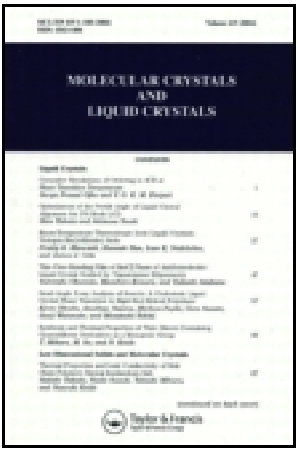

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Neutron Spin Echo Investigations on the Dynamics of Polymers

D. Richter [a]

[a] Institut Laue-Langevin, Grenoble, France

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Neutron Spin Echo Investigations on the Dynamics of Polymers

D. RICHTER
Institut Laue-Langevin, Grenoble, France

Neutron spin echo spectroscopy allows an observation of long range internal relaxation mechanisms of macromolecules simultaneously in space and time. Thereby it facilitates a microscopic study of molecular models applied for the explanation of the macroscopic viscoelastic properties of polymer materials. For *linear polymers* in solution and melt universal intramolecular relaxation mechanisms are predicted theoretically. In this talk, I review experimental results over the full range of concentration. Thereafter, I present spin echo experiments on the dynamics of *branched polymers* choosing the star molecule as a prototype. Finally, I discuss aspects of the dynamics of polymer networks and present first spin echo data on the motion of labelled cross-links.

The main part of the quasielastic neutron scattering work in the field of polymer is centered around the investigation of large scale intramolecular relaxations. While the motion of single bonds along the backbone of a polymer chain is restrained by the details of the local potential, the longer range movements tend to become independent of such constraints and are thought to exhibit universal behaviour. Entropic forces resulting from the conformational entropy in the polymer free energy, hydrodynamic interactions between different polymer segments in solution and topological constraints or entanglements in concentrated systems govern the motional properties. The discovery of the equivalence between polymer conformations in solution and spin correlations in ferromagnets near T_c led to a transfer of ideas on many body effects in the theory of phase transitions and critical phenomena to the description of polymers. Finally, the scaling ansatz was also applied to polymer dynamics.[1] On a macroscopic scale these molecular motions are the origin for the unusual viscoelastic properties of polymer systems being essential for polymer applications. Thus, besides fundamental interest neutron scattering experiments on the molecular motion of macromolecules ultimately aim on a microscopic understanding of their mechanical properties.

Experimentally, this field has been opened up to neutron scattering by the application of the neutron spin-echo (NSE) technique. Uniquely, it provides the necessary energy resolution (10 neV) at sufficiently small scattering vectors ($q > 0.02$ Å^{-1}). It is worth mentioning that NSE as a Fourier method measures directly the intermediate scattering function $S(q,t)$ a quantity of particular usefulness in the

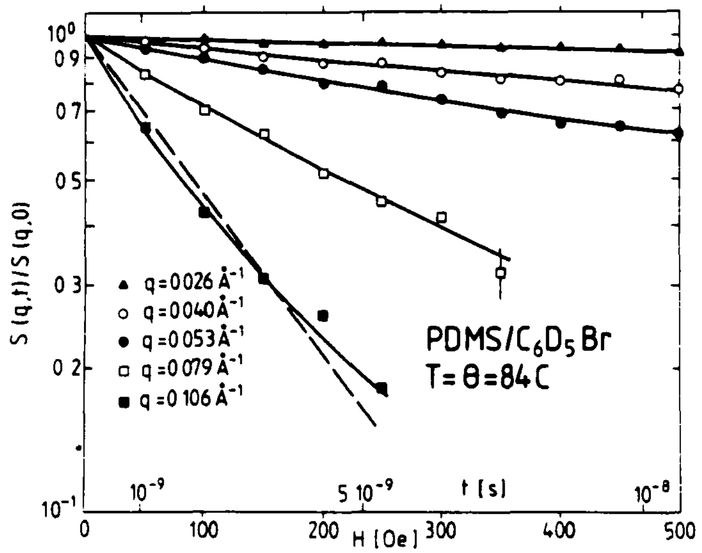

FIGURE 1 Relaxation spectra $S(q,t)/S(q,0)$ as a function of time for a dilute solution of PDMS in bromobenzene taken at the θ-temperature. Thereby $S(q,t)/S(q,0)$ is given by the neutron polarization and t by the value of the guide field H in a spin echo set-up.

