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Counter-ion dynamics in crosslinked poly(styrene sulfonate) systems studied by NMR

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Abstract

The field dependence of the longitudinal and transverse nuclear magnetic relaxation rates of $^{23}Na^+$ in aqueous crosslinked Na-poly(styrene sulfonate) (PSS) systems (ion exchange resins) has been obtained as a function of the degree of crosslinking. The relaxation is considerably enhanced relative to solutions of non-crosslinked NaPSS at equal ionizable group concentration. This is due to the dynamic constraints of the polymer chains, which render the averaging of the counter-ion chain interaction less efficient. The field dependence of the relaxation rates in the crosslinked NaPSS systems reveals two processes that are out of the extreme narrowing limit. This is in contrast to the relaxation behavior found in non-crosslinked NaPSS systems. To characterize these processes their correlation times were combined with constants of selfdiffusion to estimate the distances diffused by an ion in order to average the electric field gradient at its nucleus. These two distances are interpreted as characteristic length scales in the network. At all degrees of crosslinking it was found that the smallest of these length scales is roughly equal to the distance between two neighbouring crosslinks. The largest characteristic distance extends over several crosslinks and reflects inhomogeneities in the crosslink concentration. These conclusions were also reached from similar experiments on $^7Li^+$ in LiPSS systems.

Keywords: Polyelectrolyte; Crosslink density; Ion mobility; NMR dispersion

1. Introduction

In recent years several nuclear magnetic relaxation studies have been undertaken to obtain information on the counter-ion distribution and dynamics in polyelectrolyte solutions. Correlations between ^{7}Li and ^{23}Na relaxation on the one hand and polyelectrolyte concentration, [1-4] chain charge density [1,3,5], chain length [1,6] and low molecular weight salt concentration [1,3] on the other hand were found. The influence of these variables was shown to be partially due to changes in the conformation of the charged chains. Also a correlation between chain segmental dynamics and counter-ion relaxation was observed [6].

In a way ion exchange resins may be viewed as highly concentrated polyelectrolyte solutions. On length scales larger than the Kuhn length the concentrated solutions of linear polymer may be regarded as homogeneous systems if the polymer consists of sufficient Kuhn segments. In ion exchange resins the polymer molecules are constrained due to the presence of crosslinks. A basic problem in the study of crosslinked systems is the uncertainty in both the exact degree of crosslinking and the uniformity of the spatial distribution

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of the crosslinks [7]. The ion exchangers studied here contain divinylbenzene crosslinks so that four poly(styrene sulfonate) chains connect at a crosslink. In principle a regular network of connected crosslinks, each surrounded tetrahedrally by four neighbours, can be formed. In practice the crosslink concentration will not be homogeneous and a particular intercrosslink distance may deviate from the average value.

In the present paper nuclear magnetic resonance is used to probe the dimension of inhomogeneities in the internal structure of ion exchangers. Combining correlation times as derived from field dependent nuclear relaxation rates with diffusion constants as measured with the pulsed field gradient NMR technique, characteristic distances are determined in the polymer network. A correlation time measures the time that is needed to average the electric field gradient (efg) that couples to the electric quadrupole moment of ^{23}Na ions. Since the most probably dynamic process that modulates the efg is translational diffusion, correlation times may be transformed into characteristic distances if the diffusion constant is known.

In this way considerable differences are observed, on a microscopic scale, between polymer solutions and ion exchange resins. In the concentrated polymer solutions the "grain" size is of the order of the Kuhn length. In crosslinked systems two length scales are deduced from the nuclear magnetic relaxation of the counter-ions. The smallest characteristic length corresponds roughly to the intercrosslink distance at all crosslinkages studied.

The ratio of the larger characteristic distance and the intercrosslink distance depends on the crosslinkage. It reflects deviations from a tetrahedral distribution of neighbouring crosslinks and inhomogeneities of the crosslink density. It is found that the internal structure of the crosslinked systems is most regular at high crosslinkage.

This article is organized as follows: Section 2 reports the way by which the resins and non-crosslinked PSS were characterized and treated prior to the NMR experiments, in Section 3 the diffusion experiments are described and their results given. In Section 4 the relaxation experiments on ^{23}Na, ^{7}Li, D and ^{17}O are described and their results are discussed using the diffusion constant results of Section 3. Section 5 summarizes the conclusions.

2. Preparation and characterization of the samples

2.1 Preparation

Ion exchange resins of five different crosslinkages of poly(styrene sulfonic acid) (HPSS) were purchased from Bio-Rad (The AG-50W analytical grade series). The protonated ion exchange resin beads were kept in 2 N HCl solution for a few days to remove cations from the resins. After washing with Millipore water the Na and Li forms were obtained by adding NaOH or LiOH in small excess. Excess ions were detected with conductance measurements and removed by washing with water.

Linear HPSS of non-dialyzed quality of several degrees of polymerization was obtained from Pressure Chemicals. After dialysis, this HPSS was neutralized with LiOH or NaOH solution to obtain NaPSS and LiPSS. Excess low molecular weight salt was removed by dialysis. Potassium styrene sulfonate (monomer) was purchased from Polysciences and brought into the sodium form on a ion exchange column. It was purified by recrystallization from an ethanol/water mixture.

2.2 Characterization of the resins

The five crosslinkages were taken to be 2, 4, 8, 12 and 16% as indicated by the manufacturer. The crosslinkage is the mass percentage of crosslinking agent in the reaction mixture prior to polymerization and sulfonation. For PSS ion exchange resins the crosslinking agent is divinylbenzene (DVB) of which the molar mass is 0.130. The molar mass of styrene being 0.104, the crosslinkage is

$$X = 100 \frac{0.130\ m}{0.130\ m + 0.104\ n} \tag{1}$$

where m denotes the number of DVB moles and n equals the number of styrene moles in the reaction mixture. From the definition of the mole fraction DVB

$$f_x = \frac{m}{m+n} \tag{2}$$

it follows that

$$f_x = \frac{0.104\ X}{0.104\ X + 0.130(100 - X)} \tag{3}$$

The wet capacity (which is the number of moles of ionizable groups per kg swollen protonated resin) was obtained by tritation of fully swollen and protonated resins with NaOH. Now the sodium concentration and lithium concentration in the wet resins in the sodium and lithium forms can be calculated, provided that the water content is known. This water content depends on the type of counter-ion. The determination of the water content of the fully swollen resins was performed by weighing before and after drying under reduced pressure and 60 °C until constant weight. Then the residual water content was determined with i.r. spectroscopy to be a few weight percent. In the protonated form there were about 10% more water molecules per ionizable group than in the Na and Li form. The Na and Li forms did not differ significantly in this respect. In Table 1 some characteristic quantities of the NaPSS ion exchange resins are given.

For the calculation in this section the network will be considered as a homogeneous distribution of crosslinks connected with four neighbours. Because no line splittings in sodium spectra were observed, it is concluded that electric field gradients are averaged out to zero within distances smaller than about 500 Å, the diffused distance during the longest correlation time observed. This will be discussed in Section 4.

When the resins are immersed in water, they swell. It is expected that the intercrosslink chains stretch as a consequence. Information on the structure of the network in this situation can be obtained by calculating the amount of intercrosslink monomers and compare their added lengths with the intercrosslink distance.

The crosslink phenyl groups are not thought to be sulfonated because of sterical hindrance. This is concluded from the fact that in fuming sulfuric acid sulfonation of the phenyl group of di(dodecyl)benzene with the phenyl group attached near the center of the alkyl chains hardly occurs [8]. The amount of ionizable groups as determined by titration corresponds to the sulfonated fractions of the intercrosslink styrene monomers. The resins are sulfonated after polymerization. If the degree of sulfonation (i.e. fraction of sulfonated intercrosslink monomers) were equal to one, the total length of intercrosslink chain per unit weight of swollen gel could be calculated directly. However, the sulfonation is incomplete, as is concluded from the fact that the theoretical equivalent weight (i.e. the weight corresponding to an equivalent of ionized groups in dry crosslinked HPSS if all intercrosslink monomers are sulfonated) is, with the exception of crosslinkage 2, found to be smaller than the observed equivalent weight (i.e. the weight corresponding to an equivalent of ionized groups in dry crosslinked HPSS presently studied). From

Table 1

Some characteristic quantities of swollen NaPSS ion exchange resins at 298 K

Crosslinkage	f_x	wet capacity (eq/kg)	f_w	Molality (eq/kg H_2O)	Mole H_2O per mole Na^+
2	0.016	0.91	0.812	1.12	50
4	0.032	1.63	0.654	2.49	22
8	0.065	2.32	0.500	4.64	12
12	0.098	2.43	0.416	5.84	9.5
16	0.152	2.41	0.361	6.68	8.3

f_x: molar fraction of DVB in reaction mixture; f_w: weight fraction of water; and molality = capacity/f_w.

the titration results the water content and the mole fraction of DVB the crosslink concentration in the swollen resins was calculated.

