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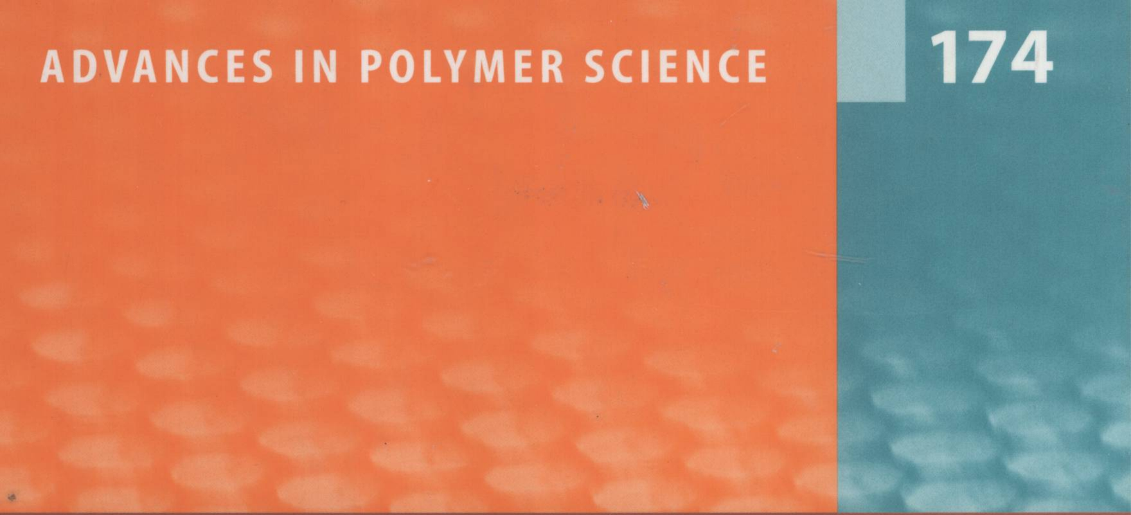

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Neutron Spin Echo in Polymer Systems

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Neutron Spin Echo in Polymer Systems

By Dieter Richter, Michael Monkenbusch,
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Springer

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Neutron Spin Echo in Polymer Systems

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Abstract Neutron spin echo spectroscopy (NSE) provides the unique opportunity to unravel the molecular dynamics of polymer chains in space and time, covering most of the relevant length and time scales. This article reviews in a comprehensive form recent advances in the application of NSE to problems in polymer physics and describes in terms of examples expected future trends. The review commences with a description of NSE covering both the generic longitudinal field set-up as well as the resonance technique. Then, NSE results for homopolymers chains are presented, covering all length scales from the very local secondary β-relaxation to large scale reptation. This overview is the core of the review. Thereafter the dynamics of more complex systems is addressed. Starting from polymer blends, diblock copolymers, gels, micelles, stars and dendrimers, rubbery electrolytes and biological macromolecules are discussed. Wherever possible the review relates the NSE findings to the results of other techniques, in particular emphasizing computer simulations.

Keywords Neutron spin echo spectroscopy · Polymer dynamics · Reptation · Glassy relaxation

1
Introduction

Among the experimental techniques for studying the structure and dynamics of polymers, neutron scattering plays a unique role for several reasons:

i. The suitability of the length and time scales. These are accessed in particular by small angle neutron scattering (SANS) and neutron spin echo (NSE) and allow the exploration of large scale properties – for instance the conformation of a large macromolecule, its diffusion in the embedding medium and its entropy driven dynamics – as well as features characteristic for more local scales, e.g. the inter- and intrachain correlations in a glass-forming polymer and their time evolution, the rotational motion of methyl groups, the vibrations and so on.
ii. By variation of the contrast between the structural units or molecular groups, complex systems may be selectively studied. In particular, the large contrast achieved by isotopic substitution of hydrogen – one of the main components of polymers – by deuterium constitutes the most powerful tool for deciphering complex structures and dynamic processes in these materials.
iii. Neutron reflectometry constitutes a unique technique for the investigation of surfaces and interfaces in polymeric systems.
iv. The high penetration of neutrons in matter allows the study of the influence of external fields, e.g. shear or pressure or the evolution of the system under processing conditions.
v. The space-time resolution of these techniques reveals the molecular motions leading to the viscoelastic and mechanical properties of polymeric systems. This knowledge is of great importance for scientific reasons and is also a basis for the design of tailor-made materials.

