

Nuclear magnetic resonance investigation of the microdynamics of vinyl chloride–vinylidene chloride copolymers

Heike Menge* and Horst Schneider

Martin-Luther-Universität Halle, Fachbereich Physik, FG Spektroskopie,
D-06099 Halle/Saale, Germany

(Received 3 March 1992; revised 11 February 1993)

Carbon-13 relaxation measurements were performed on vinyl chloride–vinylidene chloride copolymers in solution. The variations of T_1 and nuclear Overhauser enhancement were analysed over a wide temperature range including T_1 minimum. The data were analysed in terms of several motional models, including both correlation time distribution and diffusional models. Only those models that involve motion on two well separated time scales were successful. The slower motion corresponds to a damped diffusion along the chain; the faster motions are librations of limited extent about the rest position.

(Keywords: polymer physics; nuclear magnetic resonance; poly(vinyl chloride-co-vinylidene chloride); local molecular motion)

INTRODUCTION

The local dynamics of polymers in solution have been studied using a number of spectroscopic techniques. Among these techniques, nuclear magnetic resonance (n.m.r.) has proved to be a very powerful tool, because its selectivity allows a detailed analysis of the motions of the different components of the polymer chain. Many models of local polymer dynamics have been proposed^{1,2} and used successfully to investigate a number of different polymers in solution as well as in bulk^{3–5}. It therefore seemed of interest to examine whether some of these autocorrelation functions can also be used to represent n.m.r. data on polymers having a different chemical structure and mobility within the chain, e.g. copolymers.

PROCEDURE AND METHODS

N.m.r. measurements

Experiments were performed at ¹³C Larmor frequencies of 22.635, 50.3 and 20.13 MHz using Bruker HX-90 R, WP 200 and AC-80 spectrometers respectively, and ¹H- T_1 at 90 MHz. Selective relaxation times T_1 were determined by the inversion recovery technique (in the presence of proton decoupling) and selective nuclear Overhauser enhancement (NOE) factors by comparison with the peak areas in a broadband decoupled spectrum and a spectrum measured with inverse gated techniques.

The investigation was carried out on block copolymer solutions of vinyl chloride (VC) and vinylidene chloride (VDC) with different copolymer composition (4 and 40 mol% VDC, $M_w = 65\,000\text{ g mol}^{-1}$) (Figure 1, Table I). A detailed description of microstructure and composition is given in the literature^{6–8}. All samples were dissolved in deuterated tetrahydrofuran (THF-d₈). The polymer

concentrations of these solutions were 20% weight/volume. T_1 and NOE experiments were performed with varying temperatures (330–180 K). T_1 values were found to be accurate within 10% and NOEs within 15–20%.

Relaxation equation

The dominant spin relaxation mechanism in these experiments is a dipole–dipole interaction between the backbone ¹³C and its bonded proton(s)⁹. Under these conditions the longitudinal relaxation time T_1 and the NOE factor η may be expressed^{10–13} in terms of the spectral density function $J(\omega)$:

$$\frac{1}{T_{1c}} = \frac{1}{2} M_{2\text{CH}} [J(\omega_{\text{H}} - \omega_{\text{C}}) + 3J(\omega_{\text{C}}) + 6J(\omega_{\text{H}} + \omega_{\text{C}})]$$
$$M_{2\text{CH}} = \frac{1}{5} \gamma_{\text{H}}^2 \gamma_{\text{C}}^2 \hbar^2 \left(\frac{\mu_0}{4\pi} \right)^2 N_{\text{H}} \frac{1}{r_{\text{CH}}^6}$$
$$\eta = 3.976 \left[\frac{6J(\omega_{\text{H}} + \omega_{\text{C}}) - J(\omega_{\text{H}} - \omega_{\text{C}})}{J(\omega_{\text{H}} - \omega_{\text{C}}) + 3J(\omega_{\text{C}}) + 6J(\omega_{\text{H}} + \omega_{\text{C}})} \right]$$

where $M_{2\text{CH}}$ is the second moment, N_{H} is the number of protons and $r_{\text{CH}} = 0.109\text{ nm}$.