The average distance between the crosslinks can be estimated by considering the network as a diamond lattice of crosslinks. The unit cell of such a lattice contains 8 crosslinks. The volume of the unit cell is

$$\left(4/\sqrt{3}\,d_{\mathrm{x}}\right)^3 \qquad (4)$$

where d_{x} is the distance between two directly connected crosslinks. Therefore,

$$d_{\mathrm{x}} = \frac{\sqrt{3}}{20} N_{\mathrm{A}}^{-1/3} c_{\mathrm{x}}^{-1/3} \qquad (5)$$

where $\mathrm{N_A}$ = Avogadro's number, c_{x} is the crosslink concentration in molal. It is assumed that the density of the swollen resin can be taken to be 1000 kg/m^3 [9].

Each crosslink is connected to four intercrosslink chains. Therefore, the length of intercrosslink chain that is available for the connection of two crosslinks is

$$d_{\mathrm{a}} = \frac{c_{\mathrm{m}} l_{\mathrm{m}}}{2c_{\mathrm{x}}} = \frac{l_{\mathrm{m}}(1-f_{\mathrm{x}})}{2f_{\mathrm{x}}} \qquad (6)$$

where l_{m} denotes the length of a monomer (= 2.5 Å). The results of these calculations are collected in Table 2. The equivalent weights of the resins in the sodium form were obtained from those of the protonated form by subtracting 0.001 and adding 0.023 kg.

Comparing the intercrosslink distance, d_{x}, and the chain available to bridge this distance, d_{a}, an approximate agreement is observed and the trend with crosslinkage is the same for both. This indicates that the crosslink percentages are reasonably accurate. A more detailed consideration of the results shows that at higher crosslinkage there is not sufficient chain. This can be explained by the fact that crosslinks have a finite dimension of several Å.

The values for d_{x} and d_{a} indicate that at high crosslinkage the intercrosslink chains are stretched and at low crosslinkage they are bent. It should be noted, that the transition from stretched to bent chains is at a distance between neighbouring crosslinks comparable to the intrinsic persistence length of PSS, i.e. 12 Å [10].

There may be DVB monomers in the chain that not have become crosslinks. The calculated crosslink concentration is too large in that case. Both the intercrosslink distances and chain length per crosslink will then be underestimated. There exists, to our knowledge, no reliable quantitative experimental determination of c_{x}. The distance between crosslinks, d_{x}, is quite insensitive to an underestimate of c_{x} since $d_{\mathrm{x}} \simeq c_{\mathrm{x}}^{-1/3}$. The intercrosslink chain length d_{a} ($\simeq c_{\mathrm{x}}^{-1}$) is more sensitive to an error in c_{x} and will be an underestimate. Accordingly, the conclusion that the intercrosslink chains are stretched at high crosslinkage per-

Table 2

Calculated data on swollen PSS resin at 298 K

Crosslinkage	$\mathrm{M_{obs}^{eq}}$ (kg)	$\mathrm{M_{th}^{eq}}$ (kg)	p_{s}	c_{x} (mol/kg)	d_{x} (Å)	d_{a} (Å)
2	0.185	0.187	1.0	0.015	42	77
4	0.190	0.188	0.98	0.055	27	38
8	0.194	0.192	0.99	0.163	19	18
12	0.212	0.194	0.89	0.297	15	12
16	0.233	0.201	0.84	0.536	13	7.0

$\mathrm{M_{obs}^{eq}}$: equivalent weight of dry protonated resins, determined by titration; $\mathrm{M_{th}^{eq}}$: equivalent weight of dry protonated resins if the degree of sulfonation is 1; p_{s}: degree of sulfonation; c_{x}: crosslink concentration; d_{x}: distance between neighbouring crosslinks; d_{a}: chain length available to connect the crosslinks; c_{x}, d_{x} and d_{a} are calculated for resins in the sodium form.

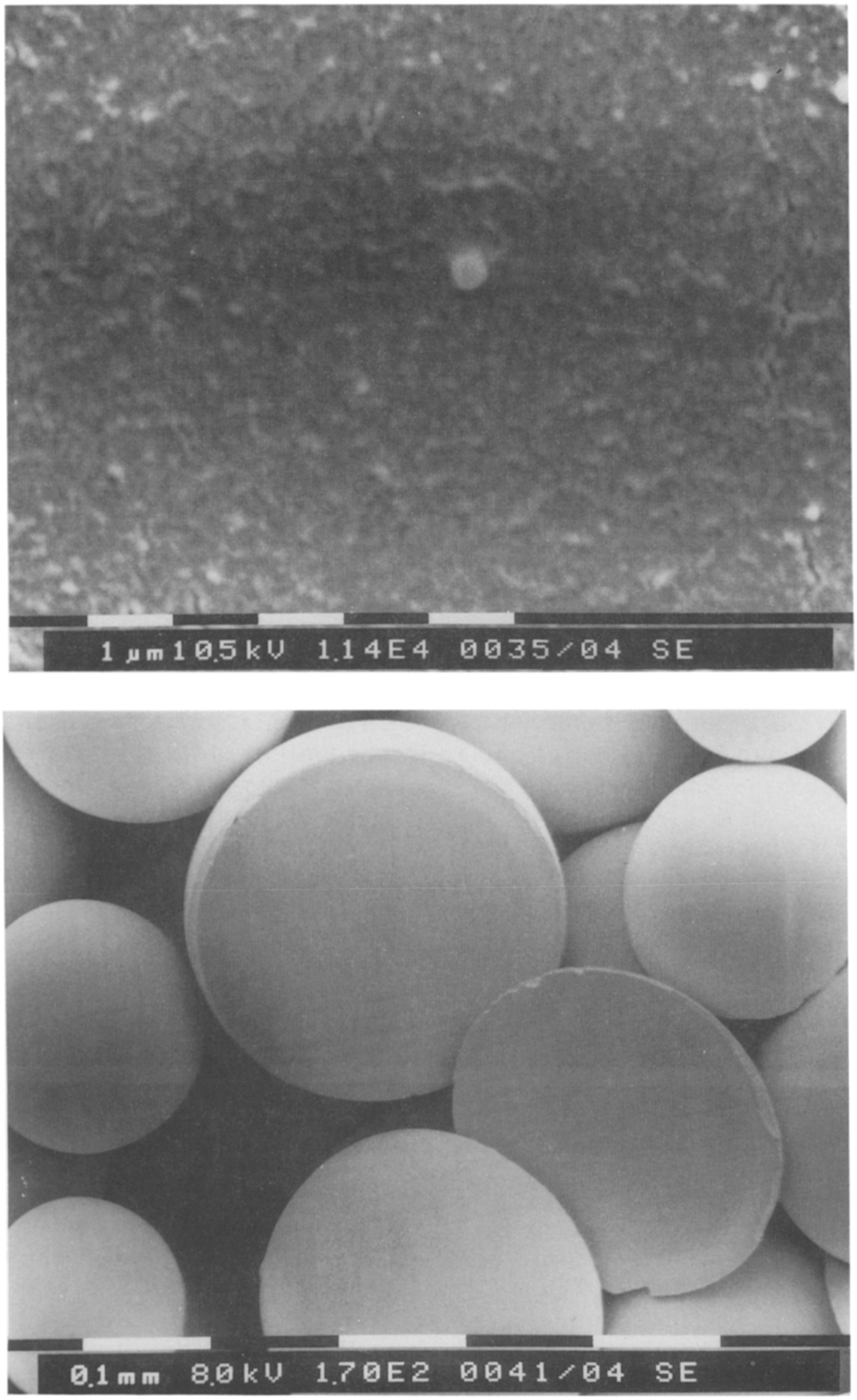

Fig. 1. Two transmission electron microscopy images of swollen NaPSS ion exchange resin of crosslinkage 12. The bars indicate the length scale.

centages is less certain than the opposite conclusion at low crosslinkages.

On a micron scale, the internal structure of the ion exchange resin has been studied with electron microscopy. The transmission electron microscope images of a swollen resin bead of crosslinkage 12 are shown in Fig. 1. On a sub-micron length scale inhomogeneities are observed. However, these photographs indicate that the resin is not macroporous. Images of resins with other crosslinkages gave similar results. Further information will be deduced from the solvent and the counter-ion nuclear relaxation.

3. Diffusion of counter-ions

The selfdiffusion of Na^+ in crosslinked NaPSS has previously been studied, by using salts of radioactive isotopes, as a function of the degree of swelling [11–14] (i.e. the weight of water per unit weight of polymer), as a function of crosslinkage [11,15] and temperature [16]. The results were compared to diffusion in solutions of linear NaPSS [11,12].

It appeared that water content and crosslinkage both have an influence on the diffusivity of sodium ions. However, no direct influence of the crosslinks on the selfdiffusion of sodium ions is found. Pikal and al. [11] found that the selfdiffusion constants were the same in crosslinked and non-crosslinked systems at the same molality (i.e. the same number of water molecules per sodium ion). A similar conclusion was reached by Timmermann [17]. It was concluded that the effect of crosslinkage is mainly exerted by way of its influence on the water and polymer content of the resin.