The unique power of neutron scattering for revealing essential features in the field of polymer science can be exemplified by two pioneering experiments that can already be considered as “classic”. The first is the experimental proof of the random coil conformation of polymer chains in the melt or in the glassy state, as proposed in the 1950s by Flory [1]. Its confirmation was only possible in the 1970s [2] with the development of SANS. Since in the bulk a given macromolecule is surrounded by identical units, Flory’s proposition could only be demonstrated by using contrast variation and deuterating single molecules. This measurement of a single chain form factor by SANS was one of the first applications of neutron scattering to polymer science. Its dynamic counterpart could only be realized 25 years later. Neutron spin echo investigations on the long time chain dynamics recently allowed the confirmation of de Gennes’ predictions [3] on the mechanism of tube-like confinement and reptation in polymer melts and dense systems [4].

In this review we will concentrate on the dynamic aspects of the polymer ensemble and describe as comprehensively as possible what has been achieved

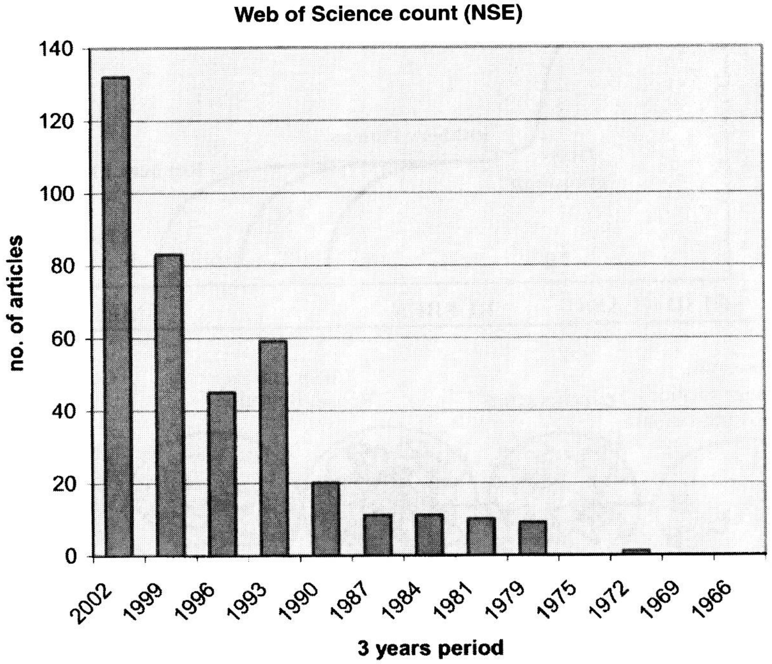


Fig. 1.1 Development of the number of NSE-related articles in 3-year periods from now to the invention of the method

so far by neutron spin echo spectroscopy. The last major review in this field appeared in 1997 [5]. Since then, a strong growth of publications on NSE results may be observed (Fig. 1.1). This figure displays the total number of publications on neutron spin echo results in three years intervals. It is evident that during recent years the publication rate on NSE results has increased dramatically. This increase is due to two reasons. First, apparently more and more scientists are discovering the power of NSE for facilitating the observation of slow dynamics in condensed matter, and, second, the number of NSE instruments available for public use has increased significantly over the last 10 years. Table 2.1 in Chap. 2 gives an overview on the NSE spectrometers that are available today for neutron users at user facilities worldwide. The table includes e-mail addresses to provide the reader access to information on these instruments.

Dynamic processes in polymers occur over a wide range of length and time scales(see Fig. 1.2 and Fig. 1.3). Figure 1.2 relates the dynamic modulus as it may be observed on a polymer melt with the length and time scales of molecular motion underlying the rheological behaviour. Our example deals with an amorphous polymer system excluding any crystallization processes. A typical relaxation map for this kind of systems is that displayed in Fig. 1.3 for the archetypal polymer polyisoprene. It is clear that we can distinguish several different regimes:

