Constraint Release mechanisms of star chains moving in a short polymer matrix

Evelyne van Ruymbeke, H. Taghipour
Bio and Soft Matter, Université catholique de Louvain, Louvain-La-Neuve, Belgium
evelyne.vanruymbeke@uclouvain.be

1. Introduction:

The linear viscoelastic properties of model polymer melts are, today, quite well understood. Also, tube-based models have shown their large capability to describe the different relaxation mechanisms. However, several questions remain, which need to be solved in order to obtain a fully quantitative model. In particular, tube models seem to fail in predicting the relaxation of binary blends of monodiperse polymers characterized by very different relaxation times, such as blends of linear and star polymers or blends of short and long star chains. The objective of this work is to further investigate the relaxation mechanisms of such blends and in particular, to study the importance of constraint release process in the slow motions of the (long) star chains. To this end, we review a series of binary blends presented in literature and analyze their relaxation based on our TMA model. This is illustrated here with a set of blends obtained from polybutadiene star chains with arms of mass 25 kg/mol and linear chains of 7 kg/mol (see [ref. 1]).

2. Star chains highly diluted in a matrix of linear chains:

We first investigate the viscoelastic behavior of the PBD stars diluted in the linear matrix at very low concentration, such as there is no entanglement between two stars, these last ones being only entangled with the linear chains. In such a case, since the linear chains are relaxing much faster than the star chains, it is expected that the stars fully relax by constraint release Rouse process (CRR), and that their corresponding Rouse time is equal to $\tau_{lin}.Z_{star}^2$ with τ_{lin}, the relaxation time of the linear chains and Z_{star}^2, the number of entanglements along the star. Their relaxation can therefore be represented by a Rouse equation. On the other hand, this CRR process should also be well described within the tube formalism, by considering that the star chains only relax by constraint release, under the condition that this relaxation cannot be faster than a Rouse process:

$$G(t) = G_N^0 .\ \varphi'(t).\phi_{tube}(t)^{\alpha} \quad , \qquad (1)$$

$$\varphi'(t) = \upsilon_{lin} .\ \varphi'_{lin}(t) + \upsilon_{star} \quad , \qquad (2)$$

$$\phi_{tube}(t) = \max\left(\varphi'(t), \phi(t'') \left[\frac{t''}{t} \right]^{\frac{1}{2}} \right) \quad , \qquad (3)$$

with G_N^0, the plateau modulus, υ_{lin} and υ_{star}, the weight fraction of the linear and star chains, $\varphi'(t)$ and $\varphi'_{lin}(t)$, the survival fractions of initial tube segments of the whole sample or of the linear chains at time *t*, , and $\phi_{tube}(t)$ the constraint release term which defines the tube diameter *a(t)* at time *t*, equal to $a(t=0).\ \phi_{tube}(t)^{-1/2}$, which cannot grow faster than by a Rouse process [ref. 2]. As described in eq. 2, the stars do not relax by CLF, since it is assumed they only relax by CRR.

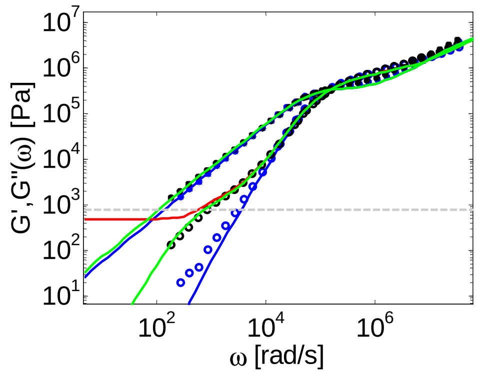

Fig.1. Storage and loss moduli of 100 wt% linear chains with M=7.5 kg/mol (blue o) and of 2 wt% star chains with M_{arm}=25.5kg/mol diluted in the linear matrix (black o). Red and blue curves: Predictions obtained based on eqs. 1-3. Dashed line: $G_{full\ rel.}$. Green curves: Eqs. 1-3 with cut-off of $\phi_{tube}(t)$.

