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# A spin-probe study of heterogeneity in the natural rubber matrix: the effect of molecular weight, molecular weight distribution and gel phase

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The electron spin resonance (e.s.r.) spin-probe method has been applied to investigate the matrix heterogeneity of natural rubbers differing in molecular weight, molecular weight distribution and gel content. The composite temperature-dependent e.s.r. spectra above the glass transition temperature ($T_g$) were evaluated in order to obtain the population of spin probes contributing to restricted and fast motion. From the ratio of spin probes distributed in the two motionally different environments, microstructural heterogeneities of the rubber matrix are observed. It is shown that the restricted spin-probe motion above $T_g$ is predominantly determined by the amount of gel phase and structure of the gel. Chemical treatment and mastication of natural rubber, which have a complex influence on gel fraction, molecular weight and intermolecular interactions, have been considered in analysis of the temperature dependence of the e.s.r. spectra. A comparison between natural rubber and a synthetic polyisoprene confirms the contribution of the gel phase and its structure to the microstructural characteristics of rubber matrices. © 1998 Elsevier Science Ltd. All rights reserved.

**(Keywords: natural rubber; spin probe; matrix heterogeneity)**

## INTRODUCTION

Various grades of Hevea rubber have been the subject of numerous studies concerning the understanding of processing and mechanical properties. Several factors are believed to account for the properties of rubber before and after vulcanization: average molecular weight and molecular weight distribution, branching of the polymer chains, gel fraction and its size and structure[1]. The gel and soluble non-rubbers have a marked effect on the relaxation behaviour of natural rubber[2,3]. Furthermore, the structure of the gel phase and interchain interactions such as hydrogen bonding between proteins and isoprene chains have an influence on the stiffening effect[4]. However, the network structure of the gel fraction in uncured natural rubber is not yet fully understood. Because of different network structures the dynamic properties are expected to differ.

The objective of this paper is to gain a deeper insight into the role of the gel fraction and its structure on matrix inhomogeneity and molecular dynamics at temperatures above the glass transition temperature ($T_g$). For this purpose a number of natural rubber samples differing in gel fraction, molecular weight and molecular weight distribution were selected for the study. Electron spin resonance spectroscopy (e.s.r.) of nitroxyl radicals (spin probes) doped in the natural rubber matrix was used. The spin-probe technique has shown inherent advantages as an indirect microscopic tool for studying molecular dynamics and polymer morphology[5]. In contrast to conventional solubility measurements, e.s.r. is a rapid method that is sensitive to the presence of natural rubber networks formed from entanglements and interchain interactions, which are not classical crosslinks formed by chemical bonding. The spin probes dispersed in a natural rubber matrix show a composite e.s.r. spectrum above the glass transition temperature that sensitively reflects two different molecular motions as a consequence of spin probes embedded in various sites of local matrix denisty[6–8]. The slow motion component refers to the gel phase of higher matrix density with restricted segmental motions, while the motionally narrowed component is ascribed to spin probes in the matrix of lower local density or larger free volume fluctuation.

In the present study we have analysed the influence of the gel, gel structure, molecular weight and molecular weight distribution of natural rubber on the matrix heterogeneity as deduced from temperature-dependent e.s.r. spectra. The effect of chemical and physical treatment of natural rubbers on the above-mentioned parameters was also considered as a factor contributing to different network structure. A change in the e.s.r. spectra of different natural rubber and some synthetic polyisoprenes at higher temperatures has been correlated to assess the prevailing factor determining the heterogeneity of natural rubber.

## EXPERIMENTAL

### *Materials*

Samples of natural rubber (Malaysian origin; SMR) covering a wide range of molecular weight, molecular weight distribution and gel content were used (*Table 1*).