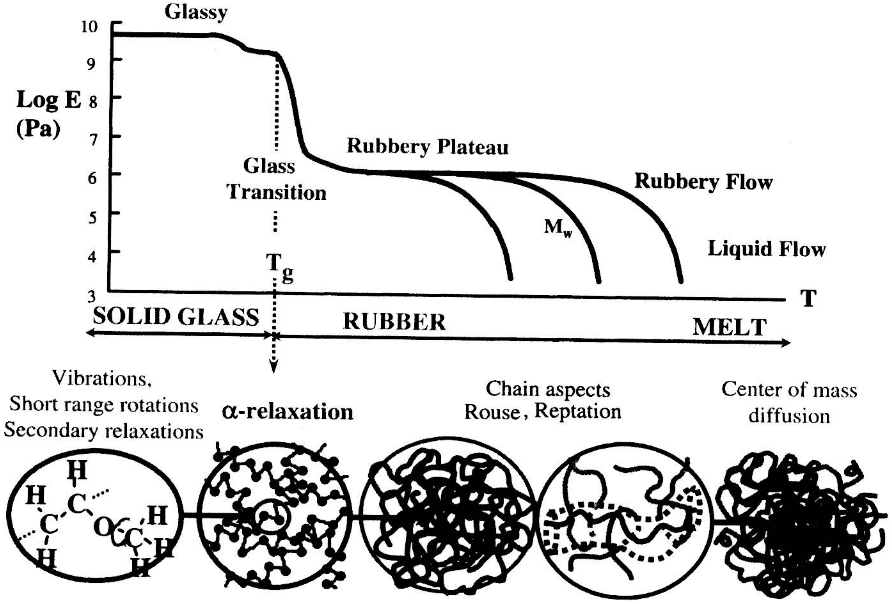


Fig. 1.2 Richness of dynamic modulus in a bulk polymer and its molecular origin. The associated length scales vary from the typical bond length (≈Å) at low temperatures to interchain distances (≈10 Å) around the glass transition. In the plateau regime of the modulus typical scales involve distances between "entanglements" of the order of 50–100 Å. In the flow regime the relevant length scale is determined by the proper chain dimensions

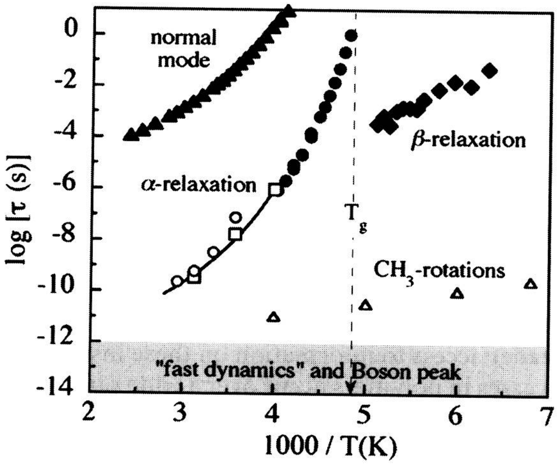
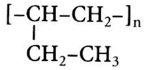
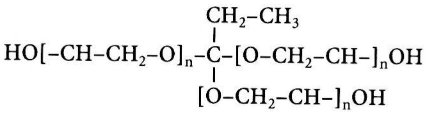
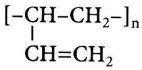
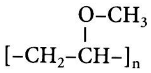
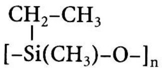


Fig. 1.3 Relaxation map of polyisoprene: results from dielectric spectroscopy (inverse of maximum loss frequency *full symbols*), rheological shift factors (*solid line*) [7], and neutron scattering: pair correlation ($\langle\tau(Q=1.44\ \text{Å}^{-1})\rangle$ *empty square*) [8] and self correlation ($\langle\tau(Q=0.88\ \text{Å}^{-1})\rangle$ *empty circle*) [9], methyl group rotation (*empty triangle*) [10]. The *shadowed area* indicates the time scales corresponding to the so-called fast dynamics [11]

