

## SEGMENTAL DYNAMICS OF CHAIN MOLECULES IN POLYMER SOLUTIONS AND MELTS AS STUDIED BY QUASIELASTIC NEUTRON SCATTERING

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**Abstract** - Quasielastic neutron scattering methods provide the unique opportunity to investigate dynamic processes of polymer molecules simultaneously in space and time. In particular, in the liquid state information on single chain behaviour is not restricted to dilute solutions but may also be obtained, if an appropriate mixture of protonated and deuterated polymers is used, from concentrated systems, the melt included.

This paper deals with recent neutron spin echo studies of liquid polydimethylsiloxane systems. Transitions of the single chain behaviour are considered in the whole range of concentration as well as the transitions from single to many chain behaviour in semidilute solutions. The results are discussed in terms of the Rouse-Zimm model and compared with the findings of other experimental methods.

### INTRODUCTION

Due to the flexible chain structure and the related large number of internal degrees of freedom the mobility of polymer molecules in the liquid state exhibits a very complex behaviour /1/. In particular this complexity is determined by the fact that different motional processes occur simultaneously on different length and time scales /2/. Roughly, with increasing length and time scales, three types of motion can be distinguished: (i) high frequency local motion to be attributed to conformational changes, (ii) diffusional processes of finite portions of the chains, which can be treated as statistical segments and (iii) slow overall diffusion of the coil-like polymer molecules. In contrast to the local processes which are strongly determined by the special chemical structure of the monomer units, and in contrast to the coil diffusion which depends on the molecular weight of the polymer, the characteristics of the segmental mobility are most universal, as this type of motion is a consequence of the chain structure of the molecules and thus expected to be largely independent from both the former mentioned properties.

The universal behaviour of the static and dynamic segmental properties became quite obvious when the analogy between polymer and magnetic systems was pointed out /3/,/4/. In the framework of this concept, it can be shown for example that the transitions from  $\theta$ - to good solvent conditions in dilute solutions or the transitions from dilute to semi-dilute solutions under  $\theta$ - and good solvent conditions exhibit the features of critical phenomena /5/ and can be described as second order phase transitions with smooth cross-over between the different phases (thermodynamic states). Consistently, the segmental diffusional processes in the transition zone have to be regarded as being different with respect to different extensions of the correlation range instead of being uniform over the whole intramolecular segmental length scale.

Another theoretical approach to the understanding of the dynamic properties of polymer solutions and melts on a scale of segmental diffusion is based on microscopic models which were initially developed to describe the time and frequency dependence of macroscopic rheological data, e.g. the viscosity of the shear modulus. The most important models are the bead and spring model /6/,/7/ and the tube or reptation model /8/-/11/. All these models provide distinct spectra of relaxation modes related to specific spatial dimension. However, a real test of both microscopic theories requires microscopic experimental methods which allow the relaxation behaviour in space and time to be probed. For these kinds of problems quasielastic light or neutron scattering methods are the best tools since they permit the analysis of the motional behaviour of a system simultaneously in space and time. In particular with the recently developed neutron spin echo technique /12/,/13/ it became possible to measure the spatial correlation function in time domain of segmental diffusion. By this method information on the single chain behaviour is not restricted to dilute solutions but may also be obtained, if an appropriate mixture of protonated and deuterated polymer is used, from concentrated systems including the melt.

This paper will give a review of recent neutron scattering studies on the segmental diffusional processes which occur in different liquid polydimethylsiloxane (PDMS) systems /14/ - /17/. Transitions of the single chain behaviour in the whole range of concentration from the dilute solution to the melt are considered as well as transitions from the single to many chain behaviour in semi-dilute solutions. The aim of this paper is to demonstrate that this microscopic experimental method is unique for the study of segmental mobility in polymers, to prove the validity of the microscopic models and the applicability of the theory of critical phenomena on dynamic properties of polymers and to judge whether microscopic and macroscopic dynamic data are compatible.

#### SOME GENERAL REMARKS ON THE QUASIELASTIC NEUTRON SCATTERING EXPERIMENTS

The neutron scattering experiments were performed at the ILL Grenoble using the spin echo spectrometer IN11. The principles of this method and instrumental details are summarized in Ref./18/.

The neutron spin echo technique yields directly the coherent dynamic structure factor  $S(\underline{q}, t)$  in the normalized form  $S(\underline{q}, t)/S(\underline{q}, 0)$ , which is identical with the normalized intermediate scattering function.  $\underline{q}$  is the scattering vector ( $q = |\underline{q}| = (4\pi/\lambda)\sin\theta$ ,  $\lambda$  wavelength of the neutrons,  $2\theta$  scattering angle) and  $t$ , the time. The  $q$  and time range were  $0.02 \leq q/\text{\AA}^{-1} \leq 0.132$  and  $10^{-9} \leq t/s \leq 10^{-8}$ .

$S(\underline{q}, t)/S(\underline{q}, 0)$  is given by /19/

$$S(\underline{q}, t)/S(\underline{q}, 0) = \frac{1}{N} \sum_{jk} \langle \exp \{-i\underline{q}(\underline{r}_j(0) - \underline{r}_k(t))\} \rangle \quad (1)$$

where  $N$  is the number of segments and  $\underline{r}_k(t)$  and  $\underline{r}_j(0)$  are the positions of the segments  $k$  and  $j$  at time  $t$  and time zero. The brackets  $\langle \dots \rangle$  denote the thermal average. In the so-called Gaussian approximation (1) can be written as

$$S(\underline{q}, t)/S(\underline{q}, 0) = \frac{1}{N} \sum_{jk} \exp \left\{ -\frac{q^2}{2} \langle (\underline{r}_k(t) - \underline{r}_j(0))^2 \rangle \right\} \quad (2)$$

Thus, to compare the predictions of the microscopic models with the experimental scattering data,  $\langle (\underline{r}_k(t) - \underline{r}_j(0))^2 \rangle$  has to be calculated for the models. For measurement of the single chain behaviour in dilute and of the many chain behaviour in semi-dilute solutions, mixtures of protonated polymers and deuterated solvents were used. In contrast for the measurements of the single chain behaviour in non-dilute solutions and in the melt the polymer fraction it-

self was a mixture of 5% deuterated and 95% protonated material which, in the case of solutions, was dissolved in an appropriate deuterated solvent so that the scattering contrast between both deuterated components became negligible. The following systems were investigated at temperature  $T$  and concentration  $c$ : PDMS ( $M_w \sim 60\,000$ ,  $M_w/M_n = 1.05$ ) in *d*-bromobenzene ( $T = 84^\circ\text{C}$ ,  $\theta$  conditions,  $c = 0.07$ ) and in *d*-chlorobenzene ( $T = 100^\circ\text{C}$ ,  $c = 0.04$ ), PDMS ( $M_w \sim 30\,000$ ,  $M_w/M_n = 1.05$ ) in *d*-benzene ( $T = 70^\circ\text{C}$ ,  $0.02 \leq c \leq 0.25$ ), PDMS (5%)/*d*-PDMS (95%) ( $M_w^H \sim 60\,000$ ,  $M_w^D \sim 60\,000$  or  $178\,000$ ,  $M_w/M_n = 1.05$ ) in *d*-chlorobenzene ( $T = 100^\circ\text{C}$ ,  $0.14 \leq c \leq 1.0$ ).

