* **1988**, *5*, 437.
[19] G. Marrucci, F. Greco, G. Ianniruberto, *J. Rheol.* **2000,** *44*, 845.
[20] G. Marrucci, F. Greco, G. Ianniruberto, *Rheol. Acta* **2001**, *40*, 98.
[21] M. Doi, *J. Polym. Sci.: Polym. Lett. Ed.* **1981**, *19*, 265.
[22] S. T. Milner, T. C. B. McLeish, *Phys. Rev. Lett.* **1998**, *81*, 725.
[23] G. Ianniruberto, G. Marrucci, *in preparation*.
[24] G. Marrucci, N. Grizzuti, *J. Rheol.*, **1983**, *27*, 433.
[25] S. Coppola, N. Grizzuti, P.L. Maffettone, *Macromolecules* **2001**, *34*, 5030.
[26] M. Rubinstein, R.H. Colby, *J. Chem. Phys.* **1988**, *89*, 5291.