ELSEVIER

Polymer 41 (2000) 3405–3410

polymer

Comparison of residual dipolar interactions in uncross-linked and cross-linked natural rubber by high-resolution solid-state NMR spectroscopy

V. Eulry[a], P. Tekely[a,*], F. Humbert[a], D. Canet[a], J. Marcilloux[b]

[a]*Laboratoire de Méthodologie RMN, UPRESA CNRS 7042, FU CNRS E008-INCM, Université Henri Poincaré, Nancy 1, 54506 Vandoeuvre-lès-Nancy, France*
[b]*Centre de Recherche Hutchinson, BP 31, 45120 Chalette-sur-Loing, France*

Received 1 June 1998; received in revised form 29 January 1999; accepted 9 July 1999

Abstract

It is shown that local residual dipolar broadening of protons coupled to ^{13}C is a sensitive way to observe motional constraints from networks and entanglements in cross-linked and uncross-linked rubber systems. This may be easily obtained from the indirect observation of proton spin system through ^{13}C resonance in the conditions of slow magic-angle spinning. The method has been used to visualise the changes in the amount of physical constraints induced during mechanical treatment, which precedes the vulcanisation process. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Natural rubber; Vulcanization process; Dipolar interactions

1. Introduction

It is well known that the decay of the transverse magnetisation of nuclear spins, induced by dipolar interactions, is an important source of information about the dynamics of polymer chains in a variety of physical conditions, e.g. in the melt of entangled molecules or in molecules cross-linked in a rubber network [1]. The dephasing of the transverse components of the magnetisation or equivalently the broadening of the resonant line due to the dipolar interaction with a coupling strength Δ_{ij} is governed by the function

$$M(t) \cong \left\langle \cos\left[\int \Delta_{ij} P_2(\cos\vartheta)\,\mathrm{d}t\right]\right\rangle \tag{1}$$

which involves the temporal average over relevant dynamic processes in a powder sample. $P_2(\cos\vartheta)$ stands for the quantity $(1/2)(3\cos^2\vartheta - 1)$, ϑ being the angle between the interaction vector (joining the two nuclei i and j) and the static magnetic field B_0. This function makes the NMR technique sensitive to angular anisotropic segmental motion that is spatially inhibited by chemical cross-links, topological chain constraints such as entanglements, or physical and chemical interactions acting as anchors for the rapid short-range processes. The persistence of angular correlations on the time scale set by the residual dipolar interactions and in the presence of temporary or permanent constraints such as entanglements or cross-links, leads to a non-exponential decay behaviour and the shape of the line broadening ('solid-like' effect) visualises the dynamic influence of these constraints [2].

Very recently, we have shown [3] that in vulcanised elastomers above T_g, a direct visualisation of the residual heteronuclear dipolar broadening on different functional groups, as well as their dependence on motional constraints, is readily obtainable from the indirect observation of the proton spin system, through ^{13}C resonance in the conditions of slow magic-angle spinning.

In the present work, by using this method, we compare the residual dipolar interactions in uncross-linked and cross-linked natural rubbers. It is shown that under certain circumstances, the residual dipolar interactions in uncross-linked natural rubber may be roughly as important as those observed in a highly cross-linked rubber.

2. Experimental

High-resolution solid-state experiments were carried out in a Bruker DSX 300 spectrometer using a standard CP/MAS probe and 7 mm rotor. The operating frequencies

---

* Corresponding author.

0032-3861/00/$ - see front matter © 2000 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(99)00506-6

