Viscoelastic response of linear defects trapped in polymer networks

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A B S T R A C T

We analyze the dynamic response of end-linked poly(dimethylsiloxane) networks containing entangled unattached guest linear polymers. Upon increasing the content of unattached guest polymers there is an increasing dissipation and a reduction in the network elasticity. It was found that the width of the relaxation spectrum is nearly insensitive to the content of guest chains, indicating that the network structure is not affected by the presence of these defects and that the effective number of entanglements associated to guest chains is independent of the equilibrium elastic modulus of the networks.

The inhibition of the constraints release mechanism for molecules trapped in polymer networks have enormous consequences on the dynamic response, producing a dramatic slowing down in the relaxational dynamics of defects. The presence of different structures of defects in polymer networks is physically unavoidable, even under optimum reaction conditions. Here we found that the slow dynamics of soluble branched structures or dangling molecules can easily hide the contribution of linear unattached molecules.

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1. Introduction

Viscoelastic and diffusional properties of entangled polymers have been successfully described by the tube model [1–8]. According to this model, the topological confinement exerted on a given molecule by the surrounding media can be modeled as a hypothetical tube that severely suppress the motion perpendicular to the tube's local axis, but permits the diffusion along the tube [3,4].

For linear chains, the long time dynamics is mainly controlled by the diffusion of molecules along its own contour, a process known as "reptation" [1]. In this case, the theory predicts that both, terminal relaxation time τ_d and shear zero viscosity η_0 scales with the molar mass of the linear

polymer chain M as $\tau_d \sim M^3$ and $\eta_0 \sim M^3$, respectively. However, several experimental studies clearly indicate a stronger dependence on molar mass, with both quantities scaling as $M^{3.4}$ [4–6]. Then, in addition to the dominating effect of chain reptation, two additional mechanisms must be considered in order to obtain a quantitative agreement with the experiments [4–6,9]: *contour-length fluctuations* and *constraint release*. Contour length fluctuations [8] account for the shortening of the primitive path as a result of fast random motions of the chain ends while the constraint release mechanism takes into account the fact that some of the chains that define the confining tube release their constraints [4–6].

Unlike a linear chain, branched molecules cannot reptate to recover equilibrium. In this case, reptation is severely suppressed and chains renew their configurations mainly through arm retraction [2,4–6,10–19]. In this case

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the end of each arm must retract partway down its confining tube to reemerge along a different path [4]. The absence of reptation due to the branching point has important consequences on the dynamics of branched polymers in both, the linear [4–6] and non-linear viscoelastic regimes [20–27]. Quite differently from the power law observed for linear polymers, arm retraction mechanism is highly unfavorable and the time scale for complete retraction in the entangled regime increases roughly exponentially with the molar mass of the branch [2,4]. This mechanism was firstly studied by de Gennes, who considered the motion of a symmetric star shaped polymer in a fixed network of obstacles and showed that the probability for a star arm of length N to retract fully to the junction point is exponentially unlikely. Then, the longest relaxation time that allows the star arm to completely lose its configurational memory becomes $\tau_s \sim \exp(\gamma N)$, where γ is a constant [2].

Stress relaxation of symmetric star polymers in a fixed network of obstacles was theoretically studied through the tube model formalism by Doi and Kuzuu [11] and Pearson and Helfand [12]. According to this model the arm free end can be thought to be undergoing Brownian motion in a potential field dictated by the effective number of entanglements per star arm. The Pearson–Helfand model predicts that the arm potential $U_{PH}(s)$ has the following quadratic form [4,12]: $U_{PH}(s) = \frac{15}{8}Zs^2$, where $s(0 < s < 1)$ is the fractional distance back along the primitive path where the arm free end has been retracted and Z is the average number of entanglements per star arm [5,16]. Within this theoretical frame, the terminal relaxation time for a star trapped in a fixed network of obstacles results [28,29]:

$$\tau_{PH}(s, n_e) = -\frac{1}{2}I\pi^3 Z^2 \tau_e \, erf(I\sqrt{vZ}s) \qquad (1)$$

where $v = 15/8$ $I = \sqrt{(-1)}$, $erf[x]$ is the error function and τ_e is the Rouse relaxation time for an entanglement segment [4,5].