### SEGMENTAL DIFFUSION IN DILUTE SOLUTIONS

The segmental diffusion of polymers in dilute solutions is largely determined by the hydrodynamic interactions which produce a long range coupling between the different chain segments in addition to the direct coupling due to the chain structure of the molecules /20/.

Using the bead and spring model and introducing the hydrodynamic interactions via the Oseen tensor, preaveraged assuming a Gaussian distribution of segments, the relaxation spectrum of segmental diffusion under  $\theta$ -conditions is given by the Rouse-Zimm modes /21/

$$\frac{1}{\tau_j^{\text{RZ}}} = \frac{6k_B T}{f_0 l^2} \left(\frac{j\pi}{N}\right)^2 \left(1 + 2\sqrt{\pi} h^* \left(\frac{j\pi}{N}\right)^{-1/2}\right) \quad j = 1, \dots, N \quad (3)$$

( $k_B$  Boltzmann constant,  $T$  temperature,  $f_0$  segmental friction coefficient,  $l^2$  mean square segment length). The draining parameter

$$h^* = f_0 / ((12\pi^3)^{1/2} l \eta_0) \quad (4)$$

( $\eta_0$  viscosity of the pure solvent) describes the extent of hydrodynamic interactions. The numerical values of  $h^*$  are between 0 and 0.25.

In the Zimm model /7/ the hydrodynamic interactions are dominant ( $h^*=0.25$ ) and the Rouse-Zimm modes are reduced to the pure Zimm modes

$$\frac{1}{\tau_j^{\text{Z}}} = \frac{\sqrt{12}}{\pi} \frac{k_B T}{l^3 \eta_0} \left(\frac{j\pi}{N}\right)^{3/2} \quad j = 1, \dots, N \quad (5)$$

On the other hand in the Rouse model /6/ if the hydrodynamic interactions are neglected completely ( $h^* = 0$ ), the pure Rouse modes

$$\frac{1}{\tau_j^{\text{R}}} = \frac{6k_B T}{f_0 l^2} \left(\frac{j\pi}{N}\right)^2 \quad j = 1, \dots, N \quad (6)$$

result in agreement with eq.(3), setting  $h^* = 0$ .

The coherent dynamic structure factors  $S(q,t)/S(q,0)$  (see eq.(2)) have been calculated for the Rouse /22/ as for the Zimm model /23/ in the range  $q_1 < 1 < q R_g$  ( $R_g$  radius of gyration). In the limit of long times they can be approximated by

$$S(q,t)/S(q,0) = \exp \{-\text{const} (\Omega(q)t)^n\} \quad (7)$$

The parameters in (7) are the characteristic frequency in Fourier space  $\Omega(q)$  and the line shape parameter  $n$ . The Zimm model leads to  $n = 2/3$  and

$$\Omega_Z(q) = \frac{1}{6\pi} \frac{k_B T}{\eta_0} q^3 \quad (8)$$

whereas the corresponding quantities for the Rouse model are  $n = 1/2$  and

$$\Omega_R(q) = \frac{1}{12} \frac{k_B T}{12 f_0} q^{4.4} \tag{9}$$

Up to now there has been no successful calculation of  $S(q,t)/S(q,0)$  for the Zimm model under non  $\theta$ -conditions.

However information on  $\Omega(q)$  independent from solvent properties are available by an approach proposed by Akcasu and co-workers /24/. Starting from Kirkwood's generalized diffusion equation,  $\Omega(q)$  is derived from static correlation functions alone via the initial slope of the coherent dynamic structure factor  $\lim_{t \rightarrow 0} \frac{\partial}{\partial t} \{-\ln[S(q,t)/S(q,0)]\}$ .

Whereas eq.(8) is confirmed in the case of  $\theta$ -solvents, for good solvent conditions  $\Omega_Z(q)$  is predicted to scale with  $(T/\eta_0)q^3$  as before but to have absolute values which are increased by about 30% compared to  $\theta$ -conditions.

Moreover, from scaling considerations which generally cannot provide any numerical prefactors it was shown by de Gennes /4/ that the dependence  $\Omega_Z(q)$  on  $T, \eta_0$  and  $q$  is identical in  $\theta$ - and non  $\theta$ -conditions.

Using the method of initial slope it became possible to estimate the errors which result from pre-averaging the Oseen tensor. Without performing this pre-averaging procedure  $\Omega_Z(q)$  is expected to increase by a factor of about 1.17 /25/,/26/.

To analyse the quasielastic neutron scattering data obtained from PDMS in a  $\theta$ -solvent (d-bromobenzene,  $T=84^\circ\text{C}$ ) and a good solvent (d-benzene  $T=70^\circ\text{C}$ ), a line shape analysis was performed according to eq.(7). The shape parameters  $n$  (see Fig.1) which are significantly different from the values  $1/2$  and  $1$ , characteristic for the Rouse model and the overall coil diffusion respectively, indicate that the hydrodynamic interaction is dominant. The distinct deviation

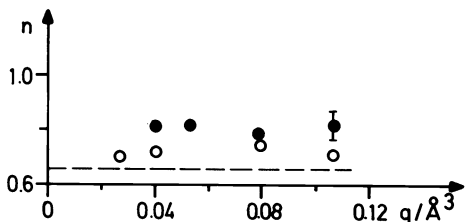


Fig.1: Quasielastic neutron scattering on dilute polymer solutions. Line shape parameter  $n$  (see eq. (7)) as a function of  $q$ .  
 - - - theoretical value  
 ● PDMS/d-bromobenzene  $T = 84^\circ\text{C}$  ( $\theta$ -conditions)  
 ○ PDMS/d-benzene  $T = 70^\circ\text{C}$  (good solvent conditions)

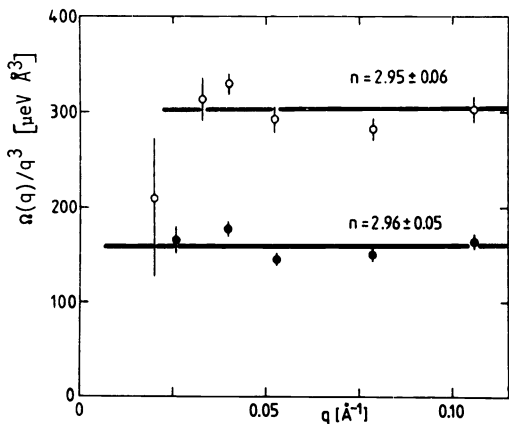


Fig.2: Quasielastic neutron scattering on dilute polymer solutions. Characteristic frequencies  $\Omega(q)$  divided by  $q^3$  as a function of  $q$ .