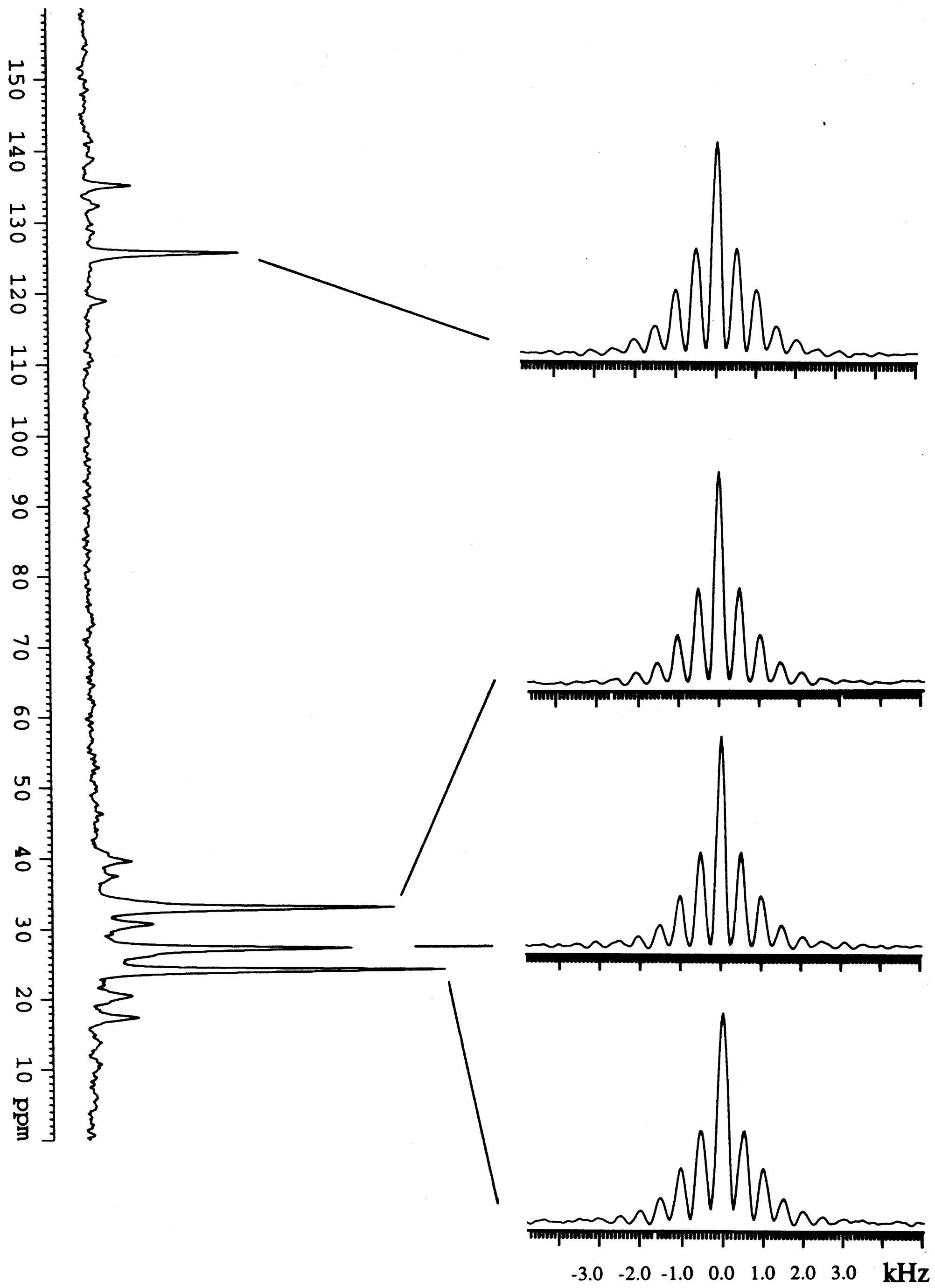

Fig. 1. Dipolar slices of different functional groups from uncross-linked natural rubber (sample B) obtained from the indirect observation of protons through ^{13}C resonance (proton on-resonance conditions for each group). Here 256 increments of 25 μs were used in t_1. CP = 5 ms, $\nu_r = 500$ Hz.

were 300.13 and 75.47 MHz for ^{1}H and ^{13}C, respectively. Liquid-like spin-echo measurements have been conducted on a homebuilt 90 MHz spectrometer.

The effect of the entanglements and of cross-links on the residual dipolar broadening and the transverse relaxation was investigated on two uncross-linked and two cross-linked natural rubber samples. The samples A and B were the natural rubbers, before and after mechanical treatment, on a two rolls mill during 5 min. at 25°C. The formulations for the cross-linked samples in units ‘phr’ or parts per hundred rubber, were: besides the natural rubber, sample C contained 1 phr S, 1 phr CBS (*N*-cyclohexyl benzothiazole 2-sulfenamide), 5 phr ZnO, 2 phr stearic acid and sample D contained 5 phr S, 5 phr CBS, 5 phr ZnO, 2 phr stearic acid. The average molecular mass between cross-links (M_c) determined by the swelling measurements, were 11 000 and 3100 for samples C and D, respectively.