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**Table 1** Characteristics of natural rubber samples

| Sample | Type[a] | $M_n$ | $M_w$ | $M_z$ | $M_w/M_n$ | Gel (%) |
|---|---|---|---|---|---|---|
| NR-1 | I | 6600 | 29200 | 78600 | 4.39 | 1.1 |
| NR-2 | I | 7900 | 46400 | 177800 | 5.87 | 5.0 |
| NR-3 | I | 9300 | 46900 | 159300 | 5.05 | 1.1 |
| NR-4 | I | 12700 | 73200 | 258000 | 5.78 | 3.0 |
| NR-5 | II | 73600 | 139300 | 224100 | 1.89 | 4.1 |
| NR-6 | II | 98300 | 199600 | 327100 | 2.03 | 8.9 |
| NR-7 | III | 170700 | 988200 | 2078800 | 5.79 | 6.7 |
| NR-8 | IV | 157300 | 796800 | 1601200 | 5.07 | 10.4 |
| NR-9 | IV | 232100 | 996100 | 1811200 | 4.29 | 10.9 |
| NR-10 | IV | 236900 | 1060900 | 1951000 | 4.48 | 22.4 |

[a] Type I—depolymerized rubber; type II—milled rubber; type III—SMR-CV rubber; type IV—bale rubber

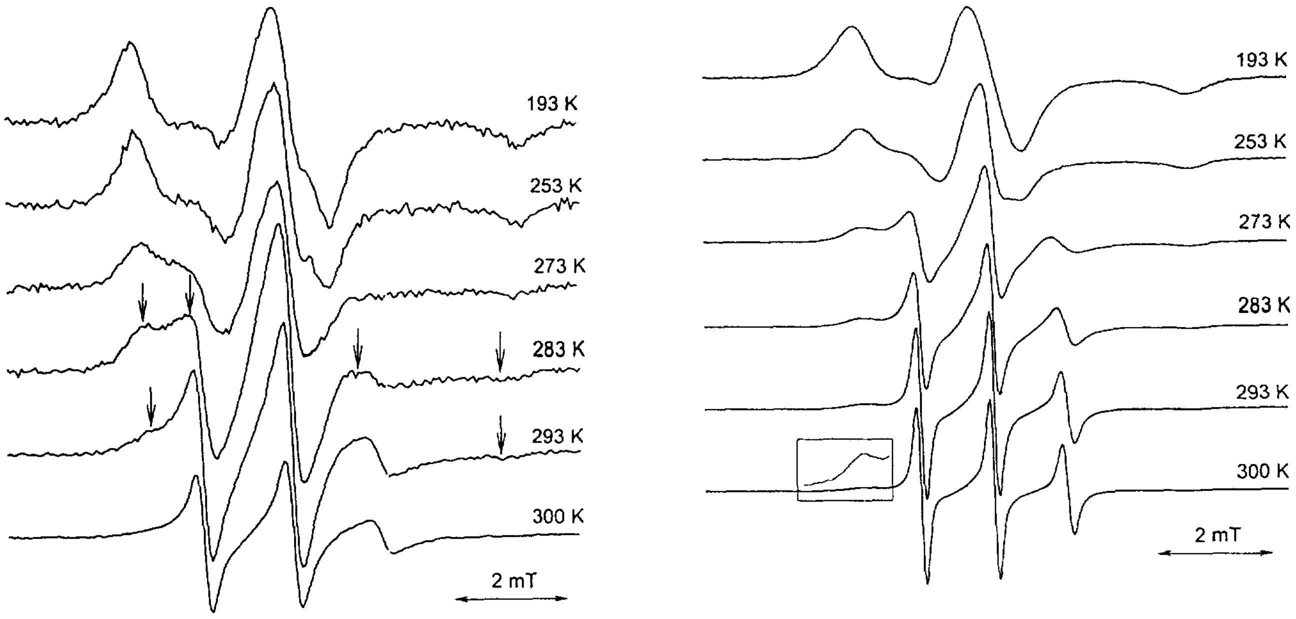

**Figure 1** E.s.r. spectra of NR-1 (left) and NR-10 (right) at indicated temperatures

The rubber samples with lower-molecular-weight (NR-1 to NR-4; $M_n < 60000$) were prepared by a variety of chemical depolymerization techniques; the intermediate rubber samples (NR-5 and NR-6) by milling; sample NR-7 (CV) is chemically treated to prevent increasing bulk viscosity with time; the high-molecular-weight samples (NR-8 to NR-10) are bale rubber grades. Typical natural rubber samples contain 99.5 mol% of *cis*-1,4-polyisoprenes and 0.5 mol% of *trans*-1,4-polyisoprenes, as determined by $^1$H nuclear magnetic resonance (n.m.r.) spectroscopy.