Constants of selfdiffusion of Li^+ and Na^+ were obtained with the pulsed field gradient NMR method [18] at a field strength of 2.1 T. The Li^+ selfdiffusion constants were determined for all crosslinkages of LiPSS. The Na^+ selfdiffusion could be measured only for crosslinkages 2 and 4 of NaPSS because of a too fast transverse relaxation at higher crosslinkages. At those crosslinkages they were estimated from the Li^+ values assuming that

Table 3

Diffusion constants of Na^+ and Li^+ in crosslinked NaPSS and LiPSS. Temperature 298 K

Crosslinkage	$D_{Na} \times 10^9$ (m^2/s)	$D_{Li} \times 10^9$ (m^2/s)
2	0.46	0.408
4	0.30	0.250
8	0.14 [a]	0.122
12	0.08 [b]	0.060
16	0.03 [b]	0.025

[a] From ref. [11].
[b] Calculated according to eq. (7).

$$D_{Na}/D_{Na,0} = D_{Li}/D_{Li,0} \tag{7}$$

where $D_{Na,0}$ and $D_{Li,0}$ are the diffusion constants at high dilution of low molecular salt. At crosslinkages 2 and 4 this could be checked to be a good estimate. The values of $D_{Na,0}$ and $D_{Li,0}$ have been taken to be 1.33×10^{-9} m^2/s [19] and 1.05×10^{-9} m^2/s [20]. In solution of non-crosslinked LiPSS, the Li^+ diffusion constants were obtained as a function of molality. The resulting diffusion constants are collected in Table 3.

The D/D_0 values of Li^+ and Na^+ differ only slightly at low crosslinkages where the D-values of Na^+ are available. So both ions appear to have a similar interaction mechanism with the charged network.

4. Relaxation experiments

4.1 Relaxation theory

The magnetic relaxation of the nuclei studied here, i.e. ^{23}Na, ^{7}Li, ^{17}O and D is, except for lithium, completely determined by the interaction of the nuclear quadrupole moment with the electric field gradient at the site of the nucleus.

As discussed in ref. [21], if the characteristic time scale of the time dependence of the electric field gradient is comparable or longer than the Larmor precession period, the ^{23}Na ($I = 3/2$) relaxation is bi-exponential. The decay of the transverse and longitudinal magnetization is expressed by

$$M_{+,-}(t) = M_0[(3/5)\exp(-R_{2f}t) + (2/5)\exp(-R_{2s}t)] \quad (8)$$

$$M_z(t) = M_0[1 - (2/5)\exp(-R_{1f}t) - (8/5)\exp(-R_{1s}t)] \quad (9)$$

M_0 is the equilibrium magnetization in the direction of the field, i.e. the z-direction. The relaxation rates are

$$\begin{aligned} R_{2f} &= J(0) + J(\omega) \\ R_{2s} &= J(\omega) + J(2\omega) \\ R_{1f} &= 2J(\omega) \\ R_{1s} &= 2J(2\omega) \end{aligned} \quad (10)$$

where the subcripts f and s mean fast and slow. $J(\omega)$ is the real part of the spectral density at the Larmor frequency of the time dependence of the coupling between the nucleus and the electric field gradient [22] which in an isotropic system can be expressed as:

$$J(\omega) = (\pi^2/5)\chi^2 \,\mathrm{Re}\int_0^\infty \frac{\langle V_{zz}(0)V_{zz}(t)\rangle}{\langle V_{zz}^2\rangle} \times \exp(-\mathrm{i}\omega t)\,\mathrm{d}t \quad (11)$$

where the square of the coupling constant is given by

$$\chi^2 = (eQ_{\mathrm{Na}}/h)^2\langle V_{zz}^2\rangle$$

in which Q_{Na} is the nuclear quadrupole moment of ^{23}Na, e the proton charge, h Planck's constant and $V_{zz}(t)$ is the zz-component of the electric field gradient tensor in the laboratory frame. Sharp brackets indicate an ensemble average. As will be discussed the time dependence of $\langle V_{zz}(0)V_{zz}(t)\rangle$ for Na$^+$ in crosslinked NaPSS systems is found to be describable by assuming contributions from several processes. These processes are considered as independent. In that case

$$\langle V_{zz}(0)V_{zz}(t)\rangle = \sum_{i=1}^{m} \langle V_{zz}(0)V_{zz}(t)\rangle_i \quad (12)$$

where m is the number of processes and $\langle V_{zz}(0)V_{zz}(t)\rangle_i$ is the autocorrelation function of the modulation by the ith process. Thus

$$J(\omega) = (\pi^2/5)\,\mathrm{Re}\sum_{i=1}^{m}\chi_i^2 \times \int_0^\infty \frac{\langle V_{zz}(0)V_{zz}(t)\rangle_i}{\langle V_{zz}^2\rangle_i}\mathrm{e}^{-\mathrm{i}\omega t}\,\mathrm{d}t \quad (13)$$

where

$$\chi_i^2 = (eQ_{\mathrm{Na}}/h)^2\langle V_{zz}^2\rangle_{\mathrm{i}} \quad (14)$$

which is the coupling constant of the ith process

Only the real part of the spectral density causes relaxation, whereas the imaginary part generates a shift of the central transition ($1/2 \rightarrow -1/2$) relative to the outer transitions [23]. The influence of this shift on the measured relaxation rates was shown to be negligibly small [24].

The D and ^{17}O longitudinal relaxations have been shown [25] to be in the extreme narrowing limit in polyelectrolyte solution even at concentrations of several molal. It turned out that also in the crosslinked systems studied here the longitudinal relaxation is in this limit. It can be expressed by [22]

$$R_{1,\mathrm{d}} = (3\pi^2/2)(eQ_d V_{zz,\mathrm{d}}/h)^2(1 + \eta_\mathrm{d}^2/3)\tau_\mathrm{d} \quad (15)$$

$$R_{1,0} = (12\pi^2/125)(eQ_0 V_{zz,0}/h)^2(1 + \eta_0^2/3)\tau_0 \quad (16)$$

where $V_{zz,\mathrm{d}}$, is the zz-component of the electric field gradient, defined in the molecular fixed principal frame of the electric field gradient in which $|V_{zz,\mathrm{d}}| \geq |V_{yy,\mathrm{d}}| \geq |V_{xx,\mathrm{d}}|$. $\eta_\mathrm{d} = (V_{yy,\mathrm{d}} - V_{xx,\mathrm{d}})/V_{zz,\mathrm{d}}$, Q_d denotes the nuclear quadrupole moment of deuterium and τ_d the correlation time; $V_{zz,0}$, η_0, Q_0 and τ_0 for ^{17}O are analogously defined.

Only the longitudinal rate of D and ^{17}O is interpreted in this study. Around neutral pH transverse relaxation may be influenced by proton or deuteron exchange which renders interpretation difficult.

The ^{7}Li ($I = 3/2$) relaxation takes place not only by way of the quadrupole mechanism, but also by a mechanism that contributes mono-exponentially to both longitudinal and transverse relaxation. Probably this is a heteronuclear dipole–dipole coupling. In this case the transverse and longitudinal relaxation rates can be expressed as

$$\begin{aligned} R_{2f} &= R_{2f,q} + R_{2,dd}\\ R_{2s} &= R_{2s,q} + R_{2,dd}\\ R_{1f} &= R_{1f,q} + R_{1,dd}\\ R_{1s} &= R_{1s,q} + R_{1,dd} \end{aligned} \qquad (17)$$

where the dipolar contributions have the subscript 'dd' and the quadrupolar contributions the subscript 'q'.

4.2 Relaxation of sodium ions in polyelectrolyte systems

When the autocorrelation of the electric field gradient decays exponentially in time the real part of the spectral density has a Lorentzian functional dependence on the Larmor frequency:

$$J(\omega)\frac{C^2\tau}{1+(\omega\tau)^2} \qquad (18)$$

where τ is the correlation time of the modulating process and C is, except from a numerical constant, the coupling constant. In many cases where Larmor frequency dependence of the relaxation rate is observed, a Lorentzian or a sum of Lorentzians describes this dependence satisfactory. Often a Lorentzian dependence is assumed because information is too scarce to make a more detailed interpretation of the Larmor frequency dependence feasible. By fitting one or a sum of Lorentzians to the ω dependence of $J(\omega)$ an estimate can be obtained of the C and τ of the modulating processes.