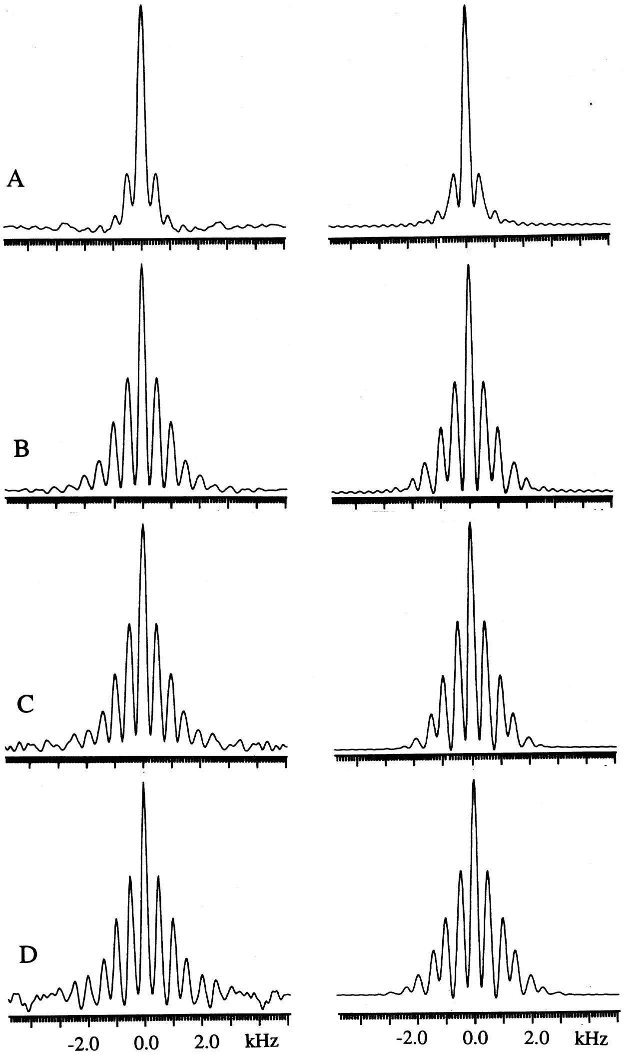

Fig. 2. Experimental (left) and calculated (right) dipolar spectra for CH groups in uncross-linked (A,B) and cross-linked (C,D) samples of natural rubber. Here CP = 5 ms, $\nu_r = 500$ Hz. Each calculated spectrum is a superposition of two components with following residual dipolar couplings and relative populations: (A) 0.1 kHz (80%), 1.5 kHz (20%); (B) 0.1 kHz (50%), 2.15 kHz (50%); (C) 0.2 kHz (45%), 2.0 kHz (55%); (D) 0.75 kHz (45%), 2.5 kHz (55%). For other simulation details see text.

3. Residual dipolar interactions as revealed by ^{13}C-detected proton spectra

It is now well established that the cross-polarisation technique offers the possibility of investigating one nucleus indirectly by means of the other nucleus involved in the polarisation transfer. In the conditions of high-resolution solid-state NMR spectroscopy, this permits to take advantage of both high sensitivity and large chemical shift dispersion offered by protons and rare spins, respectively.

We have shown previously [4,5] that the indirect observation of protons through ^{13}C resonance can be exploited so as to provide dipolar local field information when dealing with organic solids in which heteronuclear dipolar interactions dominate homonuclear dipolar interactions. This is a common situation for protonated carbons in many amorphous polymer systems. In such solids, rapid magic-angle spinning and short periods of polarisation transfer restrict the effective number of spins to the nearest neighbours that govern the dipolar local field, and this provides local structural and dynamic information. The success of this simple experiment relies on the effective isolation of the protons directly bonded to the ^{13}C nucleus [5].

The experiment starts with a 90° pulse applied to protons, and continues with a variable t_1 period during which proton magnetisation evolves essentially under effect of dipolar interactions. At the end of this period, the rare spin magnetisation is created by a cross-polarisation procedure, followed by a detection period t_2 in the presence of proton decoupling. As a consequence, the rare spin signal will be amplitude-modulated by the proton magnetisation remaining at the end of the t_1 period [6,7]. The double Fourier transformation of the data matrix leads to the 2D spectrum with the proton line-shapes displayed in the ν_1 dimension and thus separated according to the chemical shift of the rare spins in the ν_2 dimension [8,9]. For short periods of polarisation transfer and/or under conditions of slow proton spin diffusion, the local dipolar interactions are unravelled in the ν_1 cross-sections [3–5]. These dipolar slices not only provide structural information on internuclear distances but their collapse may also be used to detect the effect of molecular motions. Similar information can be gained from the ^{13}C-edited ^{1}H magnetisation relaxation [6,10,11].

