



Dynamics of Linear Chains in Polymer Networks as a Model for Drug Delivery Systems: Preliminary Results

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Abstract

Dynamic properties of cross linked polymer networks and gels are the subject of a particular interest in drug delivery applications. Here, we report preliminary results considering the effects of combined relaxations of network (as host) and linear chains (as guest). These combined relaxations are analyzed in terms of fast (host driven) and slow (guest driven) modes through response functions derived from linear response theory and accessible by quasi elastic scattering or fluorescence confocal spectroscopy. Preliminary results of the variations of frequencies and amplitudes of the modes are given under a variety of conditions depending on the polymer concentration, degree of miscibility and relative sizes of chains and network strands.

Keywords: *Cross linked polymer; Spectroscopy; Miscibility; Amphiphilic*

Introduction

Dynamics of multi component polymer systems have been the subject of a particular attention in the literature for quite a long time [1]. The driving idea is to mix different species in an attempt to combine all their properties in a single composite material having predefined functionalities. Successes in polymer chemistry opened up wide prospects for synthesizing new materials with unprecedented applications in a variety of domains such as drug delivery devices [2]. There are two typical examples of drug carriers involving polymers; cross linked networks or gels which are characterized by swelling and de swelling responses to changes in the medium conditions such as temperature and pH of the solution [3]. These responses determine the kinetics of drug delivery and may be influenced by the dynamics under equilibrium here which we would like to analyze by invoking the slow and fast relaxation processes characterizing linear chains in polymer networks. Another class of drug carriers use amphiphilic block copolymers which, under certain conditions, these systems form spherical micelles

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with a hydrophobic hard core at the center containing the drugs and a hydrophilic swollen shell [4]. We will focus on the former case by examining considering the relaxations of linear chains mimicking drug specie and the cross-linked network as the carrier.

These dynamical relaxations are stamped the interaction parameter denoted χ which controls the degree of compatibility of the species in the mixture, and their extent of miscibility or phase separation. Another important ingredient of these relaxations is the mobility of each species forming the mixture knowing that there are short ranges frictional forces opposing molecular motions and long range viscous flow effects reminiscent of hydrodynamic interactions in the fluid. We will give selected preliminary results invoking the impact of the polymer sizes, that of thermodynamic interactions inherent in the χ -parameter.

Dynamical process: Fast and slow modes

The dynamic response function is denoted $S(q,t)$, where the reciprocal space variable q^{-1} indicates the probed space range, and t the time. The complete formalism based on linear response theory will be given in more detail elsewhere. Here, we simply indicate that $S(q,t)$ may be written as a sum of two terms,

$$S(q,t) = a_f e^{-\Gamma_f t} + a_s e^{-\Gamma_s t} \quad (1)$$

Where subscripts f and s denote fast and slow, respectively; a 's are amplitudes and Γ 's relaxation frequencies. At small q 's, diffusion overwhelms the dynamics, and the diffusion coefficients for both processes are defined as

$$\frac{\Gamma_{f,s}}{q^2} \equiv D_{f,s} \quad (2)$$

Note that the static quantity $S(q, t=0)=S_0(q)=a_f+a_s$ has been discussed in reference [3], and the partial amplitudes a_f and a_s will be examined in details elsewhere. All these properties are accessible experimentally by scattering techniques such as quasi elastic light scattering or neutron spin echo, or using fluorescence confocal spectroscopy. In the next section, we present selected preliminary results.

Preliminary Results and Discussion

The fast mode is reminiscent of the network breathing process while the slow mode describes an inter diffusion process whereby linear chains find their way in between the network's strands and neighboring cross links. If the linear chains in solution are relatively short compared to network strands, then the viscosity drops and the frictional forces hindering molecular displacement get weaker. This means that relaxation frequencies go up and the dynamical processes speed up noticeably.

Opposite trends are observed for longer linear chains where both processes slow down because of hindrance of molecular motion due to combined effects of enhanced friction forces and damping in hydrodynamic interaction.

On the other hand, as the interaction between network and linear chains increases, their miscibility drops and the relaxation modes slow down substantially. This means that fluctuations in composition and in total polymer concentration take longer time to relax, possibly reaching the critical slowing down behavior as the χ parameter approaches a critical threshold.

It is interesting to note that the normalized diffusion coefficient obtained in the small q -limit exhibit opposite tendencies for both processes. While the slow mode diffusion coefficient decreases with the total polymer concentration that of the fast mode increases under similar circumstances. The relative importance of the fast mode compared to the slow one is also indicated by the relative amplitude $a_f/(a_f+a_s)$. The calculations show that this quantity exhibits a peaked variation with the total polymer concentration. Starting from the dilute regime, one finds that the fast mode tends to dominate the spectrum since its relative amplitude grows with concentration. There is a maximum at a certain concentration, then a significant drop meaning that the slow mode takes over and becomes the overwhelming process in the spectrum. This can be understood by recalling that in the bulk limit where the total polymer concentration reaches its upper bound, the spectrum is made uniquely of the slow mode describing the inter diffusive process of linear chains in the network. This process is found to be more sensitive to the degree of miscibility which is indicated by the fact that the relative amplitude of the fast mode drops significantly.

Instead of considering separately the frequencies $\Gamma_{f,s}$ and the relative amplitude $a_f/(a_f+a_s)$, one can combine both information to get the mean relaxation frequency $\bar{\Gamma} = (a_f\Gamma_f + a_s\Gamma_s)/(a_f + a_s)$ which is accessible experimentally from the initial slope of $S(q,t)$ versus time. The corresponding diffusion coefficient, which is obtained from the $q=0$ limit, shows a peaked variation with concentration except for cases where the guest composition is very low and linear chains are present at a trace amount only. There is currently a renewed interest on this case in the literature promoting the development of fluorescence confocal spectroscopy [5]. When the chain's molecular weight exceeds a certain threshold, the chain tries to avoid obstacles by executing a reptation motion [6], whose properties differ from those of the fast and slow modes considered here. Under certain conditions, cross over phenomena may take place between different processes depending on the values range of molecular sizes, concentration, composition and temperature.

Conclusion

These findings hint to the fact that the fast mode drives the dynamics of the host network while the slow one is reminiscent of the motion of linear chains embedded in the guest solution. This report was limited to the special response function $S(q,t)$ describing the network dynamics in the presence of polymer solution. Other responses can be considered probing the dynamics of guest chains that diffuse in the network or the host/guest cross correlations. Experimentally, the distinction between those functions can be achieved by labeling techniques. While the frequencies $\Gamma_{f,s}$ are the same for different functions, the amplitudes $a_{f,s}$ change. A major difficulty in handling the dynamics of polymer systems at long times is inherent in the memory effects especially for non-Markovian processes. For the case of a single chain, this problem was solved by de Gennes [6]. under certain conditions. In general, however, calculations of the memory effects remain still a big

challenge. The present results are valid if long range hydrodynamic interactions are present or not, although the formalism is much more elaborate in the former case. A detailed numerical analysis of these results will be reported in the near future.

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