- PDMS/C<sub>6</sub>D<sub>5</sub>Br  $T=84^\circ\text{C}$
- PDMS/C<sub>6</sub>D<sub>6</sub>  $T=70^\circ\text{C}$

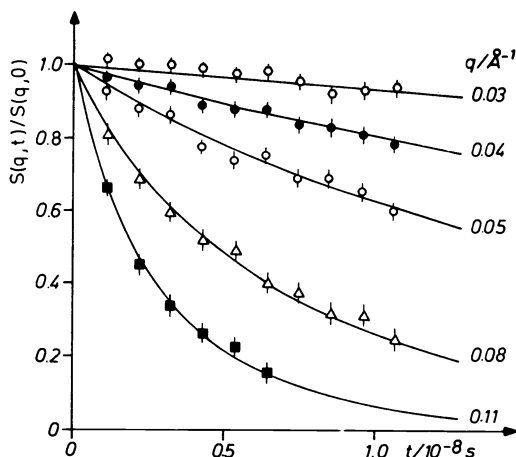


Fig.3: Quasielastic neutron scattering on PDMS/d-bromobenzene at  $T = 84^\circ\text{C}$ . Common fit of all spectra with the scattering law of the Zimm model using only one parameter ( $xT/\eta_0$ )

of the  $n$ -values from  $2/3$  predicted for the Zimm model results from the fact that the long time limit of  $S(q,t)/S(q,0)$  is not yet reached in the time range experimentally accessible by the instrument. For the numerical data analysis, the scattering law calculated for the Zimm model /23/ was fitted to the experimental data. By the results, obtained from fitting single spectra (see Fig.2) it is demonstrated that the  $q^3$  dependence of  $\Omega(q)$ , characteristic of the Zimm model, is satisfied with high precision for both samples.

In addition common fits were performed for all the  $q$  values of each sample using the scattering law of the Zimm model with  $\Omega(q) = Aq^\gamma$ , where  $A$  and  $\gamma$  are adjustable parameters. As can be seen from Fig.2 the  $\gamma$  values come very close to 3, as theoretically predicted. Finally Fig.3 shows by way of example the result of a common fit with the scattering law of the Zimm model using  $\alpha T/\eta_0$  as the only adjustable parameter for the PDMS/d-bromobenzene system. One can see that both the time and  $q$ -dependence of the spectra are quite well described by the Zimm model and that there are no indications of considerable contributions of Rouse modes in the spectra. The same is true for the PDMS/d-benzene sample in the case of good solvent conditions. For polystyrene (PS) in d-methylcyclohexane ( $T=68^\circ\text{C}$ ,  $\theta$ -conditions) and d-toluene ( $T=100^\circ\text{C}$ , good solvent conditions) similar behaviour is observed /27/.

In contrast to these results which are in full agreement with the assumption of dominant hydrodynamic interaction, the absolute values of  $\Omega(q)$  deviate from the theoretical predictions. Defining  $X = \frac{\Omega_Z^{\text{exp}}(q)}{\Omega_Z^{\text{theo}}(q)}$  where  $\Omega_Z^{\text{theo}}(q)$  is calculated using the pre-averaged Oseen tensor, values of  $X=0.88$  and  $X=0.91$  are found for  $\theta$  and good solvent conditions of the PDMS sample. Much larger deviations occur in both PS systems mentioned above.

These results indicate that the characteristic frequencies normalized by division with  $(T/\eta_0)q^3$  do not follow the universal relation predicted from eq.(8) and have to be modified by polymer specific properties.

In order to incorporate such properties in the Zimm model the hydrodynamic interaction tensor was modified, taking into account that the interaction does not result from infinitely small beads but from beads of diameter  $2l_H$  ( $2l_H$  hydrodynamic segment length related to the static segment length  $l$ ) /28/.

Thus instead of eq.(8)

$$\Omega_Z(q) = \left\{ 1 - \frac{24}{\pi} \left( \frac{2l_H}{l} \right)^2 \right\} \frac{1}{6\pi} \frac{T}{\eta_0} q^3 \quad (10)$$

is obtained.

Whereas the parameter  $2l_H/l$  is found to be small in the case of PDMS ( $2l_H/l = 0.18$ ) it increases considerably for such polymer which, due to larger side groups, are less compact than PDMS (e.g. PMMA /14/, PS /27/). Up to now all neutron scattering experiments on dilute solutions performed by other authors, deal with non- $\theta$  conditions /29/,/30/. The experimental findings are consistent with those presented here.

If the intrinsic storage and loss moduli of dilute solutions, as dependent on frequency, are calculated for the Rouse-Zimm modes (3), a continuous transition from pure Rouse to pure Zimm modes is found with  $h^*$  values increasing from 0 to 0.25 /20/. For  $\theta$ -conditions the dynamic mechanical measurements exhibit the pure Zimm behaviour in agreement with the neutron scattering data, indicating that the hydrodynamic interactions are dominant. However, for good solvent systems the mechanical data become more Rouse like which is in complete contrast to the results of neutron scattering.

This discrepancy is explained by taking into account that the reduction of hydrodynamic interactions together with the coil expansion found in good solvents may produce Rouse behaviour for the mechanical modulus. Provided that both effects are separated properly, which requires an additional independent measurement, the dominance of hydrodynamic interaction directly seen from the line shapes of the neutron scattering data, can be deduced from the dynamic mechanical measurements too.