For elastomers well above T_g, the high molecular mobility reduces dramatically the dipolar interactions and proton flip-flops are much less effective than in amorphous polymers in the glassy state. This and the other above mentioned factors lead to greatly diminished role of proton spin-diffusion (which manifests only on the time scale higher than tens of milliseconds) and make the indirect observation of protons via cross-polarisation ^{13}C spectroscopy an attractive tool for the selective visualisation of residual heteronuclear dipolar interactions in cross-linked network of elastomers. We wish to point out that due to the very low efficiency of cross-polarisation transfer in these highly mobile systems (which manifests itself by a low intensity of cross-polarisation spectra as compared with a direct (single pulse) spectra), we will access preferentially the most rigid fragments of networks and so the most mobile fragments will not be observed.

Fig. 1 presents dipolar spectra of different functional groups in uncross-linked, natural rubber (sample B). As we have shown previously [3], in the conditions of this experiment, the dipolar spectra are governed by the heteronuclear dipolar interactions and this leads to relatively narrow, well-separated dipolar spinning sidebands. We have previously demonstrated, that proton spin diffusion is not responsible for the uniform spinning sideband families on the different functional groups in natural rubbers. On the contrary, the differences in the residual proton–proton

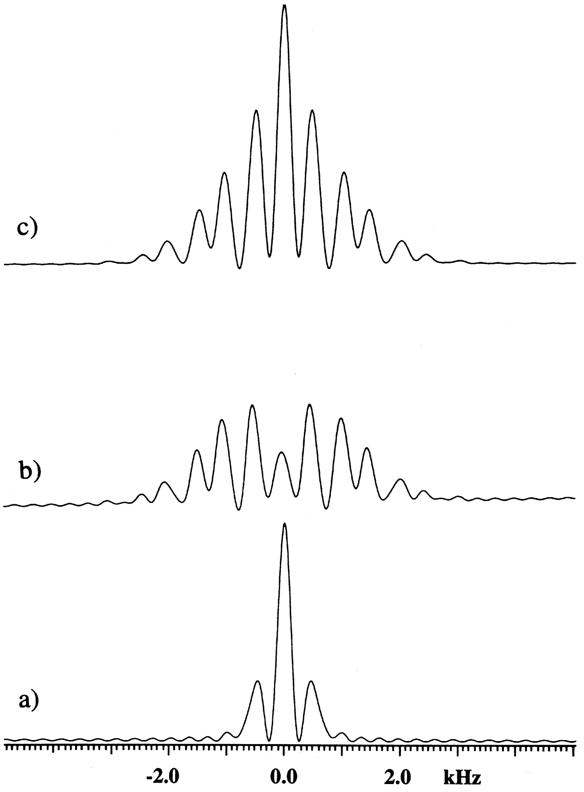

Fig. 3. Calculated dipolar spectrum for sample D (c) and its two components (a,b).

dipolar interactions on different functional groups may be observed when applying the carbon decoupling irradiation during the evolution period t_1. The fact that very similar intensity envelope of spinning sidebands in Fig. 1 is observed in the dipolar dimension on each functional group means also that the effective $^1H–^{13}C$ vectors of different chain fragments are affected, motionally, in the same manner on the time scale of this experiment.

Fig. 2 compares the experimental and simulated dipolar cross-sections for CH groups from uncross-linked natural rubber before (A) and after (B) mechanical treatment, and for two cross-linked samples with different density of cross-links (C,D). The simulated spectra were calculated from the evolution of the motional averaged dipolar interaction of an isolated CH group during t_1 under MAS conditions and by taking into account the effective CP time used to detect the dipolar evolution [5]. This is justified by our previous observations [3] that the dipolar cross-sections reveal effectively the residual local dipolar interaction felt by a methine proton bonded to a ^{13}C. However, no satisfactory fit could be obtained, when using a single spinning sideband family, and to obtain a good agreement between the experimental and simulated cross-sections, the presence of an additional single central line of unequal weight or the superposition of two spinning sideband families with different residual dipolar interactions, had to be assumed for samples A–C and D, respectively. The relative proportions of these two families are given in the legend to Fig. 2.