study of relaxation phenomena.[2] Experimental efforts commenced with studies on the motion of linear polymers. In dilute solution the internal relaxation is governed by the hydrodynamic interaction, i.e. the mutual interaction between polymer segments via the solvent backflow.[3] Under these circumstances the characteristic relaxation frequency $\Omega(q)$ should scale with the third power of the scattering vector q (Zimm modes). Within the q–t range of the spin-echo spectrometer IN11 at the ILL, such behaviour has been verified for several flexible polymer systems (PDMS, PMMA) in θ as well as in good solvents.[3,4] Figure 1 presents a typical set of spectra taken on PDMS in Bromobenzene which is a θ-solvent at 84 C. The solid lines are the results of a fit with the Zimm model which, using only one adjustable parameter, describes the data very well. It is interesting to note that dynamic experiments on macroscopic quantities like the viscosity or the frequency dependent moduli are well understood in the framework of the same molecular model. Thus, it provides a consistent description of polymer relaxation in dilute solutions starting from length scales in the order of 10 Å and time scales above 10^{-9}s. In the time-length domain of the spin echo experiments systematic deviations towards lower q-exponents are found for less flexible chains (PS,PTHF) and are interpreted as resulting from the influence of the local potential. This provides a means of studying the backbone dynamics on a more local scale and of extracting information on the potential and local hindrance, a subject upon which current interest is focussed.[5]

With increasing monomer concentration, different chains start overlapping and forming a transient network of mesh size ξ_c. With respect to chain dynamics both the collective response of the many chain ensemble as well as the single chain motion are of interest.

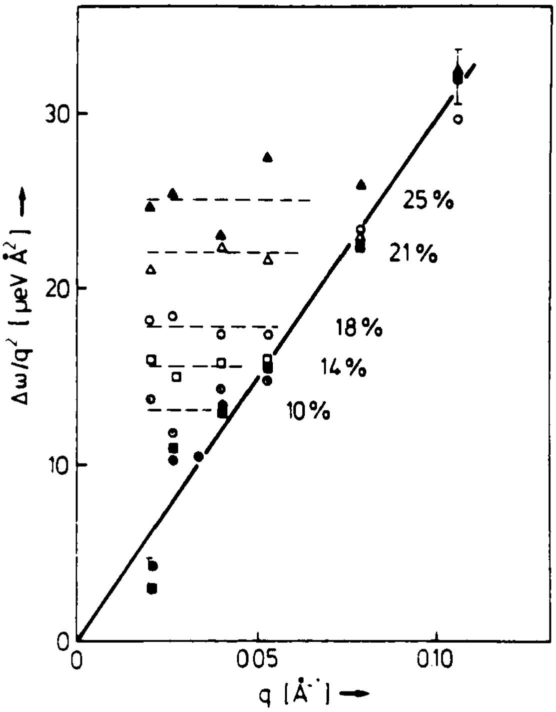

FIGURE 2 Concentration cross-over in PDMS-D-benzene. Characteristic frequencies $\Delta\omega/q^2$ for benzene different concentrations at 70°C as a function of momentum transfer q. The solid line represents the low concentration q^3-dependence due to Zimm relaxation, the dashed lines show the q^2-behaviour characteristic for collective diffusion.

(I) Many chain system: From analogy with swollen permanent networks for spatial scales $r > \xi_c$ a collective relaxation spectrum $\Omega \sim D_c q^2$ is anticipated, while for shorter distances the network is not yet effective and $\Omega \sim q^3$ should still be valid. Spatial cross-over between both regimes is expected for $q\xi \simeq 1$. Quasielastic neutron scattering on PDMS in d-benzene led to a direct observation of this cross-over. Figure 2 summarizes the experimental results. While at low polymer concentrations the observed characteristic frequencies follow the q^3-law, with increasing concentration a cross-over to a q^2-behaviour is found at increasing q-values. The plateau values at low q thereby relate to the collective diffusion coefficient D_c, the cross-over points to ξ_c. ξ_c and D_c were found to scale with the monomer concentration according to the predictions of dynamical scaling.[6]

(II) Single chain system: For the relaxation of a single chain the screening of the hydrodynamic interaction is of prime importance. For distances longer than a hydrodynamic length ξ_H the backflow field is screened out and chain relaxation is thought to be controlled by the entropic forces alone. Spinecho experiments on labelled H-PDMS chains in contrast matched semidilute PDMS solutions allowed a microscopic observation of hydrodynamic screening i.e. a gradual cross over from

hydrodynamic modes (Zimm) to decoupled entropy controlled modes (Rouse), and led to a determination of $\xi_H(c)$.[7] The experimental result of nearly coinciding ξ_H and ξ_c is in favour of one of the basic assumptions of dynamical scaling. However, other than theoretically anticipated, the hydrodynamic screening is not complete, but a residual time dependent viscosity remains which mediates the backflow field beyond ξ_H. Its microscopic explanation is still open.