The samples for e.s.r. measurements were prepared by swelling rubber samples in a benzene solution of 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl (Aldrich Chemicals) as a spin probe at 308 K. After the solvent had slowly evaporated off, the samples were annealed in a vacuum at 313 K for 24 h prior to each measurement. The concentration of the spin probe is less than $10^{-4}$ M.

### *Methods*

E.s.r. spectra were recorded with a Varian E-109 spectrometer operating at 100 kHz modulation. The attenuation power and modulation amplitude were adjusted well below saturation and distortion of the spectra. The temperature was controlled by a variable temperature unit. The complex e.s.r. spectra above the glass transition were analysed as a superposition of two motionally different spectral components. This assignment is based upon following facts: (1) the separation of the outer maxima, $2A_{zz}$, remains unchanged above $T_g$; (2) an increase in microwave power shows an enhancement of the fast component, most likely due to a shorter electronic spin–lattice relaxation time[9]. Motional components were simulated with a set of spectra generated by the Schneider–Freed program[10]; isotropic Brownian rotational diffusion was assumed with the following parameters: $g_{xx} = 2.0095$; $g_{yy} = 2.0064$; $g_{zz} = 2.0027$; $A_{xx} = 0.75$ mT; $A_{yy} = 0.70$ mT; for slow motions ($\tau_R > 1.67$ ns) $A_{zz} = 3.55$ mT and for fast motions ($\tau_R < 1.25$ ns) $A_{zz} = 3.15$ mT, which gave the best fit. The rotational correlation times are calculated by spectral simulation. The fraction of each component is determined with a deviation of less than 3%.

## RESULTS AND DISCUSSION

Depolymerized samples with lower molecular weights (NR-1 to NR-4) are in a highly viscous state while the intermediate- and high-molecular-weight samples exhibit rubbery behaviour at ambient temperature. Since the spin

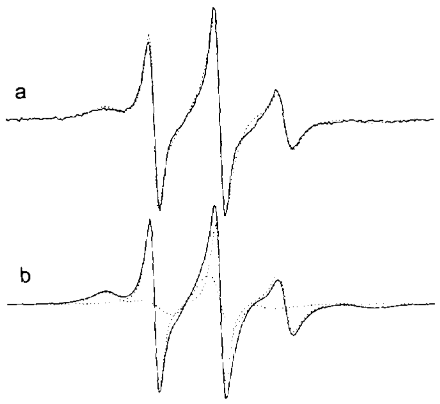

**Figure 2** (a) Experimental (——) and fitted (- - -) spectra of NR-8 at 283 K; (b) broad and narrow components (- - -) of the best fit (——) to the experimental spectrum

probe embedded in the rubber matrix is sensitive to the local density and dynamics, pertinent information is available through a comparison of the temperature-dependent e.s.r. spectra of the two sets of rubber samples.

Temperature-dependent e.s.r. spectra typical of low- and high-molecular-weight of spin-probed natural rubbers are shown in *Figure 1*. The appearance of a narrow component at about 273 K is related to $T_{5\,\mathrm{mT}}$ (the temperature at which $2A_{zz}$ becomes 5 mT owing to the onset of rapid motion of the polymer chains). $T_{5\,\mathrm{mT}}$ temperature correlates with the glass transition temperature, $T_g$, and is usually shifted to higher temperatures[5]. Since the e.s.r. spectra discussed in this paper are above $T_{5\,\mathrm{mT}}$ and above $T_g$, in further discussion we refer to the glass transition temperature only. However, the e.s.r. spectra of natural rubber above $T_{5\,\mathrm{mT}}$ appear to be a superposition of the two spectra, indicating that the spin probes are sensing different motional environments. The motionally narrowed component of the e.s.r. spectra is ascribed to spin probes located in regions undergoing main-chain segmental motions characteristic of a polymer above the glass transition temperature. The motionally broadened component corresponds to the probes embedded in sites with restricted segmental motions[9]. The dominant factor determining the presence of a slow component in the case of (uncrosslinked) natural rubber is found to be the gel phase and its structure[7,8]. Observed e.s.r. spectra with two motionally non-interconverting spin-probe populations were simulated as shown in *Figure 2*. The fraction of slow or fast spin-probe populations was determined by double integration of each spectral component. It can be seen that the fractions of the slow and fast components (*Table 2*) depend on the sample. However, the fraction of probe populations changes with temperature. This change of the spectral shape is illustrated in *Figure 1*. As the temperature is increased the intensity of the fast component (the number of spin probes attaining fast motion) is increasing at the apparent expense of the slow component. This can be expected as a consequence of a gradual increase of local free volume or segmental motion above the glass transition temperature. Irrespective of the continuous increase of the fast component, the slow component in the spectra of high-molecular-weight NR is still present well above $T_g$ and the outer maxima separation, $2A_{zz}$, of the remaining slow component does not change in the measured temperature interval. Some polyisoprene chains, being in the regions of relatively rigid chain associations due to the interchain interactions and chain entanglements, are still restricted above $T_g$[4]. Thus the spin probes located in domains with restricted segmental motion will undergo slow molecular motion (the fraction of the slow component as a function of temperature is given in *Table 2*).