MODELS

Detailed analysis of ¹³C n.m.r. in poly(vinyl methyl ether), poly(propylene oxide) and some other polymers has shown that the well known autocorrelation functions derived from models of conformational jumps in polymer chains cannot account for the particularly high value of a minimum of ¹³C spin-lattice relaxation time T_1 observed as a function of temperature. Such behaviour indicates that, in addition to the conformational jumps which induce a damped orientation diffusion along the chain, there is also a fast process. This fast process was assigned

* To whom correspondence should be addressed

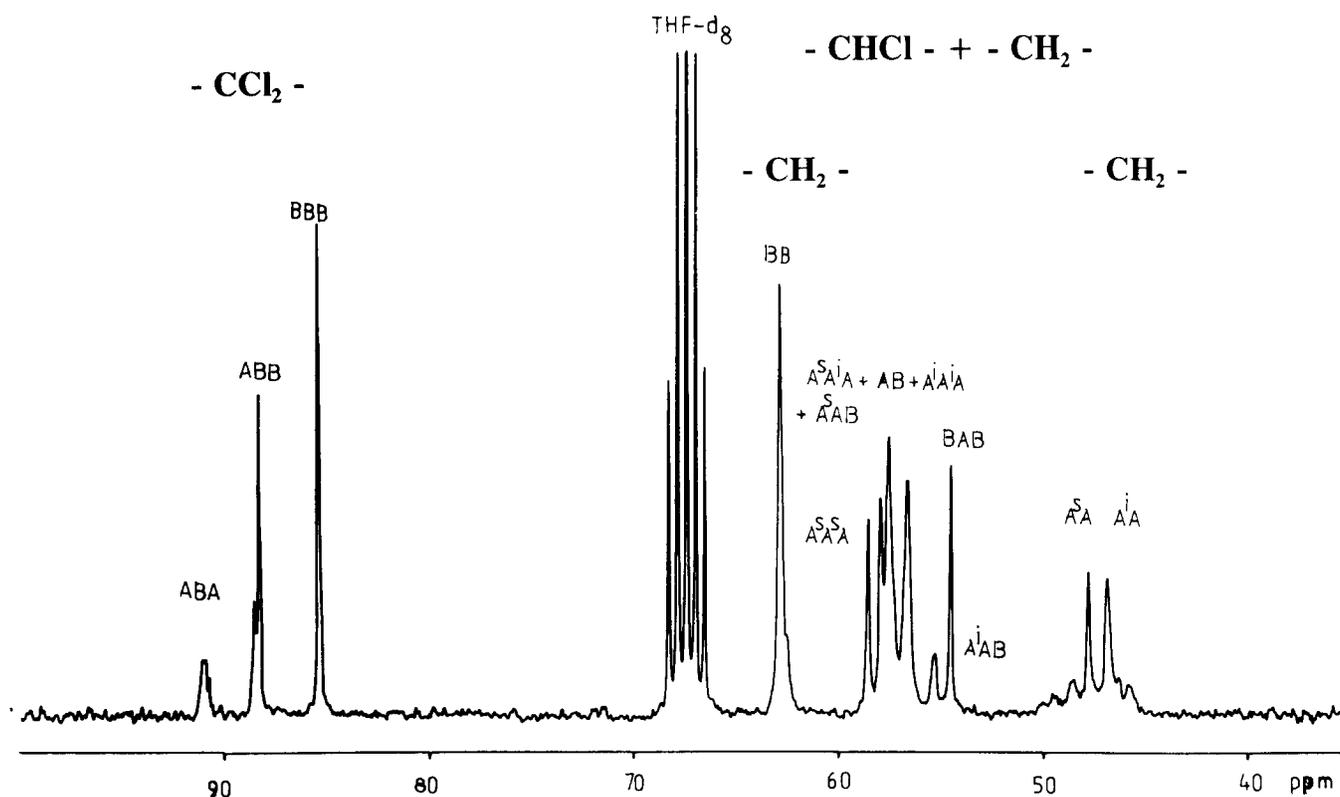


Figure 1 ¹³C n.m.r. spectra of P(VC-VDC) in THF-d₈, P(VDC)=0.4: A, vinyl chloride (VC); B, vinylidene chloride (VDC)