If $|\omega\tau| \ll 1$ the dependence of $J(\omega)$ on ω vanishes (extreme narrowing limit). In that case it is not possible to determine from the relaxation rates C and τ separately. Then, no dynamic and structural information can be obtained without additional data. For sodium ions this is found in solutions of low molecules salt solutions, in moderately concentrated isotropic polyelectrolyte solutions and in semi-dilute polyelectrolyte solutions with excess low molecular salt. A dependence of $J(\omega)$ on ω is found at ambient field strengths in semi-dilute polyelectrolyte solutions without low molecular salt added and, as will be shown, in systems of crosslinked NaPSS. Several processes may contribute to the slow modulation of the interaction between ions and the charged chains in semi-dilute polyelectrolyte solutions: chain tumbling [2,26], chain segment dynamics [6], diffusion of sodium ions parallel to a bending chain [1,4] and diffusion of ions between neighbouring chains [2]. Diffusion concentric to the chain was shown to be a modulation mechanism in 0.1 molal polyelectrolyte solution [27].

On Na^+ in crosslinked PSS some work has been done before. Goldsmith et al. [28] performed a relaxation study on Na ions in crosslinked NaPSS as a function of the dielectric constant of the solvent. Blaedel et al. [29] measured relaxation rates of Na^+ in crosslinked NaPSS as a function of degree of swelling. Creekmore et al. [30] observed a line broadening upon increase of crosslinkage. Berendsen et al. [31] observed bi-exponential relaxation in ion exchange resins and were the first to ascribe it to unequal transition probabilities for different allowed transitions in $I = 3/2$ systems. In these studies no use was made of the field dependence and bi-exponentiality of the Na^+ relaxation to obtain information on the processes that govern the Na^+ relaxation in crosslinked systems.

4.3 Experimental procedure of relaxation experiments

The nuclear magnetic relaxation of sodium ions in fully swollen crosslinked systems was measured as a function of the crosslinkage and field strength. The sodium Larmor frequencies were 4.0, 11.9, 23.9, 71.4, 105.8 and 132.3 MHZ (0.35, 1.05, 2.1, 6.3, 9.3 and 11.7 T). In solutions of linear NaPSS the relaxation was studied as a function of concentration, molecular weight and field strength (1.05, 2.1 and 6.3 T). At one field, 6.3 T, the ^{17}O and D relaxation were measured (Larmor frequencies 36.0 and 41.4 MHz, respectively) in the crosslinked systems. At two fields (2.1 and 6.3 T, Larmor frequencies 35.0 and 104.9 MHz) the ^7Li

relaxation was measured as function of the crosslinkage in fully swollen LiPSS resins.

For lithium and sodium the longitudinal and the transverse relaxation were studied. Longitudinal relaxation experiments were done by inversion recovery, whereas the transverse relaxation was recorded by the spin-echo sequence if the relaxation rate was higher than 10 s^{-1} and with the Carr–Purcell–Gill–Meiboom sequence if the rate was lower than 10 s^{-1}. The pulse distance was varied down to 500 μs. No pulse spacing dependence was observed.

All experiments on ion exchange resins were done with samples of resin beads immersed in water. As a consequence, the ^{17}O and D signals were composed of contributions from water inside and outside the resins. In all cases (except the D relaxation at crosslinkage 16), the magnetization decays could be fit satisfactory to a sum of two exponents, one of which was characteristic for bulk water. This means that ^{17}O and D show a mono-exponential relaxation inside the resins.

The transverse and in some cases the longitudinal relaxation of Na^+ and Li^+ is bi-exponential without a contribution from ions outside the resins. This can be stated because no Na^+ or Li^+ could be detected in the supernatant.

From computer simulations it is concluded that the development of three-quantum coherences during the inversion recovery experiments does not cause significant deviation from the time dependence of the longitudinal magnetization as expressed in eq. (8), as was shown [32] to be a theoretical possibility.

In many cases the decay of the longitudinal relaxation can be fit to one exponent, the difference between the two exponential contributions being too small to make a bi-exponential fit feasible. This one exponent is however often significantly smaller than R_{2s}, which means that $J(\omega) \neq J(2\omega)$. In order to determine $J(\omega)$ and $J(2\omega)$, the fact was used that their sum, R_{2s}, is known. From eqs. (9) and (10) it follows that, after a π pulse

$$M_z(t) = M_0\{1 - \exp(-R_{2s}t)[(2/5)\exp(-\Delta t) + (8/5)\exp(\Delta t)]\} \qquad (19)$$

where $\Delta = J(\omega) - J(2\omega)$. By fitting eq. (19) to the longitudinal decay Δ was found. From Δ and R_{2s}, $J(\omega)$ and $J(2\omega)$ were calculated. From R_{2f} and $J(\omega)$, $J(0)$ was calculated.

Free induction decays were recorded in 1024 points and accumulated 10 to 100 times. In the inversion recovery experiments a waiting time of 300 μs after the $\pi/2$ pulse was practiced before storing the first point of the free induction decay (FID) in the boxcar array. The inversion recovery and spin-echo relaxation decays were recorded at 128 time intervals. They were fit to a mono- or bi-exponential function with a linear least squares algorithm. Adjustable parameters were the base, the amplitude, the relaxation rate(s) and, in case of bi-exponential decay, the amplitude ratio of the two exponents. However, in case of Na and Li relaxation this last parameter was only set free if $R_f > 3R_s$; when this condition was not met the amplitude ratio was fixed at the theoretical value that was corrected to an estimated extent for the influence of the dead time. Prior to the fit this influence can only be estimated because it depends on the relaxation rates. The correction never exceeded 5%. For the bi-exponential ^{17}O and D relaxation, which is due to internal and external water, the amplitude ratio had to be set free in the fit. This resulted in nearly all cases in satisfactory results (except for D at crosslinkage 16), even when $R_f < 3R_s$, because of the high signal-to-noise ratio.

4.4 Results and discussion of relaxation experiments

4.4.1 Water relaxation in crosslinked systems

For the interpretation of the relaxation data it is assumed that the swell pressure has not influence. The swell pressure is due to the Donnan potential between the interior of the resin and the surrounding solvent, which makes water molecules enter a not fully swollen resin. Its final value is determined by the elastic force exerted by the network on the internal solution. This final pressure increases with increasing crosslinkage and is reported in case of crosslinkage 16 to be about 3 MPa [33]. Such a pressure was shown not to change significantly the pure water proton relaxation rate [34], the D relaxation in LiCl solution [35] and the constant of selfdiffusion of H_2O [36].

The longitudinal relaxation of ^{17}O and D in crosslinkage 2 to 12 is found to be mono-exponential in the resins, indicating that inhomogeneities, if present, are small enough to allow exchange of H_2O between them which is fast relative to the longitudinal relaxation of ^{17}O. At crosslinkage 12 the T_1 of ^{17}O being ca. 1 ms and the self diffusion constant ca. 1.4×10^{-10} m^2/s, this means that all physically different environments available to water molecules are sampled within 1 μm. At lower crosslinkages by a similar reasoning it can be concluded that the inhomogeneities do not exceed extensions of a few μm. The relaxation behavior of the water nuclei confirms the structural information obtained from electron microscopy. The typical size of inhomogeneities observed in electron microscope images is smaller than one μm. In terms of water relaxation, on a micrometer scale the ion exchange resins are homogeneous. Granularity in these systems occurs on a smaller length scale as will be seen from an analysis of the Na relaxation rates. The relaxation of D and ^{17}O at crosslinkage 16 was not mono-exponential. This indicates an exchange rate between inhomogeneities that is not fast on the scale of T_1. Therefore, the water relaxation at crosslinkage 16 is not considered here.

In Fig. 2 the ratio R_1/R_1^0 (where R_1^0 is the relaxation rate in bulk water) for D and ^{17}O is plotted vs. molality for crosslinked and non-crosslinked systems.

It can be concluded that the ^{17}O and D longitudinal relaxation is enhanced in crosslinked systems relative to bulk water. This enhancement is stronger than in non-crosslinked systems of the same equivalent concentration. Because the coupling is intramolecular, it can be immediately concluded that the average water mobility is reduced in the presence of crosslinks. This is probably not only due to a direct interaction between crosslinks and water molecules because the apolar phenyl groups are not expected to influence the water