When compared with experiments employing symmetric star polymer melts with different chemical structure, it has been shown that the Pearson–Helfand potential largely over-predicts the terminal relaxation time [4,15,16]. Then, in order to remove the discrepancy between the theory ($\tau_{PH}(n_e) \sim \exp[15/8Z]$) and experiments ($\tau_{exp}(Z) \sim \exp[0.6Z]$), it is necessary to reduce the strength of the arm retraction potential by a factor of about 3 [4,16,18]. This discrepancy was solved by considering not only arm retraction process but also the constraint release contribution. In a melt of entangled star shaped molecules, different arms are not moving in a fixed network of obstacles since some topological constraints can be released by other star free ends in the neighborhood. In this case the constraint release mechanism contributes to speed up the relaxational dynamics [4,6].

On the other hand, during the last decades the dynamics of macromolecules trapped in polymer networks have attracted considerable attention due to their practical and theoretical interest [28,30–41]. Since in polymer networks the confining tube remains nearly invariant, the process of constraint release is inhibited [28]. Consequently,

polymer networks can be employed as an excellent model to study the dynamics of polymers with different architectures in the absence of this important relaxational mechanism. For example, a guest linear chain trapped in a network will lose its conformational memory mainly via reptation [42–47] while the slow relaxation of a symmetric star or a linear pendant chain [28,48–57] is driven by arm retraction in the very strong arm retraction potential $U_{PH}(s)$ [28].

In this work, we employ well characterized PDMS networks with controlled amounts of unattached linear guest polymers to analyze their influence on the viscoelastic response. The results are theoretically rationalized in terms of the tube model and compared with available data for networks containing similar amounts of linear dangling chains.

Although the problem of linear guest chains trapped in a network has been previously explored to test the validity of the tube model [42–47], here we focus the attention on the effect of guest chains concentration on the elastic and dissipative properties. The role of unavoidable defects residing in the network structure and their contribution to the dynamic response is also analyzed.

2. Experimental

Model poly(dimethylsiloxane) networks were obtained by a hydrosilylation reaction, based on the addition of hydrogen silanes from cross-linker molecules to end vinyl groups present in prepolymer molecules [49,58–61]. A commercial difunctional prepolymer, α,ω-divinyl poly(dimethylsiloxane) (B_2) (United Chemical Technology, Inc.) and linear unreactive poly(dimethylsiloxane) polymers ($B_{0,1-4}$) with different molar masses were employed. The molar mass characterization of the prepolymers and other reactants used in the cross-linking reactions are listed in Table 1 where the notation $B_{0,i}$, with $i = 1–4$, was employed for the linear poly(dimethylsiloxane) chains. Phenyltris(dimethylsiloxy)silane (A_3) (United Chemical Technology, Inc.) was used as cross-linker and a Pt salt was employed as catalyst for the cross-linking reaction.

Four linear polymers ($B_{0,i=1-4}$) with relatively narrow molar mass distribution were obtained from monofunctional polymers synthesized previously by anionic polymerization, using n-butyllithium as initiator, n-hexane as solvent and tetrahydrofuran (THF) as polymerization promoter. The vinyl group chain end of the monofunctional polymers was neutralized by a hydrosilylation reaction with a monofunctional reagent containing a silane group (A_1). The monofunctional reagent A_1 employed was pentamethyldisiloxane, which was used in excess of about 100%. A Pt salt was used as catalyst for the reaction. The neutralization reaction was carried out in solution, using toluene as solvent for about 24 h. The reactive mixture was maintained under nitrogen atmosphere with mechanical stirring at a temperature of 333 K. Once the reaction was completed, the polymer was precipitated from the reaction media using methanol. The PDMSs without reactive groups was then separated from the solvent and dried under vacuum up to constant weight. The elimination of