Table 1 Microstructure of P(VC-VDC) copolymers

Sample	VDC content, P(VDC) (mol%)	Sequence length (experimental)		Product of reactivity ratios, $r_{VC}r_{VDC}$	Syndiotactic fraction, P(s) (mol%)
		l_{VC}	l_{VDC}		
1	4	33.2	1.3	10.0	58
2	40	4.2	2.9	6.2	46

to a limited but significant libration of the internuclear vectors about their rest position³⁻⁵.

The salient features of the models used in this paper are summarized here.

For the fit of the experimental data on one side, the symmetrical distribution of correlation times $\rho(s)$ by Fuoss-Kirkwood (FK)¹⁴ has been chosen:

$$s = \frac{\tau}{\tau_c}$$

$$\rho(s) = \frac{2\alpha \cos\left(\alpha \frac{\pi}{2}\right) \cosh(\alpha s)}{\pi \cos(\alpha\pi) + \cosh(2\alpha s)}$$

On the other side, motional models for chain dynamics based on conformational changes are used. They are characterized by a correlation time τ_1 , which propagates along the chain according to a damped diffusional process. The damping is described by a correlation time τ_2 . In the following discussion we will use either the Hall-Helfand (HH)¹⁵, the Valeur-Jarry-Geny-Monnerie (VJGM)¹⁶ or the Dejean-Lauprêtre-Monnerie (DLM)^{3,4} expression of the autocorrelation function $G(t)$ to describe the local polymer chain dynamics (see Table 2).

Table 2 Expression of the HH, VJGM and DLM orientation autocorrelation functions

HH	$G(t) = \exp(-t/\tau_2) \exp(-t/\tau_1) I_0(t/\tau_1)$
VJGM	$G(t) = \exp(-t/\tau_2) \exp(-t/\tau_1) \operatorname{erfc}(t/\tau_1)$
DLM	$G(t) = (1-a) \exp(-t/\tau_2) \exp(-t/\tau_1) I_0(t/\tau_1) + a \exp(-t/\tau_0)$ with $(1-a) = [(\cos \Theta)/2(1 + \cos \Theta)]^2$

The only parameter introduced in the HH expression is the ratio τ_2/τ_1 . The corresponding spectrum of time constants¹⁷ $F(\tau)$

$$F(\tau) d\tau = \frac{d\tau}{\pi \tau^2 [(\tau_2^{-1} - \tau^{-1})(\tau^{-1} - \tau_2^{-1} - 2\tau_2^{-1})]^{1/2}}$$

(if $(1/\tau_2 + 2/\tau_1)^{-1} \leq \tau \leq \tau_2$ and $F(\tau) = 0$ elsewhere) diverges at $\tau = \tau_2$ and $\tau = (1/\tau_2 + 2/\tau_1)^{-1}$.

Large values of τ_2/τ_1 provide a broad distribution of motional time constants $F(\tau)$ and a high T_1 minimum, but the HH $F(\tau)$ has sharp cutoffs at long and short τ . Allowing $\tau_1 \rightarrow \infty$ enables the recovery of the single exponential correlation function CF(t). VJGM CF(t) is similar to HH CF(t).

Dejean de la Batie *et al.*^{3,4} have combined the HH expression and an exponential function, producing the

DLM expression. This flexible function introduces three parameters: the ratios τ_2/τ_1 and τ_1/τ_0 and the relative weight a of the fast anisotropic motion τ_0 (inside a cone of half angle Θ).

RESULTS

Spin-lattice relaxation data were analysed by using several spectral density functions. The temperature dependence is given by an Arrhenius law:

$$\tau_i = \tau_i^\infty \exp\left(\frac{E_a}{RT}\right)$$

where τ_i represents either τ_1 (in the case of diffusional models) or τ (in the case of FK distribution).