In order to prove that the slow component of the e.s.r. spectra above $T_g$ reflects restricted motion of entangled and physically crosslinked chains, known as the gel phase, the extracted sol and gel phases of the NR-10 were spin-probed. The corresponding temperature-dependent e.s.r. spectra are displayed in *Figure 3*. The spectra of the gel phase (upper four spectra) between 273 K and 300 K are characteristic for restricted polymer chains below $T_g$ with a constant $2A_{zz}$ value (fraction of the superimposed narrow component is less than 2%). However, the e.s.r. spectra of the sol phase (lower four spectra) indicate a continuous increase of spin-probe motion with rise of temperature. The presence of a broad component in the isolated sol phase confirms that a certain heterogeneity in spin-probe motion is still present above $T_g$. However, the intensity of this component in the sol phase at higher temperatures disappears much faster at the expense of the narrow component, as compared with the behaviour of the extracted gel phase. A small contribution of the broad component in the sol phase could be explained either by the presence of high branching of polyisoprene chains in the sol phase[3] or by soluble microgel particles extracted in the sol phase which contain a network structure[11].

One has to consider that the slow component is related to spin probes located in domains of highly restricted

**Table 2** Fractions of e.s.r. slow components ($S_S$), rotational correlation times of slow ($\tau_{RS}$) and fast ($\tau_{RF}$) components of NR samples at various temperatures

| Sample | $T = 273$ K | | | $T = 283$ K | | | $T = 293$ K | | | $T = 300$ K | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $S_S$ (%) | $\tau_{RS}$ (ns) | $\tau_{RF}$ (ns) | $S_S$ (%) | $\tau_{RS}$ (ns) | $\tau_{RF}$ (ns) | $S_S$ (%) | $\tau_{RS}$ (ns) | $\tau_{RF}$ (ns) | $S_S$ (%) | $\tau_{RS}$ (ns) | $\tau_{RF}$ (ns) |
| NR-1 | | 10.0 | 7.2 | | 7.7 | 3.0 | | 7.2 | 2.1 | | 7.2 | 7.1 |
| NR-2 | | 8.3 | 7.2 | | 8.3 | 3.0 | | 7.2 | 2.2 | | 7.2 | 1.8 |
| NR-3 | | 8.3 | | | 7.2 | 3.0 | | 7.2 | 2.1 | | 7.2 | 1.7 |
| NR-4 | | 10.0 | 7.2 | | 8.3 | 2.6 | | 7.7 | 1.7 | | 7.7 | 1.2 |
| NR-5 | 66 | 10.0 | 2.1 | 48 | 10.0 | 1.2 | 26 | 10.0 | 0.72 | 13 | 10.0 | 0.48 |
| NR-6 | 65 | 10.0 | 2.1 | 50 | 10.7 | 1.2 | 43 | 10.0 | 0.63 | 32 | 10.0 | 0.48 |
| NR-7 | 56 | 10.7 | 2.0 | 36 | 10.0 | 1.0 | 17 | 10.0 | 0.56 | 12 | 10.0 | 0.42 |
| NR-8 | 70 | 11.0 | 1.8 | 61 | 10.0 | 1.0 | 49 | 10.0 | 0.6 | 42 | 10.0 | 0.42 |
| NR-9 | 71 | 10.0 | 1.7 | 57 | 10.0 | 1.0 | 47 | 10.0 | 0.56 | 37 | 10.0 | 0.42 |
| NR-10 | 76 | 10.0 | 1.8 | 60 | 10.0 | 1.0 | 50 | 10.2 | 0.63 | 39 | 10.0 | 0.42 |