Results are shown in Fig. 1 for 2 wt% of stars in the linear matrix. A good agreement with the experimental data is obtained, which validates the way the CRR process is taken into account. However, the tube diameter is limited to a maximum value of $a(t=0).\ \upsilon_{star}^{-1/2}$, which leads to a non-physical second plateau at low frequency. In fact, this discrepancy highlights an important limit of the present model: if a long chain is relaxing by CRR, there is no criterion which accounts for the fact that at some point, the chain should be considered as fully relaxed. On the contrary, the Rouse relaxation of a chain diluted in solvent considers that a chain is fully relaxed as soon as its longer mode is relaxed. In order to stay valid at larger time, $t > \tau_R$, the Rouse equation, expressed as a function of $t^{-1/2}$, is multiplied by a cut-off function, $exp(-t/\tau_R)$ [ref. 3]. Similarly, the end of CRR should be determined after the Rouse relaxation of segments of mass $2M_{arm}$, which corresponds to a storage modulus equal to:

$$G_{full\ rel.} = \upsilon_{star} \frac{\rho RT}{2M_{arm}} = \upsilon_{star} G_N^0 \frac{M_e}{2M_{arm}} \quad , \qquad (4)$$

with M_e, the molar mass between two entanglements and ρ the polymer density (see Fig. 1). Thus, below this level, the relaxation modulus must go towards 0, which is achieved by multiplying $\phi_{tube}(t)$ (see eq. 3) by the exponential function, $exp(-t/\tau_{CRR})$, with τ_{CRR}, the CRR time of the whole chain (here equal to $\tau_{lin}.Z_{star}^2$). In such a way, very good agreement is found for all frequencies.

3. Relaxation of star chains blended to linear chains:

At larger concentration, entanglements between two star chains are found and the picture of a dilated tube becomes valid. Results obtained based on eq.1-3, i.e. with the stars only relaxing by CRR, are shown in Fig. 2 (left, dashed curves). Surprisingly, no real plateau is observed at lower frequency and a slope of ½ is even found in G', as if the stars could relax by CRR up to larger length scale. Results obtained by allowing CRR beyond this dilated tube are represented by the continuous curve (left) and indeed, very well describe the experimental data, until the star reach their terminal flow. We explain this larger dilution effect based on monomeric tension equilibration process [ref.2], which allows the loss of initial star/star entanglements only due to the motion of the linear chains and consequently, which leads to larger tube dilution. Again, the terminal regime takes place when the full relaxation of the star ($G_{full\ rel}$) is reached and is well described by a function $exp(-t/\tau_{CRR})$ (see Fig. 2, middle), with the corresponding CRR times accounting for the lifetime of both the linear-star and the star-star entanglements (see Fig. 2, right).

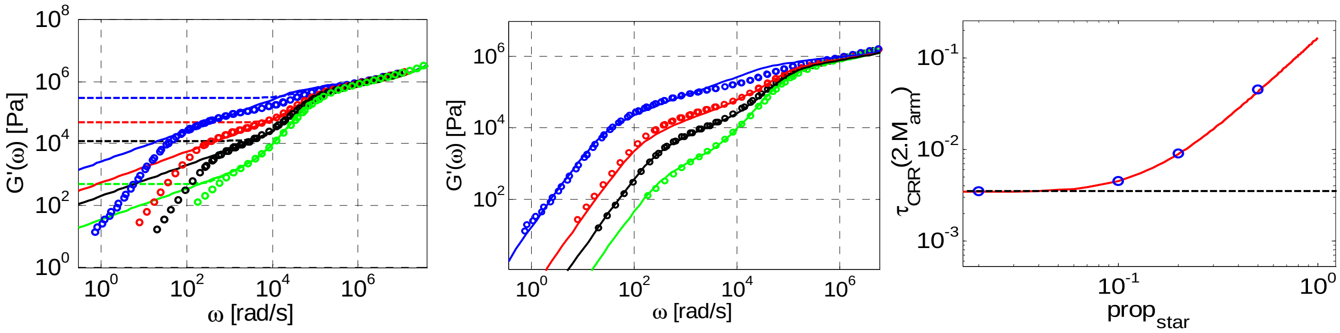

Fig. 2: Storage modulus of binary blends composed of 50 wt%, 20 wt%, 10 wt% and 2 wt% of stars in a linear matrix (o: experimental G'; theoretical curves: see text), and CRR times used in the cut-off function, in respect to υ_{star}.

Thus, from this example, we conclude that the relaxation of star chains diluted in a short matrix is well described by only considering CR mechanisms, this last process being most probably in competition with the CLF process. This assumption is then tested on other binary blends.

References:

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