All temperature-dependent T_1 s and NOEs measured at all available Larmor frequencies were fitted simultaneously utilizing a least-square algorithm. Some of the parameters E_a , a or α , τ_i^∞ depending on $J(\omega)$, τ_1/τ_0 , τ_2/τ_1 were partly introduced into the fitting routine; all other parameters were varied 'manually'. Thus the program never fitted more than three parameters at once.

Because of the resolution of the n.m.r. spectra, we will discuss only the methylene group within the VC-VC (AA) and VDC-VDC (BB) diad of the copolymer⁶⁻⁸.

Methylene T_1

The values of the experimental T_1 minima are compared with those calculated from the different models in Table 3. It can be seen that the experimental values are always at least 30% higher than the calculated ones in the case of the HH expression. The same results have been found by other authors^{3,4,17} for many other polymers. This large discrepancy cannot be accounted for by incorrect internuclear distance.

The VJGM model gives acceptable results at room temperature¹⁸⁻²⁰, but is not valid near the T_1 minimum. Even with the simultaneous fitting of all available temperature-dependent experimental data, a great variation in fitting parameters produces similar curves without describing the experimental data correctly. For this reason there will be no further discussion of the VJGM model.

The FK distribution was able to give an initial approximation only. It is possible to predict raised T_1 minima in accordance with the experiment. However, this requires broadening the distribution so much that T_1 always depends strongly on the magnetic field strength B_0 . The best compromise is shown in Figures 2 and 3 with the values from Table 4. The modification of the FK distribution by Schneider allows better agreement with the experimental data if there is an asymmetrical distribution^{21,22}.

The best overall fit to the methylene T_1 of both

Table 3 Comparison of experimental and calculated T_1 values (ms) at the minimum and 22.635 MHz

	4 mol% VDC, VC-CH ₂	40 mol% VDC	
		VC-CH ₂	VDC-CH ₂
Exp.	30.5	24.5	32.5
FK	30	24.5	27.5
HH	23	25	28
DLM	30	24.5	32.5

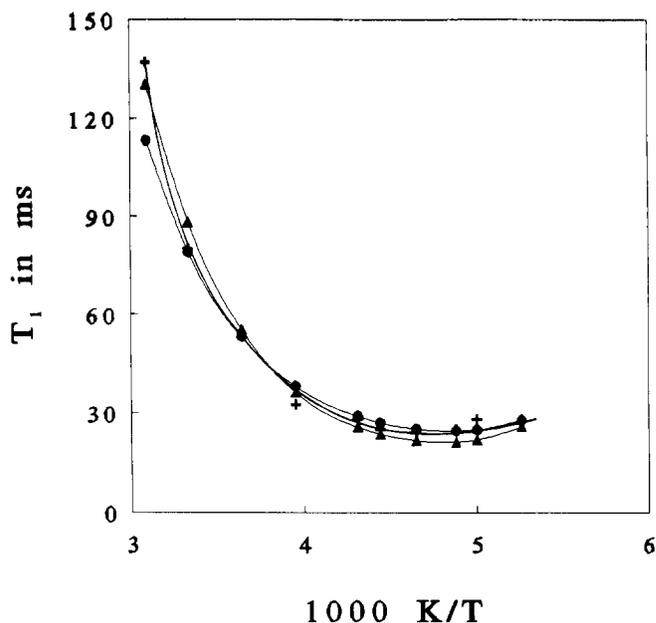


Figure 2 Best fit to spin-lattice relaxation data from methylene AA diad of P(VC-VDC) in THF-d₈ solution (40 mol% VDC) at $f(^{13}\text{C})=22.635$ MHz; parameters from Table 4. +, Experimental data; ▲, Fuoss-Kirkwood distribution; ●, DLM model