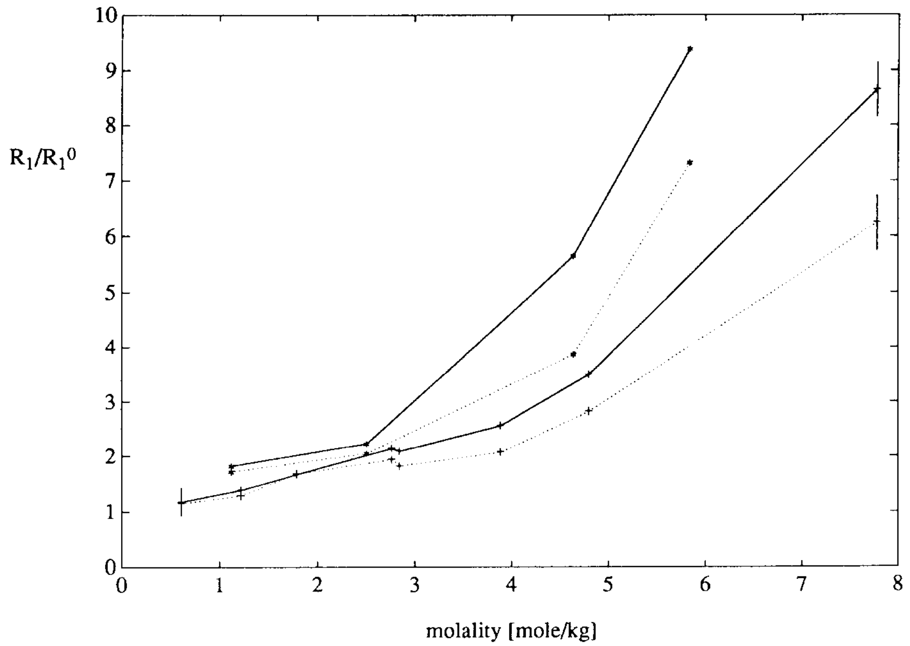

Fig. 2. ^{17}O and D relaxation in crosslinked and non-crosslinked NaPSS systems. The enhancement of R_1 relative to bulk H_2O vs. molality at 298 K. (+) and dotted line: D in non-crosslinked systems, (+) and full line: ^{17}O in non-crosslinked systems, (*) and dotted line: D in crosslinked systems, (*) and full line: ^{17}O in crosslinked systems. The full and dotted lines (for ^{17}O and D, respectively) are drawn as an aid to the eye. The error bars at 0.6 and 8.9 molal are representative for all points.

dynamics in great extent. The influence of a polyelectrolyte molecule on the molecular water dynamics in its neighborhood are mainly exerted by way of its charges [25]. The relaxation enhancement in crosslinked systems indicates that the segmental motions are slowed down due to the presence of crosslinks. More information on this point can be obtained in principle by varying the ionic species. This is however complicated by the fact that there can also be a correlation between segmental mobility and ion mobility [37].

4.4.2 Sodium relaxation in non-crosslinked systems

In Fig. 3 the transverse and longitudinal sodium relaxation rates are plotted versus equivalent concentration for several degrees of polymerization (from 1 to 5792) at 6.3 T (71.4 MHz). Between 0.5 and 2.5 molal there appears to be no influence of the degree of polymerization. The interaction between a Na^+ nuclear quadrupole moment and the surroundings of the ion is electrostatic. This interaction is expected to have a range of the order of the Debije screening length, which is not more than a few Å at these concentrations. Therefore, the nuclear quadrupole moment interacts only with its very near surroundings. Although this does not mean that isotropy in the efg is also reached within the Debije screening length, the fact that the degree of polymerization does not influence the relaxation rate is a confirmation of the short interaction range. The absence of dependence on connectivity also shows that the rate of modulation of the ion chain interaction is not influenced by connectivity in NaPSS solution from 0.5 up to 2.5 molal. This is a remarkable result. Early work on ^{23}Na relaxation in poly(phosphate) solution [3], showed a clear dependence on the degree of polymerization (dp) of the relaxation rate up to dp ≈ 100 for concentrations in the molal range. The present results show that this is not general for polyelectrolyte solutions. Further work is necessary to determine whether site binding of a small percentage of the Na^+ ions is responsible for the observations on the poly(phosphate) solutions.

The concentration dependence is very similar to that of ^{17}O and D of H_2O [25]. This is expected, because the sodium relaxation is closely connected

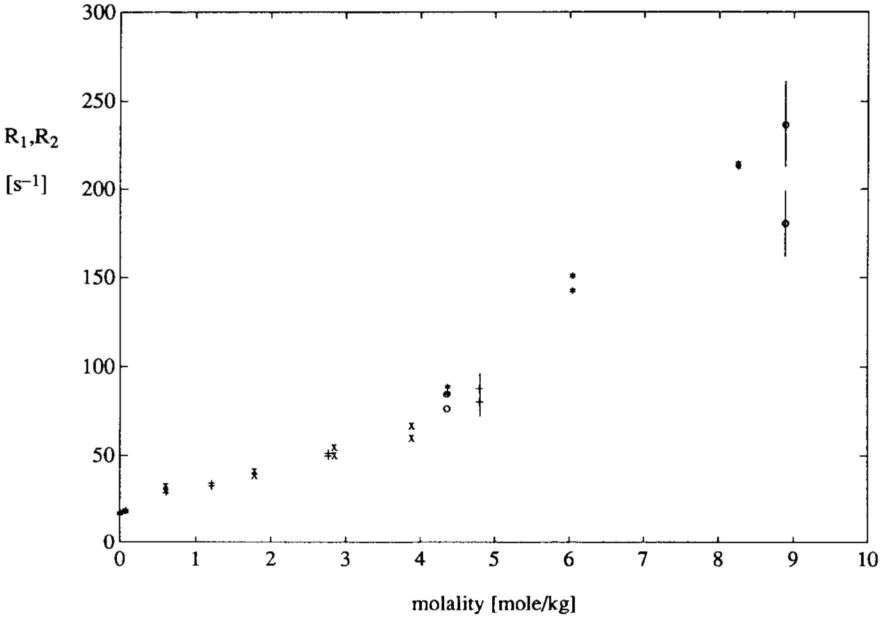

Fig. 3. Relaxation of Na^+ in aqueous NaPSS solutions. R_1 and R_2 for several degrees of polymerization vs. molality. Degrees of polymerization: (∗) 1, (+) 22, (○) 87, (×) 5792. Upper symbols are the R_2 values, the lower the R_1 values. The error bars at 4.8 and 8.9 molal are representative for all points.

to the dynamics of H_2O molecules in its neighbourhood [38].

Above a concentration of 2.5 molal an influence of the connectivity of the monomers is found (Fig. 3). At concentrations higher than 2.5 molal there is a significant difference between R_1 and R_2 which is not observed in the solution of sodium styrene sulfonate. In spite of the difference between R_1 and R_2 there is no observable bi-exponentiality in the longitudinal or transverse decay. The difference between R_2 and R_1 is however confirmed by a field dependence of $J(\omega)$, which is plotted in Fig. 4 for 8.89 molal and in Fig. 6 for 4.35 molal (dashed line). In both cases the degree of polymerization is 87. Because the longitudinal and transverse relaxation decays are mono-exponential functions within experimental accuracy, it is assumed that the rates can be interpreted as the first cumulant of the theoretical bi-exponential decays, expressed by eqs. 8 and 9.

$$\begin{aligned} R_1 &= (2/5)J(\omega) + (8/5)J(2\omega) \\ R_2 &= (3/5)J(0) + J(\omega) + (2/5)J(2\omega) \end{aligned} \tag{20}$$

R_1 and R_2 values were obtained at 0.35, 1.05, 2.1 and 6.3 T. The R_1 and R_2 values, taking into account the circumstance that the field strength 1.05 is a half times 2.1 T, form a set of eight equations with eight unknowns which can be solved.

It is assumed that the spectral density in solution of linear polymer can be expressed as

$$J(\omega) = \frac{C^2\tau}{1 + \omega^2\tau^2} + J_f \tag{21}$$

where J_f is a frequency independent contribution due to processes much faster than the Larmor frequency.

The curves in Fig. 4 and Fig. 6 (8.89 and 4.35 molal, respectively) represent the least-squares fit of eq. (21) to the experimental values of $J(\omega)$. The resulting parameter values are collected in Table 4. Because at relatively low concentrations the dispersion is very weak, there is a large experimental uncertainty in the parameters. The correlation time increases with increasing concentration,

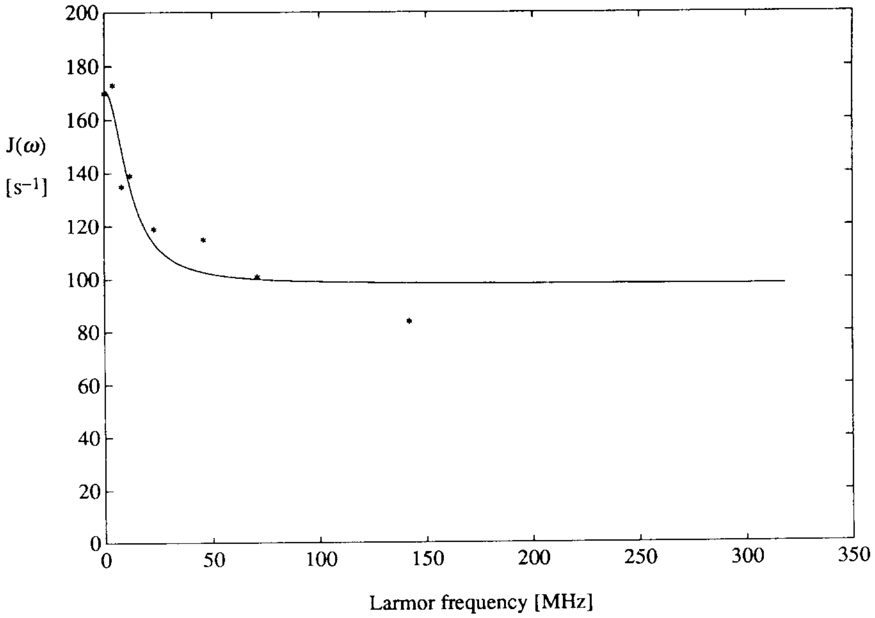

Fig. 4. Relaxation of Na^+ in solution of linear NaPSS. The Larmor frequency dependence of the spectral density in 8.9 molal NaPSS solution at 298 K. The solid curve is the best fit of eq. (21). Degree of polymerization is 87.

