NMR LINE-SHAPE ANALYSIS OF SWOLLEN CROSSLINKED POLY(ETHYLENE OXIDE) USING AN ORIENTATION-DEPENDENT GAUSSIAN BROADENING FUNCTION WITH VARYING WIDTH

Jaromír JAKEŠ

Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, 162 06 Prague 6

Dedicated to Professor O. Wichterle on the occasion of his 70th birthday.

NMR line shapes of swollen crosslinked poly(oxyethylene) were analysed as a convolution of a narrow Lorentzian function governed by rapid segmental motions, and a dipolar broadening function. An orientation-dependent Gaussian function with some distribution of its width was chosen for the dipolar broadening function. For the distribution of the width a function similar to the χ^2 distribution was used. An appreciable improvement compared to the previous analysis with the orientation-dependent Lorentz function was only obtained if the distribution used contained an essential amount of narrow widths close to zero. With this approach, it was possible to simulate the experimental spectra obtained in the $CDCl_3$ swelling agent at various temperatures within experimental accuracy. With the CCl_4 swelling agent, the agreement was slightly worse in the peak area, apparently due to the distribution of the width of the narrow Lorentzian function governed by rapid segmental motions. Even in this case, an improvement compared to the previous analysis was obtained. It was found that a simple Gaussian distribution function with the maximum at zero width, which is a special case of the general distribution function used, can reproduce the experimental spectra with almost the same accuracy as the general distribution function.

Previous papers from this laboratory[1-4] showed that the static NMR spectra of the amorphous part of crystalline polyethylene and of swollen crosslinked polymer gels of poly(oxyethylene), polystyrene, poly(methyl methacrylate), and poly(dimethylsiloxane) may be described successfully by the lineshape equation[1,3]

$$L(v - v_0) = \int_0^1 \int_{-\infty}^{\infty} S(v - v_1) \, G\left(\frac{v_1 - v_0}{|3\cos^2\Theta - 1|}\right) / |3\cos^2\Theta - 1| \, dv_1 \, d\cos\Theta \qquad (1)$$

with the orientation-dependent dipolar broadening function G of Lorentzian shape. This function leads to a good overall agreement, but in the cases of poly(oxyethylene) and polystyrene it was seen to be little lower than the experimental spectrum in the peak area and in wings, being essentially correct in the intermediate region (around

$v - v_0 = 600$ Hz). On the other hand, Wennerström[5] used an orientation-dependent Gaussian function to simulate the NMR spectra of anisotropic liquids. Therefore, it was interesting to compare the results of applying the Lorentzian and Gaussian G functions in the line shape analysis[4]. In doing so, it was found that the Lorentzian G function gave better agreement than the Gaussian function in all cases considered in ref.[2] with the exception of the CCl_4 swelling agent at 50°C. Further, as has already been pointed out in ref.[3], it is quite natural to assume a distribution of width parameters in a polymer system, and a Lorentzian line itself may be considered as a superposition of Gaussian lines with a common center and varying width. From this point of view, in refs[1–4], the form of the width distribution function was chosen quite arbitrarily; the only reason for its use was that the orientation-dependent dipolar broadening function of Lorentzian shape was easy to calculate. In the present paper, a more detailed consideration of the influence of the width distribution on the line shape was considered using a generalized χ^2 distribution. By this approach, NMR spectra of the crosslinked poly(oxyethylene) swollen to equilibrium in $CDCl_3$ and CCl_4 at various temperatures were analysed using experimental data from ref.[2]

The Form of the Dipolar Broadening Function G and of its Distribution

We assume a dipolar broadening function $G(v - v_0)$ (ref.[1,3,4]) of the Gaussian form, $G(x) = \exp(-x^2/A^2)/(\pi^{1/2}A)$, with the width parameter A having some distribution described by a distribution function $w(A)$. Two effects may be dominating in forming the distribution $w(A)$. First, in the swelling of a polymer, short intercrosslink chains may become almost stretched, whereas long intercrosslink chains may be relatively free to move and coil. A segment of a short chain has less chance of reorientation so that the averaging of the near-static dipolar interactions is less perfect and the corresponding line is broad (A is large). On the other hand, the longer intercrosslink chains, especially their centers, behave almost as a linear polymer and the corresponding lines are narrow (A is close to zero). Second, units close to the crosslink point have also less chance of reorientation, so that their lines are broad, whereas units distant from the crosslink point have greater chance of reorientation, so that their lines are narrower. Due to the complexity of statistics in a swollen polymer and without any more detailed knowledge about it, it is very difficult, if ever possible, to derive a distribution $w(A)$ from physical grounds. Therefore, a general distribution function has been selected in this work.