For the quantitative discussion of the dynamic mechanical data  $1/\tau_1^Z$  (see eq.(5)), which is directly accessible by experiment, is of similar importance as  $\Omega(q)$  in the case of the neutron scattering data. While 1 is expected for the ratio  $(1/\tau_1^Z)/(\eta_0 l^3 N^{3/2}/(12\pi k_B T))$  for all polymer systems under  $\theta$ -conditions, values of about 0.8 are found for PDMS and PS, respectively /31/,/32/. This result is different from neutron scattering, where the deviation in  $\Omega_Z(q)6\pi\eta_0/(k_B T q^3)$  obtained for both systems, supports the introduction of polymer specific properties into the Zimm model. However, in regard to this problem, the mechanical data seems less reliable since it contains two molecular quantities ( $1/\tau_1^Z$  and  $N^{3/2} l^2$ ) to be measured independently instead of only one ( $\Omega(q)$ ) in the case of neutron scattering.

#### SEGMENTAL DIFFUSION IN POLYMER MELTS

In contrast to dilute solutions the properties of polymer melts are dominated by the intermolecular interactions of chain molecules. For this reason it is surprising that for molecular weights  $M$  smaller than  $M_c$ , the frequency dependence of the viscoelastic data follows the predictions of the simple Rouse model which describes the Brownian motion of an unconstrained chain in a heat bath /20/.  $M_c$  is the critical molecular weight at which the viscosity  $\eta$  exhibits a cross-over from  $\eta \sim M$  to  $\eta \sim M^{3.4}$ .

Only for molecular weights larger than  $M_c$  does the Rouse model fail to fit the dynamic mechanical data. This is assumed to arise from entanglements between different chain molecules /33/. It is thought that the effect of entanglements is to cause the flexible polymer chain to move like a snake in a "tube" formed by the topological constraints of its neighbours /8/, /34/. The model is called the tube or reptation model. Within this model two characteristic time constants  $\tau_{rep}$  and  $\tau_D$  ( $\tau_D \gg \tau_{rep}$ ) are introduced.  $\tau_{rep}$  is the time necessary for the molecule to escape from its tube by reptational motion and  $\tau_D$  the time constant related to the tube renewal.

The tube model was supported by diffusion experiments on polyethylene melts /35/, where the diffusion coefficient  $D \sim 1/N^{2.0 \pm 0.1}$  is found to agree to the prediction  $D \sim 1/N^2$  and by viscosity experiments /20/, where  $\eta \sim M^{3.4}$  is observed and  $\eta \sim M^{3.0}$  is predicted.

On a length scale smaller than the tube diameter  $d$  the dynamic coherent structure factor of a single polymer chain is identical with the predictions of the Rouse model (see eq.(6) and (9)). However, for spatial dimensions larger than  $d$ ,  $S(q,t)/S(q,0)$  is given by /36/

$$S(q,t)/S(q,0) = \exp \left\{ -\left(\frac{qd}{6}\right)^2 u \right\} \quad u \ll 1 \quad (11a)$$

$$S(q,t)/S(q,0) = \left(\frac{qd}{6}\right)^2 (\sqrt{3}u)^{-1} \quad u \gg 1 \quad (11b)$$

where

$$u = \frac{q^2 l^2}{6} (Wt)^{1/2} \quad \text{and} \quad W = \frac{3k_B T}{12f_0} \quad (12)$$

The tube model either leads to an exponential scattering law with a very strong  $q$  dependence of the corresponding characteristic frequency  $\Omega_T(q)$  ( $\Omega_T(q) \sim q^8$ ) (see eq.(11a)) or to a  $q$  independent, non exponential decay of  $S(q,t)/S(q,0)$  as in eq.(11b).

The line shape analysis of the neutron scattering spectra obtained from the PDMS melt /16/ yields  $n$ -values between 0.5 and 0.55 (see Fig.4), which is consistent with both the Rouse- and the tube model. However, if in addition the  $q$ -dependence of the characteristic frequencies  $\Omega(q)$  is checked, the tube model fails totally, since  $\Omega(q) \sim q^{4.2}$  is found.

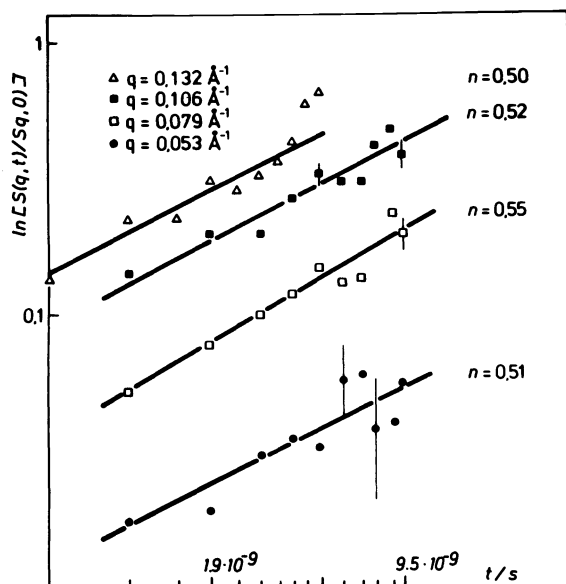


Fig.4: Quasielastic neutron scattering on a PDMS melt. Line shape analysis: double logarithmic plot of  $-\ln[S(q,t)/S(q,0)]$  vs  $t/s$

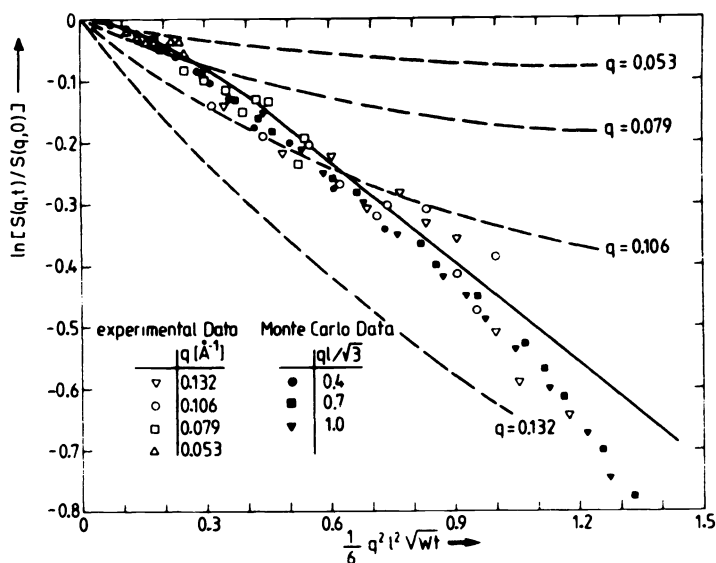


Fig.5: PDMS melt: scaling plot of quasielastic neutron scattering and Monte Carlo data.