Table 4

Sodium relaxation in solution of linear NaPSS. Degree of polymerization is 87. The parameters τ, C and J_f result from the fit of eq. (21) to the experimental values of the spectral density; d is the distance travelled by diffusion during the correlation time, calculated with eq. (22). The absolute standard deviations are between brackets.

Molality (mol/kg)	τ (ns)	C (MHz)	J_f (s^{-1})	d (Å)
2.75	1.0(1.4)	0.07(0.1)	18(8)	15(6)
3.71	2.2(1.2)	0.06(0.02)	29(3)	19(4)
4.35	2.4(2)	0.07(0.05)	35(7)	19(5)
8.89	9.3(3)	0.09(0.02)	94(7)	29(5)

whereas the coupling constant turns out to be no function of the concentration.

To explain the dispersion in the spectral density of sodium above 2.5 molal it is informative to calculate the distance that an ion diffuses during the correlation time, i.e. during the time it needs to average to zero the electric field gradient at the site of its nucleus.

With

$$d^2 = 6\tau D \tag{22}$$

the root mean square distance, d, travelled during the correlation time can be calculated. The diffusion constants can be obtained by interpolation of the data of ref. [12] on sodium ion diffusion in NaPSS solution. The results for d are in Table 4. This distance can be directly interpreted as the distance beyond which the electric field gradient tensor at the site of the nucleus is completely uncorrelated with its initial value. If diffusion of the sodium ion is the only relaxation source, this distance should be interpreted as the correlation length of the electric field gradient tensor in the laboratory frame. If also chain dynamics are a relaxation source, the diffused distance during the correlation time is a lower bound to the instantaneous correlation length of the electric field gradient.

In the concentration range from 2.5 to 8.89 molal a diffused distance during the correlation time is found to range from 15 to 28 Å, i.e. in the

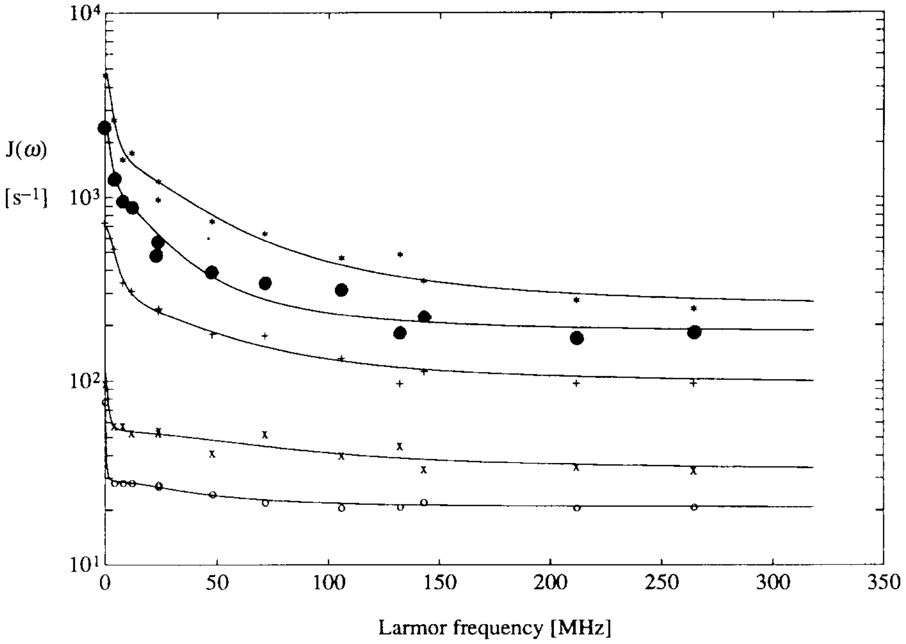

Fig. 5. Relaxation of $^{23}Na^+$ in crosslinked NaPSS systems. Larmor frequency of the spectral density. Crosslinkages (∗) 16, (●) 12, (+) 8, (×) 4 and (○) 2. The curves are the best least-squares fits of eq. (23).

order of the Kuhn length (24 Å) [10], which is twice the intrinsic persistence length. (No electrostatic contribution to the persistence length is expected because of the high electrostatic screening at this concentration.) The observation of this characteristic length scale can be explained by the fact that on a length scale larger than the Kuhn length the solution is isotropic. Below 2.5 molal the small difference disappears due to the increase of the ionic and polymer mobilities. Below 0.1 molal the relaxation of the counter-ions shows a complicated behaviour (not shown here) discussed previously [1,6].

4.4.3. Sodium relaxation in crosslinked systems

The sodium transverse and longitudinal relaxation at all crosslinkages is exponential in the way to be expected for a homogeneous sample. The sodium relaxation data is therefore interpreted assuming that the sodium ions sample all environments on a time scale which is small with respect to T_1.

In Fig. 5 the spectral densities of Na^+ deduced from the relaxation measurements are plotted for resins with different crosslinkages. For comparison, in Fig. 6 the spectral density deduced from sodium relaxation in a solution of non-crosslinked NaPSS with a similar equivalent concentration is shown. It is noted that, in the presence of crosslinks, the spectral density shows a sharp decrease between 0.3 and 3 MHz, followed by a slower decrease until a constant level is reached. These observations are most simply interpreted as two dispersions and an additional contribution of processes on a time scale too short to be monitored by NMR at the present field strengths. It is, therefore, assumed that the observed dispersions correspond to three independent processes with exponentially decaying autocorrelation functions. After this, the three processes will be referred to by "slow", "middle" and "fast". Thus, the spectral density is expressed by

$$J(\omega) = \frac{C_s^2\tau_s}{1+\omega^2\tau_s^2} + \frac{C_m^2\tau_m}{1+\omega^2\tau_m^2} + J_f \qquad (23)$$

where C_m and τ_m denote the coupling constant and the correlation time of the middle process,

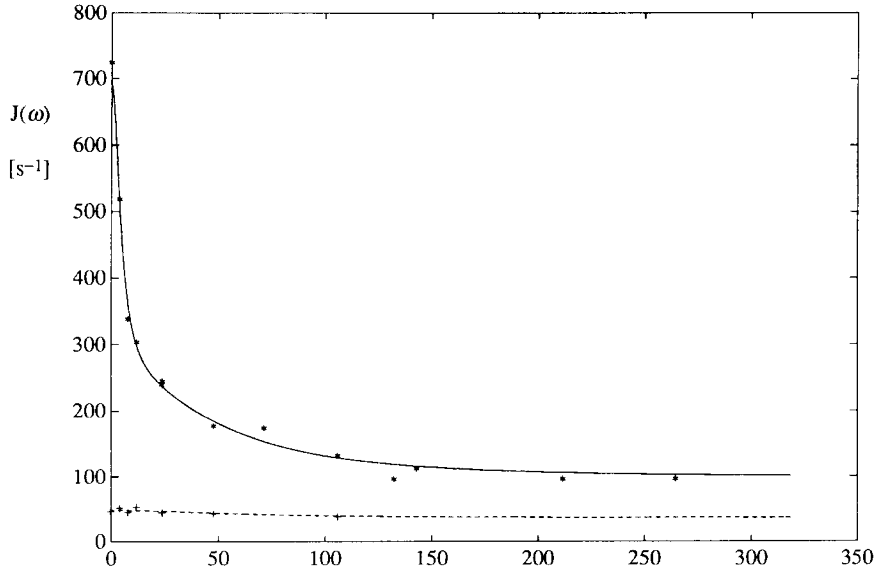

Fig. 6. Na^+ relaxation in crosslinked (crosslinkage 8) and non-crosslinked NaPSS at 298 K. The Larmor frequency dependence of the spectral density. (∗) crosslinked, (+) the spectral density of Na^+ in a solution of non-crosslinked NaPSS (degree of polymerization is 87) of the same molality as crosslinkage 8. The solid curve is the best least-squares fit of eq. (23). The dashed line is the best fit of eq. (21).

respectively. For the slow process C_s and τ_s are analogously defined. The spectral density of one or more fast processes is indicated by J_f.