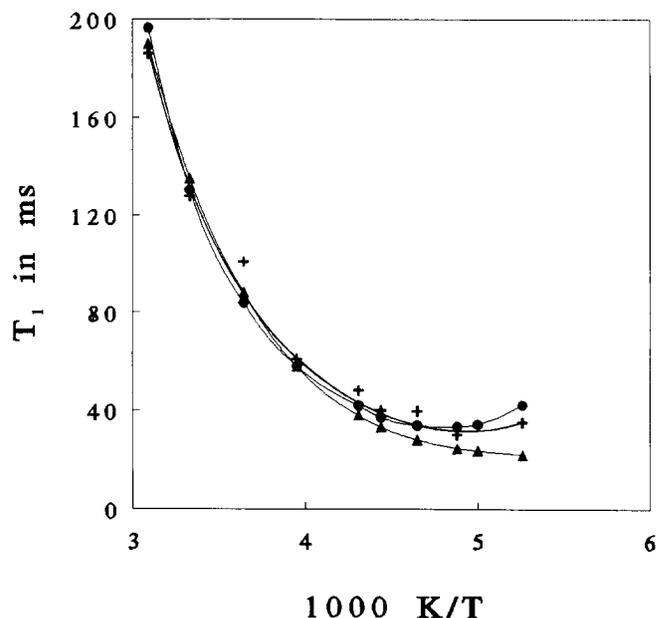


Figure 3 Best fit to spin-lattice relaxation data from methylene BB diad of P(VC-VDC) in THF-d₈ solution (40 mol% VDC) at $f(^{13}\text{C})=22.635$ MHz; parameters from Table 4. +, Experimental data; ▲, Fuoss-Kirkwood distribution; ●, DLM model

co-components (VC and VDC) is produced by the DLM model. In order to fit the DLM function over the whole temperature range under study, the parameter a has been assumed to be independent and equal to the value determined from the minimum. As observed by Dejean de la Batie *et al.*^{3,4}, the relative size of the angle Θ (and a respectively) can be anticipated from the steric hindrance at the sites considered: the larger the steric hindrance, the smaller the value of Θ ^{3,4}.

For the P(VC-VDC) copolymer with 40 mol% VDC this model predicts $\Theta \approx 16 \pm 3^\circ$ for the methylene group within the VC-VC diad and $\Theta \approx 29 \pm 3^\circ$ for those within the VDC-VDC diad. Because of the correlation of Θ to steric hindrance, the VDC methylene group is the more

Table 4 Best fit parameters: A, VC; B, VDC

VDC content (mol%)	Model	N.m.r. signal	a	τ_2/τ_1	τ_1/τ_0	τ_1^∞ (ps)	E_a (kJ mol ⁻¹)	τ^∞ (ps)	α
4	FK	CH ₂ (AA)	—	—	—	—	17.25	0.103	0.50
40		CH ₂ (AA)	—	—	—	—	18.7	0.097	0.75
40		CH ₂ (BB)	—	—	—	—	16.9	0.1	0.72
4	DLM	CH ₂ (AA)	0.21	40	300	0.180	16.4	—	—
40		CH ₂ (AA)	0.11	20	300	0.087	18.6	—	—
40		CH ₂ (BB)	0.33	50	400	0.011	22.3	—	—

mobile co-component of the copolymer P(VC-VDC). For the methylene group within the VC-VC diad of the other sample (4 mol% VDC) the calculated value a ($a=0.21$) corresponds to $\Theta \approx 23 \pm 3^\circ$. This means a small change in the shape of the potential wall and, following the argument of Dejean de la Batie *et al.*^{3,4}, a greater mobility of this group in the sample with the lower VDC content. In the same way as the half angle Θ , the correlation times τ_1 (DLM) and τ (FK), respectively, are changing a little. Thus at 300 K (for example) the DLM correlation time τ_1 of the methylene group within the VC-VC diad increases from 130 to 151 ps (± 10 ps) with increasing VDC content of the copolymer (the FK correlation time τ shows the same behaviour: from 104 to 175 ps). For the CH₂ group within the VDC-VDC diad of the 40 mol% VDC sample at $T=300$ K a τ_1 of 85 ps was calculated. Therefore not only a smaller τ_1 , but also a larger Θ indicate a higher segmental mobility.