In dense polymer systems the influence of entanglements is supposed to determine their dynamic properties. The experimental results on macroscopic diffusion and zero shear viscosity support the reptation idea. It postulates that due to mutual entanglements significant chain motions only occur inside a tube along the chain profile. These constraints should also influence the internal chain relaxation modes. In particular the mean square displacement of a given segment is predicted to increase only with the time to a power of one quarter as opposed to Rouse modes where an exponent of one half is expected. This time exponent was directly measured on a randomly labelled melt. There, the self-correlation function of a polymer segment is observed. Figure 3 presents the obtained exponents n for different values of the momentum transfer q.[8] All data are consistent with an exponent 1/2 and thus are not influenced by entanglement constraints. Experiments were also undertaken on protonated PDMS[7,9] and PTHF[10] molecules dissolved in their respective deuterated melts. They measured the coherent scattering from a single chain in a melt and were sensitive to pair correlations along the chain. The outcome of both experiments was similar but was interpreted in opposite ways. While the experimental line-shape seems to follow the local reptation model, its dependence on the scattering vector q disagrees strongly. This can be seen best in a scaling representation of the experimental data[11] (Figure 4). While the scattering function $S(q,t)$ for the Rouse model depends only on the product $q^2\sqrt{t}$, $S(q,t)$ derived for local reptation contains an additional explicit q-dependence. As Figure 4 clearly shows, experimental as well as Monte Carlo results[9] follow the universal curve of the Rouse model while local reptation leads to different curves for each q-value. However, though both coherent and incoherent experiments appear to favour the

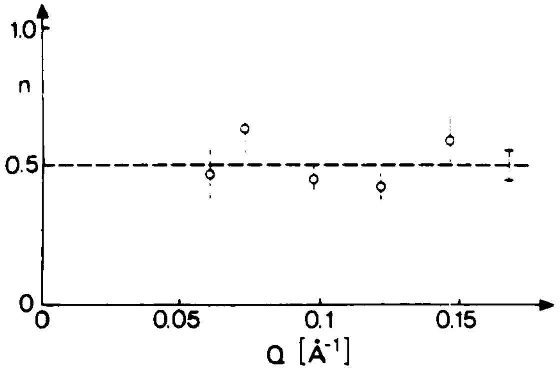

FIGURE 3 Time exponent in the stretched exponential form of $S(Q,t) = \exp - Q^2(t/\tau)^n$ as a function of Q for a randomly labelled PDMS melt.

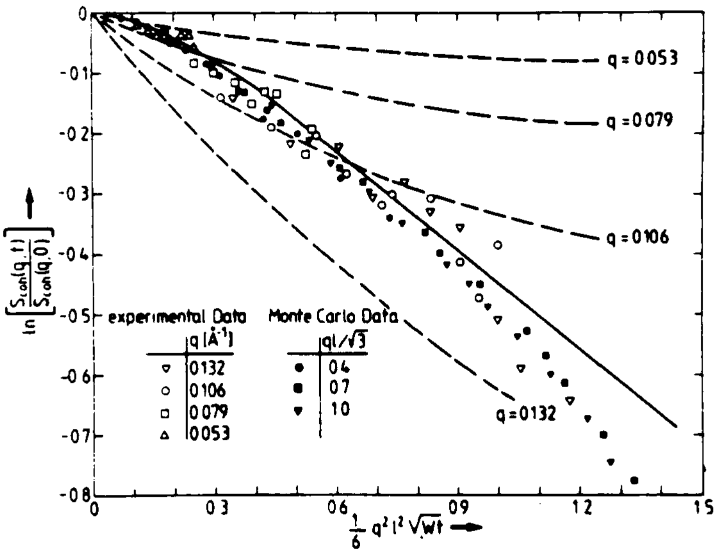

FIGURE 4 Scaling representation of the measured relaxation function $S(q,t)$ for 5% protonated PDMS chains in a deuterated melt. Solid line: Rouse model, dashed lines: prediction of the local reptation model.