The best fit results of eq. (23) to the experimental field dependence of $J(\omega)$ for the coupling constants and correlation times are in Table 5. In Fig. 5 eq. (23) is drawn for these parameters. J_f is supposed to be not significantly different from J(264 MHz), i.e. $J(2\omega)$ at the highest field used. It was therefore fixed at this value during the fit. At crosslinkage 2 it is not possible to get a reliable result for τ_s and C_s separately, so only $C_s^2\tau_s$ could be determined. The values of C_s and τ_s at this crosslinkage were obtained from extrapolation of the plot of C_s vs. crosslink concentration. However, from multiple pulse quadrupolar echo experiments, indications are obtained that τ_s at crosslinkage 2 may even be longer than 200 μs (J.R.C. van der Maarel, unpublished results). So the value used here of 0.5 μs is regarded as a lower bound. At crosslinkage 4 the results for the slow process are very inaccurate.

From Table 5 it is noticed that the correlation time τ_m does not show a clear dependence on crosslinkage, while τ_s decreases upon increase of crosslinkage. The coupling constants increase with increasing crosslinkage (Fig. 7). Also the frequency independent contribution to the spectral density increases upon increase of crosslinkage.

The relaxation of sodium nuclear magnetism takes place by modulation of the electrostatic interaction between the nucleus and its surroundings. As the crosslinks probably do not bear charges, they are not supposed to exert their influence on the ions by direct interaction, but by way of structural and dynamic changes relative to non-crosslinked systems which they impose on the chains.

At a crosslink two charged polymer chains are forced to "cross", i.e. to approach each other at a distance which is less than the average distance in a solution of non-crosslinked polyelectrolyte of the same concentration. This additional non-uniformity of the charge distribution in crosslinked polyelectrolyte systems may lead to increased field gradients near crosslinks. Stronger field gradient than in absence of crosslinks, combined with a less efficient averaging of these gradients due to the dynamic restrictions of the chains, may cause enhanced relaxation in crosslinked systems, compared to solutions of linear polyelectrolyte.

4.4.4 Crosslinkage dependence of coupling constants

The fast, middle and slow processes will be assumed to be independent in the sense of eq. (13), even though the coupling constants of the middle and slow processes both depend on the crosslink percentage. At this stage there is no justification for this assumption; it reflects the lack of detailed knowledge of the dynamics in the resins.

To explain the increase of the coupling constants of the middle and slow processes with increasing crosslinkage, it is assumed that the ions are distributed over two phases. One phase contains the ions in the sphere of influence of a crosslink, the other the ions outside of this sphere. This division is plausible because of the short

Table 5

Na^+ in crosslinked NaPSS. Fit results of eq. (23) to the experimental values of the spectral density of Na^+. J_f was fixed during the fit. Absolute standard deviations are between brackets

Crosslinkage	J_f (s^{-1})	τ_m (ns)	C_m (MHz)	τ_s (ns)	C_s (MHz)
2	20.8	3.9(0.5)	0.05(0.02)	538 [a]	0.009 [a]
4	32.8	1.9(0.6)	0.10(0.01)	146(100)	0.02(0.01)
8	96.5	2.9(0.5)	0.23(0.01)	34(3)	0.12(0.01)
12	182	6.1(1)	0.36(0.2)	68(12)	0.15(0.02)
16	247	3.6(0.7)	0.57(0.02)	53(2)	0.25(0.02)

[a] Only $C_s^2\tau_s$ could be determined from the field dependence of the relaxation rates. The C_s value given is the result of extrapolation of Fig. 7. Using this value τ_s was calculated.

interaction range between charges as discussed above. It is supposed that the increase of the coupling constant with increasing crosslinkage is due to the fact that at higher crosslinkage a larger fraction of the ions is in the sphere of influence of a crosslink and experiences the modulation of the chain ion interaction associated with the presence of crosslinks. In that case, C_s^2 and C_m^2 in eq. (23) should be proportional to the fraction of ions in the sphere of influence of a crosslink. Assuming, as a first approximation, an uniform distribution of the sodium ions, this fraction is

$$p_{\mathrm{Na}} = V_{\mathrm{x,Na}} n_{\mathrm{x}} c_{\mathrm{Na}} / V_{\mathrm{w}} c_{\mathrm{Na}} = V_{\mathrm{x,Na}} c_{\mathrm{x}} W / V_{\mathrm{w}}$$
$$= V_{\mathrm{x,Na}} c_{\mathrm{x}} d_{\mathrm{w}} / f_{\mathrm{w}} \qquad (24)$$

where $V_{\mathrm{x,Na}}$ is the volume of the sphere of influence of a crosslink per mole crosslinks, n_{x} is the number of moles of crosslinks in the sample, c_{Na} is the sodium ion concentration in the volume accessible to sodium ions, which volume is assumed equal to the volume accessible to water, V_{w} is the volume accessible to water and sodium ions, W is the sample weight, c_{x} is the number of moles of crosslinks per unit weight and f_{w} is the weight fraction of water. The density of the mixture of water and ions, d_{w}, is assumed to be 1000 kg/m^3. It is also assumed that the partial molar volume of water and Na^+ is the same at all sites in the gel. So C_s and C_m should be proportional to $(c_{\mathrm{x}}/f_{\mathrm{w}})^{1/2}$.,

$$C_s = (V_{\mathrm{x,Na}} d_{\mathrm{w}})^{1/2} C_{\mathrm{x,s}} (c_{\mathrm{x}}/f_{\mathrm{w}})^{1/2} \qquad (25)$$

In eq. (25), $C_{\mathrm{x,s}}$ is the contribution from a crosslink to the coupling constant of an ion in the sphere of influence of a crosslink. An analogous expression is valid for C_m. In Fig. 7 this linearity is indeed observed. The slopes for the fast and the slow process are 0.49 and 0.23 MHz kg$^{1/2}$ mol$^{-1/2}$.

To get a rough estimate of $C_{\mathrm{x,s}}$ and $C_{\mathrm{x,m}}$, it is assumed that the sphere of influence of a crosslink extends over a spherical shell concentric with a

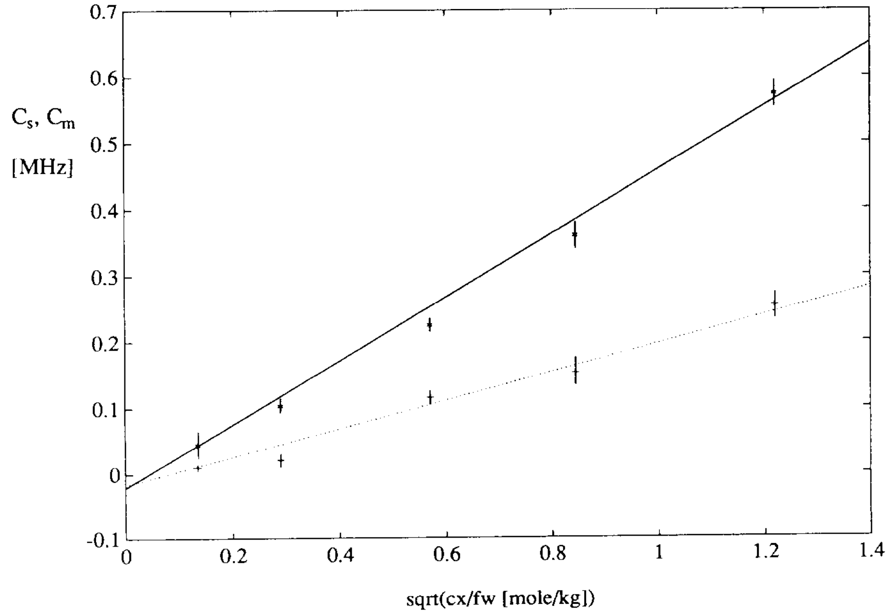

Fig. 7. Na^+ in crosslinked NaPSS systems. The coupling constants C_m and C_s of the middle and slow processes vs. the square root of $c_{\mathrm{x}}/f_{\mathrm{w}}$, where c_{x} is the crosslink concentration and f_{w} the weight fraction of water. The lines are the best linear fits. Full line: C_f, dotted line: C_s.

Table 6

Na^+ in crosslinked NaPSS. Distances diffused during correlation times τ_m and τ_s; d_x is the distance between neighbouring crosslinks (see Table 2)

Crosslinkage	d_m [Å]	d_s [Å]	d_m/d_x	d_s/d_x
2	33	300	0.8	> 9
4	18	162	0.7	6.0
8	16	53	0.8	2.8
12	17	57	1.1	3.8
16	8.0	31	0.6	2.4

crosslink with a thickness equal to one monomer length (2.5 Å) and an inner radius of 4 Å. The influenced volume per mole crosslinks is then

$$V_{x,Na} = (4\pi N_A/3)\left[(6.5\times10^{-10})^3 - (4\times10^{-10})^3\right]$$
$$= 5.3\times10^{-4}\ \mathrm{m^3/mol}$$

where l_m is the length of a monomer. Assuming the density in the sphere of influence to be 1000 kg/m^3, one obtains $C_{x,m} = 0.67$ MHz and $C_{x,s} = 0.32$ MHz. This is to be compared to the coupling constant of the relaxation due to hydration sphere water molecular dynamics of 1.5 MHz (if the correlation time is taken to be 4 ps [40]).