— Rouse model with  $l^2\sqrt{\omega}/(\text{Å}^2 \text{s}^{-1/2}) = 5.5 \times 10^6$

- - - tube model with  $l^2\sqrt{\omega}/(\text{Å}^2 \text{s}^{-1/2}) = 5.5 \times 10^6$  and tube diameter  $d=40\text{Å}$

The inconsistency between the experimental data and the predictions of the tube model can be seen directly from a scaling graph (see Fig.5), where  $\ln[S(q,t)/S(q,0)]$  is plotted against  $(ql)^2(Wt)^{1/2}/6$ , which is the universal parameter of the Rouse model. In this presentation all spectra are reduced to a master curve which is expected from the Rouse model, whereas the tube model requires a  $q$ -dependent splitting.

The Rouse model is also confirmed by recent Monte Carlo calculations /16/, /37/ (see Fig.5). Other coherent neutron scattering data, obtained from a melt of polytetrahydrofuran /38/, show a similar behaviour as that observed in the PDMS melt. On a length scale, extending to  $30\text{\AA}$  there are no indications that segmental diffusion is restricted by topological constraints.

Assuming on the Rouse model and taking  $l^2=39.6\text{\AA}^2$  /39/ the segmental friction coefficient  $f_0$  is determined to  $2.0 \times 10^{-12}$  kg/s which is in satisfactory agreement with the results of viscoelastic measurements where  $f_0=2.8 \times 10^{-12}$  kg/s is found for PDMS at  $100^\circ\text{C}$  /20/. Despite the obvious superiority of the Rouse model over the tube model it should be mentioned that the Rouse model does not describe all details of the dynamic scattering of polymer melts properly. This lack is mainly due to the fact that the asymptotic form of the scattering law of the Rouse model fits the experimental data at small times better than the full form, actually appropriate to the time range of the experiment.

The experimental scattering data presented here do not exhibit any characteristic features of the tube model. This, however, does not yet demonstrate the invalidity of the model since there are two rather restrictive conditions which have to be satisfied /36/. These are  $qd < 1$  and  $t > (d/l)^4 W^{-1}$ . If for example tube diameters of  $40\text{-}50\text{\AA}$ , as estimated from the plateau moduli /40/ are realistic, it is impossible to reach both these limits with the experimental parameters, accessible at present.

However, there are also some serious objections to the relevance of the tube model to polymer melts. Monte Carlo calculations demonstrate clearly that reptational motion is only effective for simulations of single chains in a completely frozen environment whereas without restricting the mobility of the neighbouring chains, a Rouse like segmental diffusion is obtained /16/,/37/. On the other hand it was shown by an analytical treatment /41/ that reducing the constraint that  $\tau_D$  greatly exceeds  $\tau_{rep}$  by introducing a Rouse like mobility of the entanglement points, still restricts the Rouse like segmental diffusion to dimensions smaller than the tube diameter but gives the molecular weight dependence of the diffusion coefficient ( $D \sim l^2/N^2$ ) and of the viscosity ( $\eta \sim M^{3.5}$ ) both in good agreement with the experimental data.

Although a lot of problems concerning the dynamics of polymer melts remain unsolved at the moment, the neutron scattering data reveal that the Rouse model is an appropriate description of segmental diffusion in polymer melts on a length scale up to  $30\text{\AA}$ , even if the critical molecular weight is exceeded.

#### TRANSITION FROM SINGLE TO MANY CHAIN BEHAVIOUR

As the polymer concentration in a solution is increased above a critical level  $c^*$ , there is a uniform distribution of chain segments. This is defined by

$$c^* = M/(L R_g^3) \quad (13)$$

( $L$  Avogadro's constant) and divides the regimes of dilute and semidilute behaviour.



In the semidilute solution ( $c > c^*$ ) the polymer coils are no longer separated but interpenetrate and form a transient network /42/. This network is characterized by a concentration dependent correlation length,  $\xi(c)$  which represents the average distance between the contact points of different molecules. In a good solvent  $\xi(c)$  is also the distance beyond which excluded volume effects are screened.

From static scaling theory,  $\xi(c)$  is predicted to be independent from molecular weight  $M$  and to vary with the concentration as  $c^{-\beta}$  with  $\beta=3/4$  /42/. This concentration dependence has been confirmed by static neutron scattering experiments /43/.

A general scaling hypothesis postulates that static and dynamic correlation lengths are equal /4/ and so  $\xi(c)$  is believed to be the characteristic distance beyond which the hydrodynamic interaction is screened completely. The fact that the hydrodynamic screening is in reality incomplete, as observed recently by quasielastic neutron scattering /17/, is unimportant for the cross-over from single to many chain behaviour. It will be discussed in detail in the following section concerned with transition effects of the single chain behaviour occurring as concentration increases.

The effect of entanglements on the dynamics of the transient network is to introduce an additional elastic rigidity into the system. By analogy with permanent networks swollen with a solvent, the coherent dynamic scattering law in the many chain regime  $q\xi(c) < 1$  is given by /42/

$$S(q,t)/S(q,0) = \exp\{-D_c q^2 t\} \quad (14)$$

where

$$D_c = \frac{1}{6\pi} \frac{k_B T}{\eta_0} \frac{1}{\xi(c)} \quad (15)$$

which is independent from molecular weight, is the collective diffusion constant of the pseudo gel. From (14) the characteristic frequency

$$\Omega(q) = D_c q^2 \quad (16)$$

and the line shape parameter  $n = 1$  are derived.

For spatial dimensions smaller than  $\xi(c)$  ( $q\xi(c) > 1$ ) the network is not yet effective and the single chain behaviour as described by eq.(8) with  $n = 2/3$  is retained. The cross-over from single to many chain behaviour is expected to occur at  $q\xi(c)=1$ . The condition of a smooth transition implies  $D_c \sim 1/\xi(c) \sim c^\beta$  ( $\beta=3/4$ ). The requirement of continuity between the two regimes yields the following relationship between the exponents  $\gamma$  (see eq.(8)) and  $\beta$  /44/

$$\gamma = 2 + [(3\nu - 1)/\nu]\beta \quad (17)$$

where  $\nu$  is the Flory exponent which has the value  $3/5$  in good solvents.

The theoretical treatment of the transition from single to many chain behaviour under  $\theta$ -conditions is much more complex since self entanglements have to be taken into account in addition to the intermolecular contact points which form the transient network /45/. The discussion of this problem will be ignored here because the related experiments are not yet completed /46/.