An explanation of this somewhat unexpected behaviour (a lower segmental mobility of the VC-CH₂ group with increasing VDC content, the more mobile co-component) could be given by dielectric investigation^{23,24}. Dielectric investigation of VC-VDC copolymers in solution (THF) performed by time domain spectroscopy shows some small changes in the intensity $\Delta\epsilon$ (and thus also in the resultant dipole moment μ). (1) $\Delta\epsilon$ of the copolymer is smaller than that of the pure PVC (less dipoles) because the large Cl atoms attached symmetrically to the same carbon within the VDC unit partially compensate each other. (2) For the copolymers it was found that the smaller the syndiotactic mole fraction and also the reactivity ratio $r_{VC}r_{VDC}$, the larger the $\Delta\epsilon$ value and the larger the dipole moment. So due to the changes in the sequence distribution there could exist a larger hindrance caused by intermolecular interaction between the VC unit and the solvent (THF-d₈). The τ_2 values of all considered methylene groups are in the same magnitude (about 3–5 ns), only the ratio τ_2/τ_1 of the VC methylene group decreases when the VDC content increases. This could be interpreted as a larger (but a relatively weak) damping of the diffusion of bond orientation along the chain. This is in agreement with the fact that the segmental mobility is higher in long subchains than in shorter ones and reflects the differences in the sequence distribution due to copolymerization (Table 1).

Methylene NOEs

In some respects, NOEs provide a more stringent test of motional models than do T_1 s. If T_1 reaches an extreme narrowing regime at high temperatures, the NOE should equal 3, its maximum value. As T_1 approaches a minimum, the NOE decreases. Once the T_1 data have been fitted, yielding a temperature dependence, no new

parameters are required to predict NOE as a function of temperature (within the range of error). A better agreement could be reached if T_1 measurements at another Larmor frequency were fitted simultaneously (¹H- T_1 or ¹³C, for example). But the conclusions from T_1 analysis are supported by NOEs. Precisely those models that successfully describe T_1 data simultaneously describe NOE results.

DISCUSSION

The most important finding is that motion occurs on two well separated time scales. Neither the HH nor the VJGM model can adequately describe T_1 or NOE data. Although the VJGM and the HH autocorrelation function have two time scales, they cannot reproduce the experimental T_1 data. On the other hand, the DLM model provides a good agreement with the experimental results (see Figures 2 and 3). The slower class of motions is characterized by a correlation time τ in the vicinity of $1/\omega_C$. This slower overall motion seems to reflect conformational changes about backbone C-C single bonds (propagation of a damped diffusional process along the chain). The other class is much faster ($\tau \ll 1/\omega_C$). These fast anisotropic motions reflect the wobbling motion of a C-H bond within a cone. Rapid motion within this cone quickly reduces the value of $G(t)$ to $(1-a)$. Conformational dynamics are responsible for the remaining decay of $G(t)$.

The conformational and librational motions are separated in the time scale by a factor of 300–400 (see Table 4). The amplitude of the librational motion can be estimated from experimental data. Howarth²⁵ has proposed a restricted rotation model which assumes that the C-H bond can adopt with equal probability any orientation within a cone of half angles Θ with²² $(1-a) = [(\cos \Theta)/2(1 + \cos \Theta)]^2$.

In accordance with experimental data, this model predicts a greater mobility of the VDC co-component. This agrees with the linewidth of methylene groups of VC and VDC co-components observed in n.m.r. spectra. However, the differences in the sequence distribution (Table 1) in both samples (4 and 40 mol% VDC content) will be reflected by a lowering of the segmental mobility of the VC co-component in the 40% sample due to changes in the strength of the intermolecular interaction between the VC unit and the solvent.

The fit yields^{18–20} the activation energy of the solution $E_{sol} \approx 16–22$ kJ mol⁻¹. The activation energy of the conformational jumps associated with the τ_1 correlation time can be estimated from:

$$E_a = E_{sol} - E_\eta$$

where E_{η} is the activation energy from the solvent (in the case of THF, $E_{\eta}(\text{THF})=6.9 \text{ kJ mol}^{-1}$) and therefore $E_a \approx 9\text{--}14 \text{ kJ mol}^{-1}$. This is in the range of values found for pure PVDC and other alkanes^{26,27} and it agrees with conformational energy calculations^{28,29}. This result also indicates that mainly type 2 motion, according to Helfand's notation, occurs,

The best agreement with experimental data is given by simultaneously fitting temperature-dependent T_1 at several ^{13}C Larmor frequencies. Temperature-dependent NOEs and/or $^1\text{H}\text{--}T_1$ could be used as a test, but this would result in a greater degree of experimental uncertainty.