4.4.5 Distances diffused during the correlation times

As in non-crosslinked systems, the distances travelled during the correlation times can be calculated with eq. (22). The diffusion constants are in Table 3. The resulting distances are in Table 6.

It is seen from Table 6 that the characteristic distance of the "middle" process is about equal to the distance between neighbouring crosslinks d_x, independent of the crosslink percentage. The occurrence of a characteristic distance of this magnitude is reasonable. If each crosslink is surrounded tetrahedrally by its four neighbours, an ion has to diffuse a distance of the order of d_x to average the electric field gradient to zero.

Complete isotropy is only obtained, however, for lengths larger than the intercrosslink distance. This is concluded from the existence of a large correlation time which is reflected in the Na relaxation rates. The occurrence of a larger characteristic distance, d_s, is, of course, to be expected. The four crosslinks neighbouring a crosslink are probably not distributed perfectly symmetrically in the space around the central crosslink. It is, therefore, reasonable that an ion needs to diffuse over a few intercrosslink distances before the spherical average of the electric field gradient is reached.

From the dependence of d_s/d_x on the crosslink percentage it is seen that in terms of intercrosslink distances at low crosslink percentage lack of tetrahedral symmetry exists over longer distances than at high crosslink percentage. Two causes may be suggested for this. The intercrosslink distance is larger than the persistence length for the low crosslink percentages. This may lead to fluctuations in time in the intercrosslink distance, and therefore in the local crosslink density, which relax slowly with respect to the ionic correlation time τ_s. Also, at low crosslink concentration local deviations from a uniform distribution of crosslinks in the reaction product are relatively more important than in the case of high crosslink concentrations.

In conclusion it can be remarked that the Na relaxation results indicate two levels of "granularity" in crosslinked NaPSS. One with a characteristic size of the average neighbouring intercrosslink distance. The second characteristic length depends on the degree of crosslinking and it spans a few crosslinking distances. At the lowest crosslinkage, 2, isotropy is obtained for lengths larger than roughly 0.5 μm.

4.4.6 Results from lithium relaxation measurements

In Table 7 are the longitudinal and transverse relaxation rates of ^{7}Li ions in crosslinked LiPSS at two fields, i.e. 2.1 and 6.3 T at crosslinkages 12 and 16. At crosslinkages 8, 12 and 16 bi-exponential transverse relaxation is observed. At crosslinkage 12 and 16 the longitudinal relaxation is observed to be bi-exponential, too. Because relevant calculations can be made only when bi-exponential longitudinal relaxation is observed, only the rates for crosslinkages 12 and 16 are given. The two exponential contributions have amplitude

Table 7

Li^+ in crosslinked LiPSS. Relaxation rates at two Larmor frequencies. Relative standard deviations are about 10%. Temperature 298 K

crosslinkage	frequency (MHz)	R_{2f} (s^{-1})	R_{2s} (s^{-1})	R_{1f} (s^{-1})	R_{1s} (s^{-1})
12	34.9	6.71	2.96	1.82	0.94
	104.9	5.98	2.35	0.66	0.47
16	34.9	32.4	9.3	2.37	1.64
	104.9	48.9	6.09	1.32	0.92

ratios of 1.5 and 0.25 for transverse and longitudinal relaxation, respectively. These ratios show that the bi-exponentiality is due to quadrupolar relaxation (See eqs. 8 and 9). Quadrupolar relaxation is not the only relaxation mechanism. This is demonstrated by the fact that R_{2s} is not equal to but larger than the average of R_{1f} and R_{1s}. Therefore, an additional mono-exponential contribution exists. Coupling to water proton magnetic moments as the source of a dipolar contribution is ruled out because equal relaxation rates for Li^+ were found in resins swollen in D_2O. The lithium–lithium dipolar coupling is far too weak to be observable for physical distances of closest approach. For the same reason, coupling to polymer protons is an improbable source. Therefore, the source of this mono-exponential contribution is probably coupling of the lithium nuclear magnetic moment to paramagnetic centers, perhaps radicals, on the network. A more detailed explanation for this contribution can not be given.

This dipolar relaxation mechanism is not expected to contribute significantly to the relaxation rates reported here of other nuclei. For instance, the contribution to the transverse relaxation of Li^+ is at most 8 s^{-1} (at crosslinkage 16). Since dipolar relaxation rates are proportional to the squares of the gyromagnetic ratios involved, the contribution to sodium relaxation is 4 s^{-1} (if it is assumed that the dynamics are roughly the same), which has to be compared to quadrupole contributions of 5391 s^{-1} and 904 s^{-1}. The contributions to the longitudinal rates of deuterons and ^{17}O are even less important.

The Li^+ relaxation rates are expressed as follows:

$$\begin{aligned}
R_{1f} &= \frac{2C_m^2\tau_m}{1+(\omega\tau_m)^2} + 2J_f + R_{1,dd}(\omega) \\
R_{1s} &= \frac{2C_m^2\tau_m}{1+(2\omega\tau_m)^2} + 2J_f + R_{1,dd}(\omega) \\
R_{2f} &= C_s^2\tau_s + C_m^2\tau_m + \frac{C_m^2\tau_m}{1+(\omega\tau_m)^2} + 2J_f \\
&\quad + R_{2,dd}(\omega) \\
R_{2s} &= \frac{C_m^2\tau_m}{1+(\omega\tau_m)^2} + \frac{C_m^2\tau_m}{1+(2\omega\tau_m)^2} \\
&\quad + 2J_f + R_{2,dd}(\omega)
\end{aligned} \tag{26}$$

where $R_{1,dd}(\omega)$ and $R_{2,dd}(\omega)$ are the dipolar contributions to the longitudinal and transverse relaxation rates, respectively. The other symbols have the same meaning as in the case of sodium (eq. 23). It has been assumed, that R_{1f}, R_{1s} and R_{2s} of Li^+ are not influenced by the process that causes the large difference between R_{2f} and R_{2s}. Considering the sodium results and taking into account that the Larmor frequency of $^7Li \approx 1.5$ times the Larmor frequency of ^{23}Na this assumption is justified. It can be shown, that when both longitudinal and transverse relaxation are bi-exponential, τ_m can be calculated from the four relaxation rates. The distance diffused by a lithium ion during τ_m, d_m, is calculated with eq. (22) and the diffusion constants from Table 3. The results are 14 and 6.2 Å for crosslinkages 12 and 16, respectively. Comparison to Table 6 shows that these distances are very similar to those in crosslinked NaPSS. This is an indication of a similar structure of the resins in the lithium and sodium form on the scale of about one intercrosslink distance. The observed similarity confirms the conclusions about the network structure drawn from the sodium results.

5. Conclusions

The nuclear magnetic relaxation behaviour of $^{23}Na^+$ in crosslinked aqueous NaPSS systems (ion exchange resin) is strongly influenced by the presence of crosslinks. In crosslinked systems the Na relaxation is faster than in systems of non-crosslinked NaPSS at equal molality. The increased relaxation rate in the presence of crosslinks is ascribed to stronger field gradients near crosslinks and a less efficient averaging of this electric field gradient due to the dynamic constraints imposed on the charged chains by the crosslinks.

From the field dependence of the longitudinal and transverse relaxation rates it turns out that at least two non-extreme narrowing limit processes, not present in non-crosslinked systems, are modulating the ion nucleus chain interaction. By calculating the diffused distance during the correlation times of the processes two characteristic length scales in the crosslinked systems can be identified. One length scale nearly equals the distance between neighbouring crosslinks at all crosslink densities investigated. The other length scale extends over several intercrosslink distances and the ratio of this length and the intercrosslink distance increases with decreasing crosslink density.

The shorter length, in the order of an intercrosslink distance, is also observed in systems of crosslinked LiPSS, studied by ^{7}Li NMR.

It is concluded that in the crosslinked systems with the lowest degree of crosslinking, the ions have to diffuse the largest distances to average the electric field gradient. For the present samples the largest distance is 0.5 μm (crosslinkage 2%). Therefore, as detected with ionic quadrupolar relaxation, the crosslinked resins are more coarse grained than the equivalent polymer solutions. In the polyelectrolyte solutions the spherical average of the electric field gradient is achieved on a length scale of roughly a Kuhn length in the present high concentrated regime. Due to the presence of crosslinks, the ion exchange resins are granular on a scale of several intercrosslink distances. At high crosslink percentage a fairly regular and homogeneous internal structure is found: after diffusing over two or three intercrosslink distances ($\simeq 30$ Å at a crosslinkage of 16%) a spherical average is obtained, i.e. on a larger scale the material is homogeneous from the point of view of quadrupolar ionic relaxation. It is concluded that the nuclear relaxation of quadrupolar counter-ions yields detailed information on the internal structure of charged polymer networks.

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