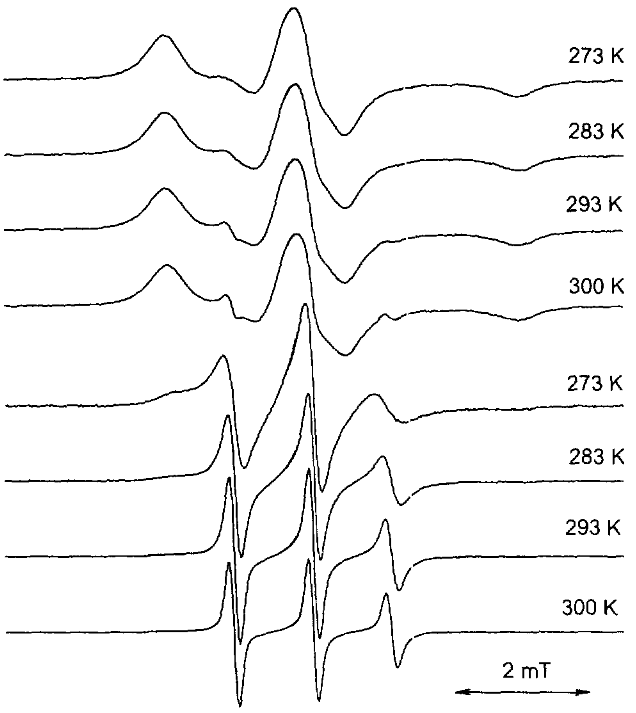

**Figure 3** E.s.r. spectra of the gel (upper four spectra) and sol (lower four spectra) fractions of NR-10 at indicated temperatures

segmental motions or higher local density. The constraints in the gel phase are imposed both by highly entangled chains and specific interchain interactions owing to the non-hydrocarbon constituents[12,13]. There is also a possibility of specific interactions with the spin probe which would contribute to its motional restriction.

At this point we should comment that the fraction of the e.s.r. broad component at a given temperature also depends on the shape and size of the probe[14]. Therefore, different rubber samples should be compared only if the same spin probe is incorporated and by following the same doping procedure. Thus the percentage of the broad component, when compared with that of the gel phase, should be considered as a relative measure[8]. *Table 2* depicts fractions of the e.s.r. slow component and the corresponding rotational correlation times, $\tau_R$, of the slow and fast components at four different temperatures above $T_g$. The population of spin probes in domains with the restricted segmental motion for both intermediate- and high-molecular-weight natural rubber exhibits a similar change with increasing temperature. For example, the two masticated samples (NR-5 and NR-6) at 273 K show similar e.s.r. spectra with 66% and 65% of broad component, respectively. Irrespective of the higher molecular weight of NR-6 and double the gel content (*Table 1*) determined from the extraction experiment, the population of spin probes having restricted motion reflects similar heterogeneity of the rubber matrix. However, as the temperature is increased, the intensity of the slow component changes much faster in the NR-5 sample and at 300 K is approximately 60% lower than in the NR-6 sample. The greater probe mobility with increasing temperature in NR-5 indicates the extra breakdown by mastication. Thus, the secondary interactions which can persist between the fragments of broken gel and which reduce chain mobility will be diminished. On the other hand, the high-molecular-weight sample NR-7 exhibits the lowest possible percentage of the slow component (56%) at 273 K, while the temperature change of the e.s.r. spectrum is similar to that for NR-5. Since NR-7 has been chemically treated to prevent the increase of bulk viscosity, it is reasonable to expect a smaller reduction of segmental mobility even at lower temperatures and, consequently, greater spin-probe motion.