Rouse model and do not show any effect of topological constraints on the chain dynamics, a definite experimental answer on the existence of local reptation on a microscopic scale cannot yet be given. As indicated by the rather large "tube diameter" of d_t = 50 Å for PDMS entanglements may become effective only at distances and times outside the present experimental range. Further experiments at smaller scattering vectors with better resolution, as will be possible on the new ultra high resolution spin-echo machine IN15, presently under construction at the ILL, are required to solve the puzzle. Finally, NSE results are compared with macroscopic dynamic mechanical data on PDMS melts. For short enough chains also the macroscopic data are in agreement with simple Rouse dynamics. The obtained model parameter, namely the friction coefficient/(segment length)^2 agree better than by a factor of two and display again internal consistency of microscopic and macroscopic results.[7]

So far, solely relaxation phenomena of linear chains were discussed. Synthetic polymers, however, exhibit a large variety of architectures involving e.g. branching and cross-linking. Star type polymers, where several linear chains are connected at one point, can be considered as the simplest prototype materials for branching systems. Figure 5 presents first measured internal relaxation rates on polyisopren stars with different functionalities.[12] The rates are reduced by q^3 and are plotted vs a scaling variable v being the product of q and the radius of gyration of one chain in the star (arm length). At large arguments Zimm relaxation as in the case of linear polymers is found and leads to Γ/q^3 = const. While for the 4-arm star this behaviour prevails until the cross over to translational diffusion $\Gamma/q^3 \sim 1/q$,

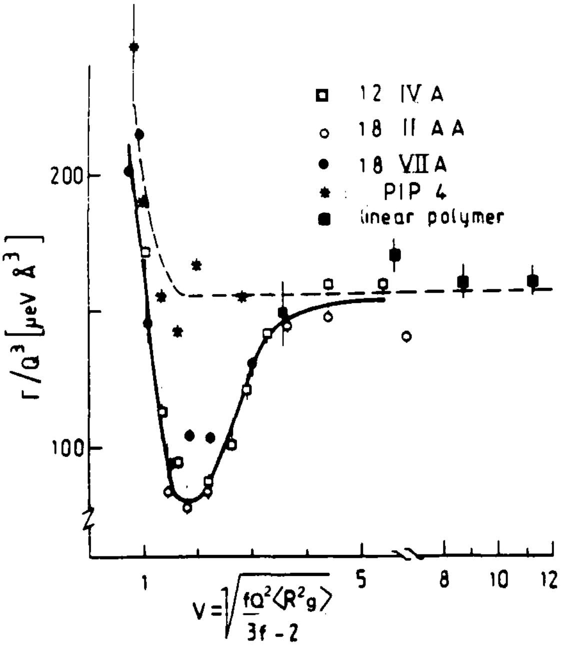

FIGURE 5 Reduced relaxation rates Γ/Q^3 from polyisoprene star molecules in dilute solution (d-benzene). The numbers in the sample name note the functionalities of the stars. The scaling variable v is a product of Q and the mean square radius of gyration of one arm. The solid and dashed lines are guides to the eyes.

for the stars of higher functionalities, the reduced rates pass a sharp minimum before they bend upwards into the regime of translational diffusion. The scaling with the variable v as well as the position of the minimum find its counterpart in the behaviour of the static structure factor which in a Kratky representation exhibits a maximum where Γ/Q3 shows a minimum. Thus, the minimum in the reduced relaxation rate is directly related with pecularities of the star architecture. In the theory of liquids such a phenomenon is well known under the term of de Gennes narrowing. There $S(Q)$ renormalizes the relaxation rate for density fluctuations. While in the liquid this is an effect involving different independent particles, in the case of the star it occurs for the internal density fluctuation of one entity.

Finally, first NSE experiments on the dynamics of polymer networks aiming on the motional properties of cross links are presented. They were performed on a four functional deuterated PDMS network with a mesh size of $R_E \simeq 50$ Å containing labelled cross-links. As a reference an end labelled melt without cross-links of chains identical to those of the mesh was also studied.[8] Figure 6 displays NSE data from both samples and shows a much weaker decay of $S(q,t)$ in the case of the cross-links as compared to the chain ends. This strongly reduced relaxation is caused by two effects: (i) since a cross-link is 4-fold connected while a chain end has only one topological neighbour, the intrinsic Rouse rate is changed[13]; (ii) while a non cross-linked chain is free to move over macroscopic distances, due to the inter-