Here, except the central line, the relative ratio of dipolar spinning sideband intensities is governed by the local residual dipolar interactions leading to the inhomogeneous broadening which forms 'solid-like' contribution of the decaying proton magnetisation. This permits to separate effectively Zeeman interactions such as those associated with chemical shifts or field inhomogeneity, as well as the relaxation effects arising from rapid (pre-averaging) fluctuations of the dipolar interactions responsible for the

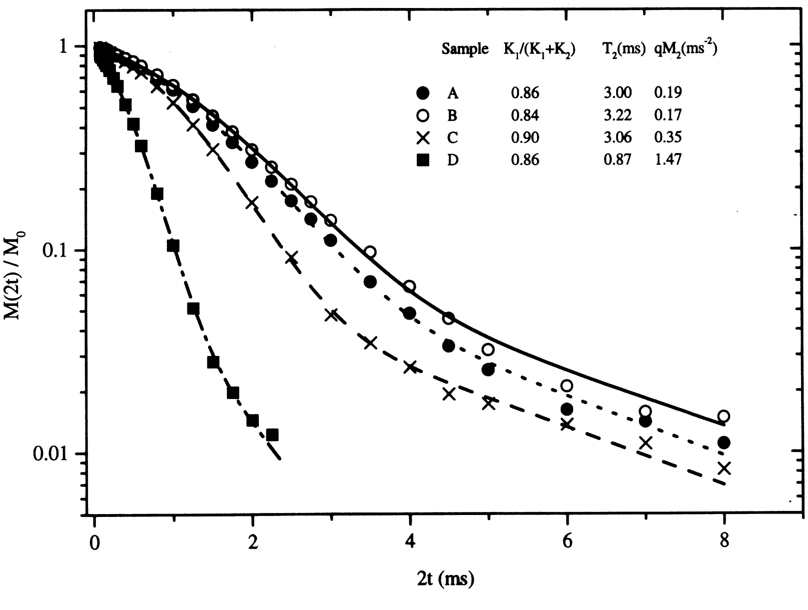

Fig. 4. ^1H Hahn spin-echo decay at 90 MHz for the samples under investigation: (●, ○) natural rubber before and after mechanical treatment (samples A and B, respectively); (×, ■) cross-linked rubber C and D, respectively. The echo time $2t$ was varied between 80 μs and 8 ms. The 90 pulse length was 2.6 μs. The solid lines are the fits to Eq. (2).

homogeneous broadening. For this purpose, other NMR techniques combining the ‘solid-echo’ pulse trains, the free induction decay ‘Hahn-echo’ and a single pulse sequences [12,13] may be useful. However, by using indirect observation of protons via ^{13}C resonance, we benefit from the selective observation of individual functional groups.

Fig. 3 shows the calculated spectrum for sample D and its two components with two different residual dipolar interactions. The fact that the presence of at least two components, which lead to different dipolar spinning sideband families, had to be assumed for highly cross-linked sample D suggests, that they may belong to two different parts of rubber chains, located in the inner and outer part of chain fragments constrained by entanglement and cross-link points. For uncross-linked samples A, B and for sample C with a relatively low density of cross-links, the more mobile parts of chains may contribute themselves to the central single line component. Obviously, due to the complex structural and dynamic nature of topological and chemical constraints, the assumption of only two components belonging to highly and less mobile fragments located far and near cross-links and entanglements, respectively, is certainly oversimplified and should rather be considered as an indication for a distribution of correlation times of polymer chains.

The changes in the homogeneous broadening, resulting from relaxation effects, and proton–proton residual dipolar interactions, which may be partially responsible for the presence of central line in the dipolar spectra, can be visualised by the magnetisation decay obtained as the envelope of echoes in a liquid-like standard spin-echo experiment. In Fig. 4 the proton decays obtained by using a spin-echo pulse sequence are plotted for static samples under investigation. In this experiment, the smallest echo time was 80 μs and this leads to the lost of the initial part of decay governed by the residual proton–proton dipolar coupling. However, no magnetisation decay in Fig. 4 can be fitted by a single exponential function. For this we have applied the relaxation function successfully exploited in rubber materials [14,15]. This function in its simplest form takes the form [15]:

$$M(t) = K_1 \exp\left(\frac{-t}{T_2} - \frac{-qM_2t^2}{2}\right) + K_2 \exp\left(\frac{-t}{T_2}\right) \qquad (2)$$