On the contrary, the high-molecular-weight bale rubber samples (NR-8 to NR-10) have undergone a certain bulk viscosity increase before the e.s.r. measurements. The e.s.r. spectra of NR-10, irrespective of the much higher gel content, show similar temperature behaviour to NR-8 and NR-9. The comparison of fractions of the slow component indicates only slightly higher motional restrictions in the NR-10 at 273 K. Generally, the intensity of the slow component is decreasing more slowly with increased temperature in unmasticated rubber (type IV) than in the masticated (type II) or chemically treated rubber (type III). One should anticipate that the spin probes are dispersed in the rubber matrix and their molecular motion is determined by the local density and segmental motion of polyisoprene chains. Segmental motion in natural rubber will depend not only on the chain entanglements but also on the intermolecular interactions between proteins or between proteins and polyisoprene chains which contribute to different network structures. In the case of unmasticated rubbers (type IV) much of the non-hydrocarbon material is probably preferentially incorporated into the gel phase and therefore its effect diminishes in the sol phase (*Figure 3*). A slight difference between the samples in the e.s.r. broad component could be explained by the motional restriction imposed by several factors such as density distribution of the rubber network, different network structure and possible spin-probe interactions with non-hydrocarbon constituents in the gel phase.

The importance of gel phase in natural rubber has been discussed widely in the literature. It has been shown that the gel phase exhibits much higher strength and correspondingly lower relaxation rate than the sol phase[4]. The difference in their mechanical behaviour is attributed to the gel structure influenced by non-rubbery components such as proteins. Generally, the amount of protein materials in the gel phase is much higher than in the sol phase. The proteins apparently contribute to the specific interactions between polyisoprene chains. Furthermore, the effect of gel in natural rubber having higher molecular weight is more predominant than that of lower molecular weight[15]; it has a stiffening effect on the tensile relaxation modulus and decreases the rate of relaxation significantly.

$^1$H n.m.r. spin–spin relaxation time measurements, $T_2$, on natural rubber of different molecular weights have shown that higher molecular weight polyisoprene, $M_n \geq 30000$, exhibits a complex $T_2$ decay[16]. The short $T_2$ component is attributed to chains in a network structure with a pseudo solid-like behavior and the long $T_2$ component to non-network chains. The $T_2$ time, which relates to long-range motions, is affected by chain entanglements and crosslinks. A certain correspondence is noted between the $T_2$ *versus* temperature behaviour and mechanical properties. This reflects that both properties are sensitive to the same motional process. On the contrary, low-molecular-weight polyisoprenes ($M_n \leq 30000$) show a single exponential decay at temperatures above $T_g$. Long-range molecular motions in those samples are sufficiently high for averaging off the dipolar interactions[16].

The e.s.r. spin-probe measurements presented in this paper reveal complex spectra for natural rubber with low

**Table 3** Extrema separation of slow ($A_{zz(S)}$) and fast ($A_{zz(F)}$) e.s.r. components of low-, medium- and high-molecular-weight NR samples

| Temperature (K) | NR-3 | | NR-5 | | NR-10 | |
|---|---|---|---|---|---|---|
| | $A_{zz(S)}$ | $A_{zz(F)}$ | $A_{zz(S)}$ | $A_{zz(F)}$ | $A_{zz(S)}$ | $A_{zz(F)}$ |
| 253 | 67.5 | — | 67.2 | — | 67.7 | — |
| 273 | 65.4 | — | 67.2 | 34.9 | 67.5 | 34.5 |
| 293 | 63.5 | 35.1 | 68.1 | 32.9 | 67.2 | 32.9 |

molecular weight (*Table 1*, *Figure 1*) above $T_g$. Both the broad and motionally narrowed components of NR-1 are present between 273 K and 293 K. Such spectra are salient characteristics of the microheterogeneous environment. However, the attempt to simulate the spectra with the same parameters as in the case of intermediate- and high-molecular-weight natural rubber failed. With increasing temperature the broad component slowly disappears and the outer extrema indicate a gradual increase of spin-probe motion, in contrast to the constant slow molecular motion of spin probes located in the restricted rubbery matrix of high-molecular-weight rubber (*Table 3*). At the same time, the intensity of the fast component is increasing as expected, but the corresponding rotational correlation time shows slower spin-probe motion than the fast motion determined in the solid matrix (*Table 2*). The reason for such a behaviour of the rotational correlation time could be looked for in the depolymerization of low-molecular-weight rubber samples (NR-1 to NR-4). During this process rubber samples have experienced a substantial amount of chemical reactions to achieve their reduced molecular weights. One of the consequences is an increase of chain ends which may have non-hydrocarbon functionality and thus increase the specific interactions with spin probes having –OH groups, which reduces spin-probe motional reorientation similar to the interaction of a probe with polar polymers[17]. At elevated temperatures above $T_g$ a fraction of spin probes may still remain 'bonded' which would lead to a reduction of motional freedom and consequently to a mutual linewidth broadening, as can be seen in *Table 3*. A possible exchange broadening of the e.s.r. spectra of viscous rubbers is excluded[18] since the nitroxyl radical concentration is less than $10^{-4}$ M.