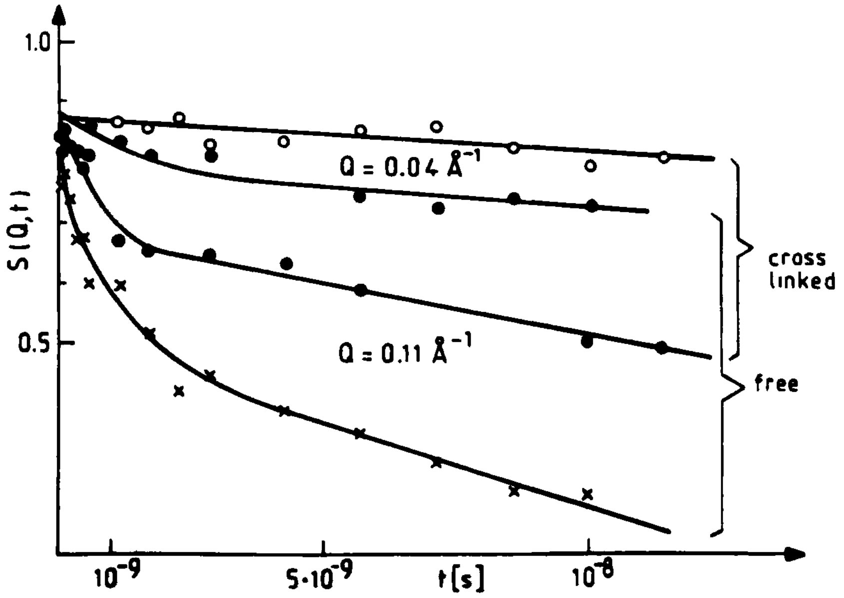

FIGURE 6 NSE-spectra from labelled cross-links and labelled ends of free PDMS-chains in a melt at two different Q-values.

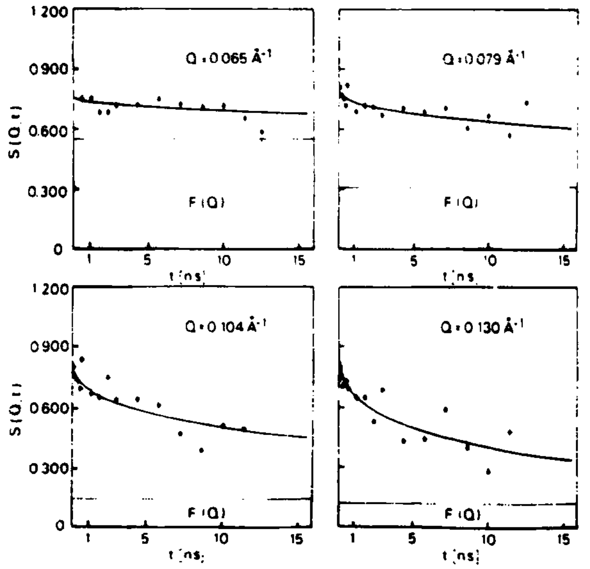

FIGURE 7 NSE-results for labelled cross links at 4 different Q-values. Included is a result of a fit with a sum of a constant contribution $F(Q)$ and a Rouse relaxation spectrum resulting in the following values for σ: (Q = 0.065 Å^{-1}, σ = 23.5 ± 3.3 Å; Q = 0.079 Å^{-1}, σ = 28.1 ± 2.8 Å; Q = 0.104 Å^{-1}, σ = 27.0 ± 3.4 Å; Q = 0.130 Å^{-1}, σ = 22.6 ± 2.4 Å). During this fit the Rouse relaxation rate $W\sigma^4 = 0.84 \cdot 10^{13}$ Å^{4}s^{-1} was kept fixed.

connectivity of the network, the motional range for a cross-link is strongly limited. In the framework of the so-called phantom network which considers fluctuations of cross-links the fluctuation range is given by a Gaussian distribution exhibiting a width $\sigma^2 = 4/3f\langle R_E^2\rangle$ where f is the functionality.[14] As a consequence even for infinite time, the self-correlation function of a cross-link does not decay to zero but is given by the above Gaussian distribution. Consequently, also $S(q,t)$ does not decay to zero but contains a constant time independent contribution $F(q) = S(q,t \rightarrow \infty) = \exp(-q^2\sigma^2/4)$. Thus a measurement of $S(q,t)$ reveals both: the time constant for the cross-link motion and its spatial limitation. Figure 7 displays the experimental data at different q-values including a fit with a Rouse type decay function sitting on a constant contribution $F(q)$. With increasing q,$F(q)$ diminishes and the decaying part gains importance. The fit results in σ values between 22.6 Å and 28.1 Å slightly smaller than the prediction of the phantom network of σ = 30 Å. The time constant is reduced by a factor of two compared to that of a randomly labelled melt and is a factor of 4.3 smaller than that of the chain ends, both results in good agreement with a calculation of Warner[15] predicting a 4:2:1 ratio. These experiments constitute the first direct determination of cross-link fluctuations and will have implications for the understanding of the rubbery state.

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