Qualitatively the change from single to many chain behaviour under good solvent conditions can be seen from a line shape analysis of the neutron scattering data (see Fig.6). For the dilute solution ( $c=0.05$ )  $n$  is equal to about 0.7 for all  $q$  values, a characteristic of the Zimm behaviour, in the semidilute solution  $n$  values of 0.7 are restricted to larger  $q$ -values

and n-values of about 1.0 are obtained at small q-values as predicted for the collective diffusion.

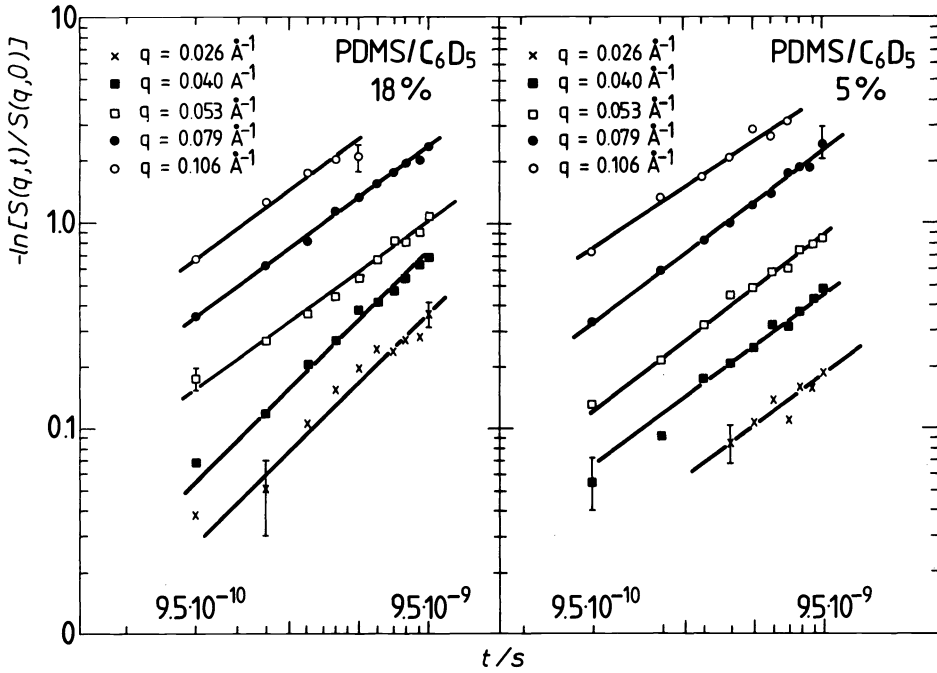


Fig.6: Cross-over from single chain to many chain behaviour in PDMS/d-benzene. Line shape analysis: double logarithmic plot of  $-\ln[S(q,t)/S(q,0)]$  vs  $t/s$

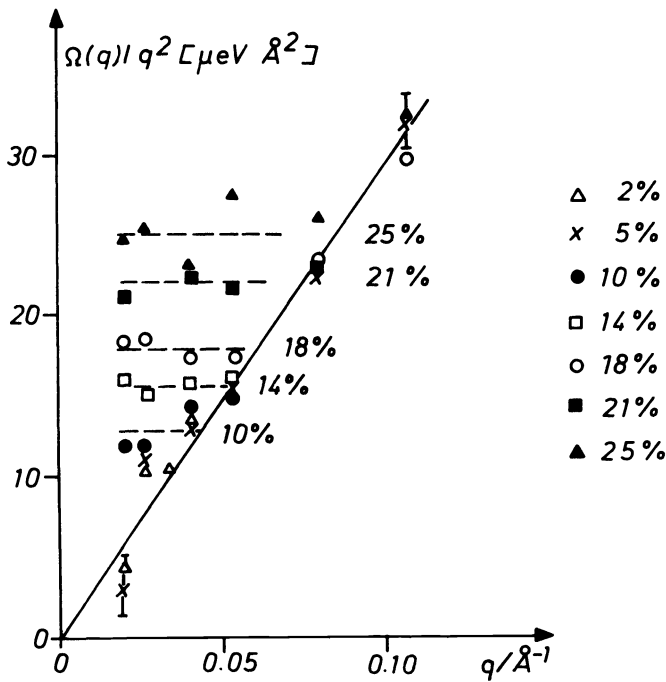
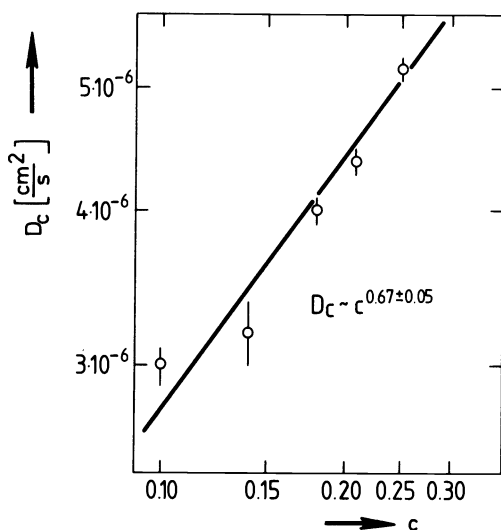


Fig.7: Cross-over from single chain to many chain behaviour in PDMS/d-benzene. Characteristic frequencies  $\Omega(q)$  divided by  $q^2$  as a function of  $q$ .

Figure 7 presents the deviations from the single chain behaviour which occur above  $c^*$  and are extended to larger  $q$ -values with increasing concentration. In this figure  $\Omega(q)$  as obtained from the scattering law of the Zimm model is divided by  $q^2$  and plotted vs.  $q$ . For both dilute solutions ( $c=0.02$  and  $c=0.05$ )  $\Omega(q) \sim q^3$  is found in the whole  $q$ -range of the experiment. With increasing concentration a transition from  $q^3$  to  $q^2$  behaviour takes place as  $q$  increases. The position of the critical point  $q^*(c)$  and the plateau level at small  $q$  are a direct measure of the dynamic correlation length  $\xi(c)$  ( $\xi(c) = 1/q^*(c)$ ) and the collective diffusion constant  $D_c$ , respectively. The concentration dependence and the numerical values of  $D_c$ , determined from fitting simultaneously all those spectra which decay according to a simple exponential decay ( $n=1$ ) are:

$$D_c = (1.3 \pm 0.1) 10^{-5} \times c^{0.67 \pm 0.05} \frac{\text{cm}^2}{\text{s}}$$