where K_1 and K_2 are the fractions of a Gauss-like relaxation function and a pure exponential function, respectively, qM_2 represents the mean residual part of the second moment of the dipolar interactions in relation to the physical and chemical constraints, and T_2 is the transverse relaxation time related to the fast local motion. By using this function, the experimental data in Fig. 4 are well fitted in each case. No significant difference may be observed when comparing the decay curves and the relevant parameters for both uncross-linked samples. On the contrary, important differences appear for both cross-linked networks. This proves that in the conditions of our measurements, the dominant effect in the transverse relaxation decay is due to permanent motional restrictions such as cross-links and that the physical entanglements have a lifetime smaller than the time of the observed magnetisation decay.

Finally, we wish to comment on the origin of a rather unexpected increase of the residual dipolar broadening observed for sample B as compared to sample A. This must result from some physical modifications induced during mechanical treatment. Two possible explanations may be evoked. First, this may be due to a higher amount of topological constraints such as entanglements. Motional changes may be also induced by morphological changes of the samples, i.e. formation of regions with different densities. In fact, it has been demonstrated [16] that the mechanical properties (hardness, elongation at break, modulus, etc.) and the cross-link density are affected by the moulding method used during the manufacture of the rubber piece. In our case, we are dealing with mixing, not moulding. However, the use of two rotating rolls leads to shear and compression gradients responsible for the orientation of polymer chains [17]. In viscoelastic materials, the viscous elements will be responsible for maintaining the state at which the process of deformation ceased [18]. Consequently, it is suggested that the mechanical treatment which precedes the vulcanisation influences the amount of physical constraints which can modify the mechanical properties of cross-linked rubber. In fact, the physical properties of a cross-linked natural rubber depend not only on the density of cross-linking (M_c), initial molecular mass and additives, but also on the morphology and molecular arrangement of chains, especially during the cross-linking process. Consequently, different mechanical properties may be found with the same cross-link density and additives due to the changes in the above mentioned physical parameters.

4. Conclusions

Local residual dipolar broadening of protons coupled to ^{13}C, is a sensitive way to observe motional constraints from networks and entanglements in cross-linked and uncross-linked rubber systems. We have shown that this may be easily obtained from the indirect observation of proton spin system through ^{13}C resonance in the conditions of slow magic-angle spinning. It has been demonstrated that the mechanical treatment which precedes the vulcanisation of natural rubber results in greater residual dipolar couplings. This may be due to the higher amount of topological constraints and/or regions with a higher density induced during mechanical process.

Acknowledgements

The authors thank Prof. D.E. Demco for helpful discussions.

References

[1] Cohen-Addad JP. Prog NMR Spectrosc 1993;25:1 and references therein.
[2] Brereton MG. Macromolecules 1990;23:1119 and references therein.
[3] Malveau C, Tekely P, Canet D. Solid State NMR 1997;7:271.
[4] Tekely P, Palmas P, Mutzenhardt P. Macromolecules 1993;26:7363.
[5] Palmas P, Tekely P, Canet D. Solid State NMR 1995;4:105.
[6] Tekely P, Nicole D, Brondeau J, Delpuech JJ. J Phys Chem 1986;90:5608.
[7] Tekely P, Canet D, Delpuech JJ. Mol Phys 1989;67:81.
[8] Zumbulyadis N. Phys Rev B 1986;33:6495.
[9] Schmidt-Rohr K, Clauss J, Spiess HW. Macromolecules 1993;25:3273.
[10] Fülber C, Demco DE, Weintraub O, Blümich B. Macromol Chem Phys 1996;197:581.
[11] Sotta P, Fülber C, Demco DE, Blümich B, Spiess HW. Macromolecules 1996;29:6222.
[12] Cohen-Addad JP. J Chem Phys 1975;63:4880.
[13] Callaghan PT, Samulski ET. Macromolecules 1997;30:113.
[14] Simon G, Baumann K, Gronski W. Macromolecules 1992;25:3624.
[15] Kuhn W, Barth P, Hafner S, Simon G, Schneider H. Macromolecules 1994;27:5773.
[16] Dinzburg BN, Bond R. Inter Polym Processing VI 1991;1:3.
[17] Klostermann R, von Bose S, Mewes D. Adv Polym Technol 1994;3:187.
[18] Treloar LRG. The physics of rubber elasticity, Oxford: Claredon Press, 1975.