i. At low temperature the material is in the glassy state and only small amplitude motions like vibrations, short range rotations or secondary relaxations are possible. Below the glass transition temperature T_g the secondary β-relaxation as observed by dielectric spectroscopy and the methyl group rotations may be observed. In addition, at high frequencies the vibrational dynamics, in particular the so called Boson peak, characterizes the dynamic behaviour of amorphous polyisoprene. The secondary relaxations cause the first small step in the dynamic modulus of such a polymer system.
ii. At the glass transition temperature T_g the primary relaxation (α-relaxation) becomes active allowing the system to flow. The temperature dependence of its characteristic relaxation time is displayed in Fig. 1.3 combining dielectric, rheological and neutron scattering experiments. The time range over which this relaxation takes place easily covers more than ten orders of magnitude. This implies the necessity to combine different experimental techniques to fully characterize this process. As shall be demonstrated in this review, the length scale associated with α-relaxation is the typical interchain distance between two polymer chains. In the dynamic modulus, the α-relaxation causes a significant step of typically three orders of magnitude in strength.
iii. The following rubbery plateau in the modulus relates to large scale motions within a polymer chain. Two aspects stand out. The first is the entropy-driven relaxation of fluctuations out of equilibrium. Secondly, these relaxations are limited by confinement effects caused by the mutually interpenetrating chains. This confinement is modelled most successfully in terms of the reptation model by de Gennes [3] and Doi and Edwards [6]. There, the confinement effects are described in terms of a tube following the coarse grained chain profile. Motion is only allowed along the tube profile leading to the reptation process – the snake-like motion of a polymer chain.
iv. When a chain has lost the memory of its initial state, rubbery flow sets in. The associated characteristic relaxation time is displayed in Fig. 1.3 in terms of the "normal mode" (polyisoprene displays an electric dipole moment in the direction of the chain) and thus dielectric spectroscopy is able to measure the relaxation of the end-to-end vector of a given chain. The rubbery flow passes over to liquid flow, which is characterized by the translational diffusion coefficient of the chain. Depending on the molecular weight, the characteristic length scales from the motion of a single bond to the overall chain diffusion may cover about three orders of magnitude, while the associated time scales easily may be stretched over ten or more orders.

In this review we will present the outcome of NSE studies on polymer systems covering results beyond those reported in an earlier review in *Advances in Polymer Science* [5] eight years ago. Table 1.1 shows the chemical structure and information on the chain dimensions of the systems considered here. In Chap. 2 we will commence with a brief description of neutron scattering principles and a discussion of the two different ways neutron spin echo may be implemented – the traditional NSE approach with precession coils and the neu-

Table 1.1 Names, acronyms and structure of the repeat unit of the polymers that appear in this work. The ratio between the average end-to-end distance $\langle R^2\rangle_0$ and the molecular weight *M* at 413 K is also shown [12]

Common name	Acronym	Structure of the repeat unit	$\langle R^2\rangle_0/M$ (Å^{2}mol/g)
Polyisoprene	PI	$[-CH_2-CH=C(CH_3)-CH_2-]_n$	0.625
Polydimethyl siloxane	PDMS	$[-Si(CH_3)_2-O-]_n$	0.457
Polyethylene	PE	$[-CH_2-CH_2-]_n$	1.21[a]
Poly(ethyl ethylene)	PEE	 $[-\underset{\substack{\mid \\ CH_2-CH_3}}{CH}-CH_2-]_n$	0.507
Poly(ethylene propylene)[b]	PEP	$[-CH_2-CH_2-CH(CH_3)-CH_2-]_n$	0.834
1,4-Polybutadiene	PB	$[-CH_2-CH=CH-CH_2-]_n$	0.876
Polyisobutylene	PIB	$[-CH_2-C(CH_3)_2-]_n$	0.570
Atactic polypropylene	aPP	$[-CH(CH_3)-CH_2-]_n$	0.670
Polyurethane	PU	 $HO[-CH-CH_2-O]_n-\overset{\substack{CH_2-CH_3 \\ \mid}}{\underset{\substack{\mid \\ [O-CH_2-CH-]_nOH}}{C}}-[O-CH_2-CH-]_nOH$	
Poly(vinyl chloride	PVC	$[-CH_2-CClH-]_n$	
Poly(vinyl ethylene)	PVE	 $[-\underset{\substack{\mid \\ CH=CH_2}}{CH}-CH_2-]_n$	0.664[c]
Poly(vinyl methyl ether)	PVME	 $[-CH_2-\overset{\substack{O-CH_3 \\ \mid}}{CH}-]_n$	
Polyethylmethylsiloxane	PEMS	 $[-\overset{\substack{CH_2-CH_3 \\ \mid}}{Si}(CH_3)-O-]_n$	
Poly(ethylene oxide)	PEO	$[-CH_2-CH_2-O-]_n$	0.805