REFERENCES

- 1 Skolnick, J., Perchak, D. and Yaris, R. *J. Magn. Res.* 1984, **57**, 204
- 2 Heatley, F. 'Annual Reports on NMR Spectroscopy', Academic Press, London, 1986, Vol. 17, p. 179
- 3 Dejean de la Batie, R., Lauprêtre, F. and Monnerie, L. *Macromolecules* 1988, **21**, 2045, 2052
- 4 Dejean de la Batie, R., Lauprêtre, F. and Monnerie, L. *Macromolecules* 1989, **22**, 122, 2617
- 5 Monnerie, L. *Makromol. Chem., Macromol. Symp.* 1991, **48/49**, 125
- 6 Schlothauer, K. and Herold, H. *Acta Polym.* 1985, **36**, 200
- 7 Schlothauer, K. and Wiss, Z. *THLM* 1987, **29**, 373
- 8 Schlothauer, K., Wulff, D. and Thiele, K. *Acta Polym.* 1988, **39**, 112
- 9 Glowinkowski, S., Gisser, D. J. and Ediger, M. D. *Macromolecules* 1990, **23**, 3520
- 10 Heatley, F. *Prog. Nucl. Magn. Res. Spectrosc.* 1979, **13**, 47
- 11 Heatley, F. *Ann. Rep. NMR Spectrosc.* 1986, **17**, 179
- 12 Abragam, A. 'The Principles of Nuclear Magnetism', Clarendon Press, Oxford, 1961, Ch. VIII
- 13 Farrar, T. C. 'An Introduction to Pulse NMR Spectroscopy', Farragut Press, Chicago, 1987
- 14 Beckman, P. A. *Phys. Rep.* (review section of *Phys. Lett.*) 1988, **171**, 3, 85
- 15 Hall, C. K. and Helfand, E. *J. Chem. Phys.* 1982, **77**, 3275
- 16 Valeur, B., Jarry, J. P., Geny, F. and Monnerie, L. *J. Polym. Sci., Polym. Phys. Edn* 1975, **13**, 667, 675, 2251
- 17 Gisser, D. J., Glowinkowski, S. and Ediger, M. D. *Macromolecules* 1991, **24**, 4270
- 18 Bergmann, H. and Schlothauer, K. *Acta Polym.* 1988, **39**, 694
- 19 Bergmann-Menge, H. Thesis (Promotion A), TH Merseburg, 1990
- 20 Lebek, B., Menge, H., Schlothauer, K., Schneider, H., Kivajeva, L. S. and Fedotov, V. D. *Polymer* 1991, **32**, 2335
- 21 Schneider, H. *J. Polym. Sci. (B), Polym. Phys.* 1991, **29**, 1171
- 22 Fedotov, V. D. and Schneider, H. in 'NMR — Basic Principles and Progress', Springer, Heidelberg, 1989, Vol. 21
- 23 Menge, H., Feldman, Yu. D., Polygalov, E., Fedotov, V. D. and Schneider, H. *Acta Polym.* 1992, **43**, 247
- 24 Salem, M. B., Oun, A. M. and Omar, M. M. *Polym. Int.* 1991, **26**, 209
- 25 Howarth, O. W. *J. Chem. Soc., Faraday Trans. 2* 1979, **75**, 863
- 26 Matsuo, K. and Stockmayer, W. H. *Macromolecules* 1981, **14**, 544
- 27 Nedeá, E. M., Marchessault, R. H. and Dais, P. *Polymer* 1992, **33**, 1831
- 28 Alig, I., Hauptmann, P. and Schlothauer, K. *Acta Polym.* 1986, **37**, 342
- 29 Alig, I., Lochmann, R. and Wartewig, S. *J. Polym. Sci., Polym. Phys. Edn* 1984, **22**, 1097