The difference between the n.m.r. $T_2$ single decay and composite e.s.r. spectra of the low-molecular-weight rubber above $T_g$ could be explained by the physical origin of the measurements. Since long-range motions reflected in $T_2$ are influenced by the presence of intermolecular couplings such as entanglements and crosslinks, their absence or very weak constraints in the present viscous gel phase of shorter chains explains a single long $T_2$[16]. On the other hand, in the e.s.r. measurement, the spin probe reflects a segmental motion which does not extend more than a few bonds along the main-chain motion[19,20]. Apparently, local small-scale motions are limited to only those few local chain segments surrounding the probe. Therefore the probe motion will depend on the fluctuation of the local free volume in its close vicinity with an increase of temperature. Complex e.s.r. spectra of low-molecular-weight natural rubber above the glass transition temperature indicate that all the spin probes are not in the same local environment or do not demonstrate the same motional freedom. Although the sample is in the highly viscous state, some probes find themselves in local denser parts—probably between the chains participating in the gel phase with insufficient free volume to permit rapid rotation characteristic for a motionally narrowed spectrum.

Simulation of these spectra with the isotropic Brownian rotational diffusion model, used successfully for medium- and high-molecular-weight rubbers, results in a deviations larger than 10%. The reason why the same model is not a suitable for motion of spin probes in a matrix with relatively short polymer chains is a certain motional anisotropy of the spin probes participating in the interaction with the chain ends[17]. Since the type of anisotropic motion is not known, the correct unique values of $\tau_R$ cannot be calculated. Although the $\tau_R$ values for low-molecular-weight rubbers (NR-1 to NR-4) are only approximate, they are slower in comparison with the high-molecular-weight rubbers irrespective whether the motion is isotropic or anisotropic.

The sensitivity of the spin probe to the morphology of polyisoprene matrices is illustrated in *Figure 4*. While both high- and low-molecular-weight natural rubber show an e.s.r. spectrum characteristic for the microheterogeneous system, synthetic polyisoprene (SKI-3) reflects a 'homogeneous' matrix above $T_g$. The absence of a broad component in the synthetic polyisoprene with $M_n$ = 142 800, molecular weight distribution of 4.82 and a gel phase of 4.4% could be explained by a specific structure and interactions in the gel phase of natural rubber. Since the molecular weight, molecular weight distribution and amount of gel phase of synthetic polyisoprene are similar to those of some of the natural rubber samples in which the motionally slowed component is always present, their absence justifies a specific network structure of natural rubber which contributes to the overall matrix heterogeneity.

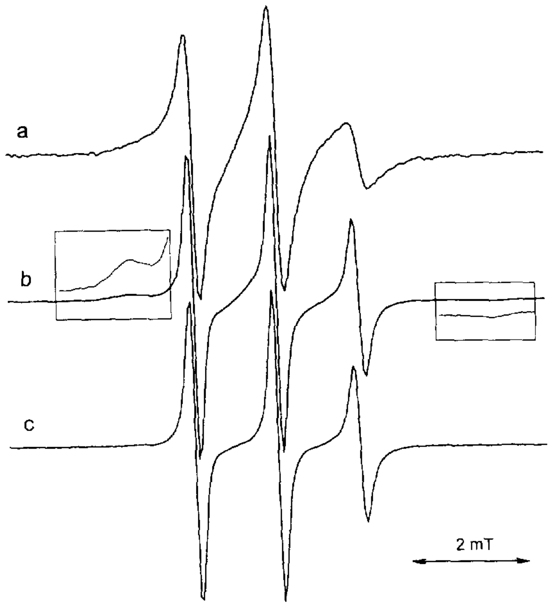

**Figure 4** E.s.r. spectra of NR-1 (a), NR-10 (b) and synthetic polyisoprene SKI-3 (c) at 300 K

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