**Fig.8:** Quasielastic neutron scattering on PDMS/d-benzene: collective diffusion constant  $D_c$  as a function of polymer concentration  $c$

This is shown in Fig.8 where the different  $D_c$  values, obtained from separate fits at each concentration, are also presented. The dynamic correlation length  $\xi(c)/\text{\AA} = (3.4 \pm 0.7) \times c^{-0.67 \pm 0.05}$  is of the same order of magnitude as the value obtained from a static experiment on the PS/d-cyclohexane system /43/. The exponent  $\beta$  of the concentration dependence of  $D_c$  and  $\xi(c)$  is in good agreement with the results of light scattering experiments /44/,/47/ which probe a much larger length scale. The values  $\beta=0.67$  and  $\gamma=2.95$  (see Fig.2) satisfy the requirements of eq.(17) within experimental error. The discrepancy that  $\beta$  is both smaller than theoretically predicted and found in the static experiments must not be attributed to a fundamental difference in the static and dynamic scaling laws, but results from the finite chain length which causes the dynamic properties to converge much more slowly to their asymptotic values /48/,/49/.

With non-scattering methods, e.g. dynamic mechanical relaxation or sedimentation, the transition from single to many chain behaviour can also be observed. However with these techniques the transition is only visible with increasing concentration: scattering experiments offer the additional possibility to investigate this transition by variation of the range of spatial correlation at a fixed concentration in the semi-dilute regime.

In dynamic mechanical measurements, the intermolecular interactions that occur with increasing concentration cause a shift of all relaxation times  $\tau_j$  to larger values. In addition, the

relaxation spectrum at long times seems to resemble much more closely the Rouse model /33/. This is in disagreement with the results of quasielastic neutron scattering which suggest that the transition from single to many chain behaviour can be explained as a transition from Zimm to collective diffusion behaviour and not as a transition from Zimm to Rouse behaviour. In contrast to dynamic mechanical relaxation data, sedimentation experiments give direct information on the correlation length  $\xi(c)$  /50/. However the experiments yield exponents for the concentration dependence of 0.8-0.9 which are considerably larger than the values predicted by theory or determined by dynamic neutron and light scattering experiments. The reason for these discrepancies has not yet been clarified in detail /50/.

#### TRANSITIONS OCCURRING IN THE SINGLE CHAIN BEHAVIOUR BETWEEN THE DILUTE SOLUTION AND THE MELT

As mentioned in the previous section, the chain overlap which takes place with increasing concentration above  $c^*$  is assumed to screen both the excluded volume and the hydrodynamic interactions /42/. There is experimental evidence /43/ that the screening of excluded volume interactions described by the correlation length,  $\xi(c)$  is in agreement with the theoretical analysis /51/. This theory predicts a complete screening for distances larger than a  $\xi(c)$  with a dependence on concentration of  $c^{-3/4}$ .

No experimental data on the screening of hydrodynamic interactions were previously available to allow us to decide whether the screening is complete for distances larger than the hydrodynamic screening length  $\xi_H(c)$  and to demonstrate if  $\xi_H(c)$  is identical with  $\xi(c)$  /52/.

Assuming that in semi-dilute solutions a complete screening occurs for spatial dimensions larger than  $\xi_H(c)$ , unscreened Zimm relaxation (eq.(7) with  $n=2/3$  and eq.(8)) is found only for  $q\xi_H(c) > 1$ . For  $q\xi_H(c) < 1$  a Rouse like relaxation, characterized by the line shape parameter  $n=1/2$ , a  $q^4$ -dependence of the characteristic frequency  $\Omega(q)$  (see eq.(9)) and a rate  $W$  (see eq.(12)) enhanced compared to the melt, is predicted. Consequently the transition between the regimes is expected when  $q\xi_H(c) \sim 1$  /42/.

The situation is more complex if, due to the residual viscosity  $\eta(c)$  of the solution some residual hydrodynamic interaction over large distances remains so that the effective screening of hydrodynamic interactions is incomplete for distances larger than  $\xi_H(c)$ .

From the incompletely screened hydrodynamic interactions another type of Zimm like relaxation results /17/, /53/ in addition to the unscreened Zimm and the enhanced Rouse modes just mentioned. When the corresponding dynamic scattering law  $S(q,t)/S(q,0)$  is calculated /52/ one can see that unscreened Zimm relaxation is restricted to the regime  $q\xi_H(c) > 1$  as in the case of complete screening. However, in the regime  $q\xi_H(c) < 1$  one may either have enhanced Rouse relaxation with

$$\Omega(q) = \frac{1}{6\pi} \frac{k_B T}{\eta_0} q^4 \xi_H(c) \quad \text{for } \eta_0/\eta(c) \ll q\xi_H(c) \quad (18)$$

in agreement with existing theories or a screened Zimm relaxation

$$\Omega(q) = \frac{1}{6\pi} \frac{k_B T}{\eta(c)} q^3 \quad \text{for } \eta_0/\eta(c) \gg q\xi_H(c) \quad (19)$$

Throughout these calculations entanglement effects are neglected, since no evidence for them was found even in the melt /16/, where they should be more important than in the present case.

The line shape analysis of the quasielastic neutron scattering spectra /17/ obtained at different concentrations between the dilute solution and the melt show clearly that two different cross-over effects occur in the segmental diffusion of single polymer chains as the concentration is increased (see Fig.9)

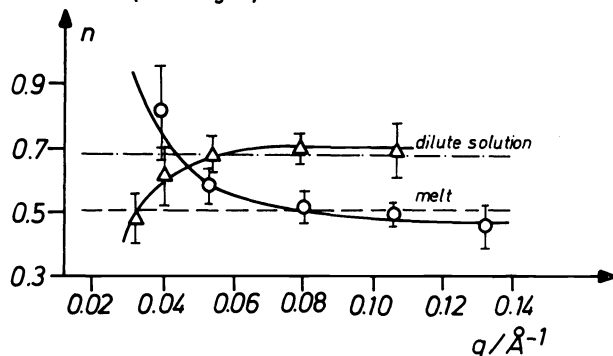


Fig.9: Line shape parameter  $n$  (see eq.(7)) as a function of  $q$ , indicating the occurrence of two transition effects in the single chain behaviour  $\Delta c = 0.18$ ;  $o c = 0.45$   
(-.-.-), (- - -) theoretical asymptotic values for the dilute solution (Zimm model) and the melt (Rouse model), respectively

At  $c=0.18$  the line shape parameter  $n$  decreases with decreasing  $q$ -values indicating that the transition from Zimm to a more Rouse like relaxation is first visible at small  $q$  values while at larger  $q$  values the Zimm like behaviour remains dominant. With further increases in concentration the theory of completely screened hydrodynamic interactions /42/ predicts an extension of the Rouse like regime towards larger  $q$  values until finally the whole  $q$ -range is governed by this motion. However, before this state is reached a second cross-over characteristic of the incompletely screened hydrodynamic interactions occurs. This can be seen unambiguously at  $c=0.45$ , where the  $q$ -dependence of  $n$  is reversed to that in the semi-dilute case. For the quantitative data analysis which will be described in detail in ref./53/ the scattering law calculated for the case of incompletely screened hydrodynamic interactions was fitted to experimental spectra. The fitting procedure was performed by treating all spectra at a given concentration simultaneously.

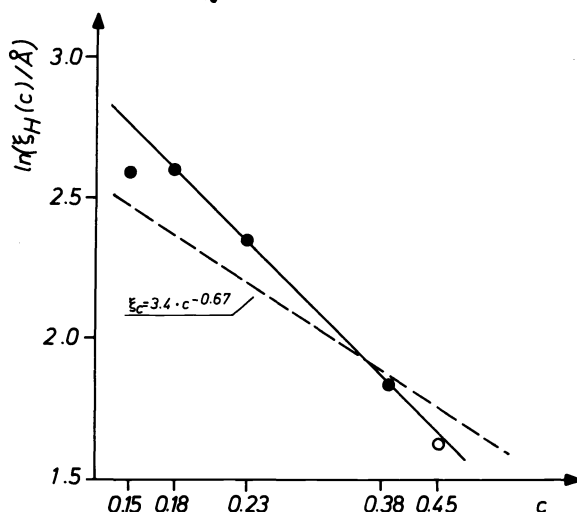


Fig.10: Hydrodynamic screening length  $\xi_H(c)$  as a function of concentration: semi-dilute regime ( $\bullet$ ) and extrapolation ( $\circ$ ) to higher concentrations, where the double cross-over is observed. (The magnitude of the errors is twice the size of the symbols).

From the spectra measured at concentrations  $0.15 \leq c \leq 0.38$ , the hydrodynamic screening lengths  $\xi_H(c)$  are determined. In Fig.10 they are plotted against the concentration  $c$  on a double logarithmic scale. For comparison  $\xi(c)$ , the screening length of the excluded volume interactions /16/, are also shown. Although the data are insufficient to find the power law for  $\xi_H(c)$ , one can see that the absolute values of both quantities are similar. Moreover, the resulting  $\xi_H(c)$  agree reasonably with the corresponding values estimated from the cross-over behaviour of the line shape parameter  $n$  (see Fig.9). For example at  $c=0.18$  the transition occurs at  $q^* \approx 0.06\text{\AA}^{-1}$  from which  $\xi_H(c) = 1/q^* \approx 16.6\text{\AA}$  is calculated, compared to the fitted  $\xi_H(c) \approx 15\text{\AA}$ .

In the case of concentrated solutions ( $0.5 < c < 1.0$ ) enhanced Rouse relaxation is dominant in the whole  $q$  range of the experiment. All spectra are well described by the scattering law /22/ calculated for the Rouse model as has been demonstrated for the melt data.

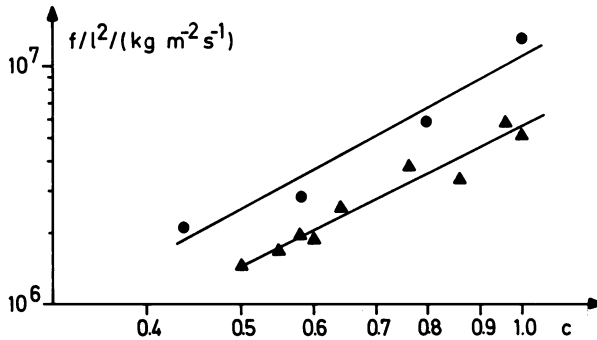


Fig.11: Segmental friction coefficient  $f$  divided by the mean square segment length  $l^2$  as a function of concentration

▲ derived from neutron scattering data

● derived from measurements of the viscosity

The microscopic parameter to be extracted from the characteristic frequencies  $\Omega_R(q)$  (see eq. (9)) is the segmental friction coefficient  $f$  divided by the mean square segment length  $l^2$ . Its concentration dependence is shown in Fig.11 on a double logarithmic scale. For comparison the values /54/ obtained from the macroscopic viscosity  $\eta_c$  of solutions of PDMS in *d*-chlorobenzene at  $T=100\text{C}$  are also plotted. In order to avoid entanglement effects on the viscosity a low molecular weight PDMS ( $M=7.400$ ) was used. For unentangled polymer solutions the relation /55/

$$\eta_c - \eta_0 = \frac{f}{12} R_0^4 \frac{\rho L}{36M} \quad (20)$$

holds. ( $R_0^2$  mean square end to end distance,  $\rho$  polymer density).

Although there are systematic deviations between the values of  $f/l^2$  determined by macroscopic and microscopic methods, one can see that the concentration dependence of both quantities is given by power laws which are very similar. This result may be taken as further evidence that segmental diffusion in concentrated polymer solutions and melts is unaffected by entanglements in length scales extending to  $30\text{\AA}$ .

#### CONCLUSION

Quasielastic neutron scattering methods show that segmental diffusion in dilute polymer solution is governed by hydrodynamic interactions as described by the Zimm model. This is true for  $\theta$  and good solvents. However, in contrast to the results of viscoelastic experiments

the neutron scattering data require properties to be incorporated in the Zimm model specific to chemical structure. For polymer melts and concentrated solutions the Rouse model was found to be an adequate microscopic model. There is no indication that segmental diffusion is restricted by topological constraints on a length scale extending to  $30\text{\AA}$ .

In semi-dilute solutions the transition from single to many chain behaviour was observed. This transition manifests itself in a change of the scaling behaviour of the characteristic frequencies and in a change of the line shapes. The concentration dependence of the related correlation length was found to be in agreement with dynamic scaling predictions modified to allow for finite chain length.

Investigations on the single chain behaviour in polymer solutions at various concentrations reveal the existence of a double transition. The complex transition behaviour which includes a cross-over from unscreened Zimm to enhanced Rouse and from enhanced Rouse to screened Zimm relaxation, results from incomplete screening of hydrodynamic interactions. For the first time the hydrodynamic screening length  $\xi_H(c)$  was determined experimentally.

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