Schaefer[6] used a χ^2 distribution of correlation times, τ_c, to explain the experimental T_1, T_2, and NOEF values in some polymers, with a logarithmic scale for τ_c to cover the distribution widths over many orders of magnitude. For our purposes, the logarithmic scale is unnecessary and the simple χ^2 distribution can be formulated as

$$w(A) = A^{p-1} A_0^{-p} \exp(-A/A_0)/\Gamma(p), \qquad (2)$$

where A_0 and p are the parameters of the χ^2 distribution and Γ is the gamma function. The averages of this distribution are $\overline{A} = A_0 p$, $\overline{A^2} = A_0^2 p(p + 1)$ and the mean square deviation is $\sigma = (\overline{A^2} - \overline{A}^2)^{1/2} = A_0 p^{1/2} = \overline{A} p^{-1/2}$. On the other hand, from statistical considerations the χ^2 distribution is known to apply to the square of a variable rather than to a variable itself, leading to the distribution

$$w(A) = 2A^{p-1} A_0^{-p} \exp\left(-A^2/A_0^2\right)/\Gamma(p/2) . \qquad (3)$$

Equations (2) and (3) may be generalized to a common form

$$w(A) = |n|\, A^{p-1} A_0^{-p} \exp\left(-A^n/A_0^n\right)/\Gamma(p/n) . \qquad (4)$$

In Eq. (4), p and n must be either both positive or both negative, otherwise the distribution function cannot be normalized. If we let p go to plus or minus infinity and simultaneously change A_0 so that $\overline{A}$ is kept constant, then distribution (4) goes to $\delta(A - \overline{A})$ and becomes infinitely narrow. For $n \to \infty$, the distribution function becomes $w(A) = pA^{p-1}/A_0^p$ for $0 < A < A_0$ and $w(A) = 0$ for $A > A_0$, experiencing a jump from p/A_0 to zero at $A = A_0$. For $n \to -\infty$, the distribution function becomes $w(A) = 0$ for $0 < A < A_0$ and $w(A) = -pA^{p-1}/A_0^p$ for $A > A_0$, having a jump from zero to $-p/A_0$ at A_0. Note that p is negative in the latter case.

The distribution function defined by Eq. (4) is a flexible three-parameter distribution which may well approximate many functions which are either monotonic or exhibit one maximum. The parameter A_0 controls the width of the distribution and is just a scaling factor of the A axis. For positive values of p and n, the parameter p controls the behavior of the function at $A = 0$. For $p < 1$, $w(A)$ is infinite at $A = 0$ and decreases monotonically with increasing A. For $p = 1$, $w(0) = n/(A_0\Gamma(1/n))$ is finite and the function decreases monotonically with increasing A. For $p > 1$, and also for negative p and n, $w(0) = 0$, the function increases to a maximum and decreases beyond it. For positive n, the parameter n controls the steepness of the decrease in the function $w(A)$ around $A = A_0$. The greater the parameter, the steeper the decrease, and for $n = \infty$ a jump appears. Changing signs of both p and n leads to the application of the original distribution $w(A)$ to the variable $1/A$ instead of the original A, replacing simultaneously A_0 by $1/A_0$ and respecting the fact that $d(1/A) = = -dA/A^2$, i.e. $w(A; A_0, p, n) = w(1/A; 1/A_0, -p, -n)/A^2$. The scaling relation of the A axis may be written as $w(A; A_0, p, n) = w(A/A_0; 1, p, n)/A_0$.

The average value $\overline{A}$ is given by

$$\overline{A} = A_0 \Gamma\left(\frac{p + 1}{n}\right)\Big/\Gamma(p/n) \quad \text{for} \quad p < -1 \ \text{ or } \ p > 0 , \qquad (5a)$$

$$\overline{A} = A_0 p/(p + 1) \quad \text{for} \quad n = \pm\infty \ \text{ and } \ (p < -1 \text{ or } p > 0), \qquad (5b)$$

$$\overline{A} = \infty \qquad\qquad \text{for} \quad -1 \leqq p < 0 . \qquad (5c)$$

A generalized average $\bar{A}^{(\alpha)} = \overline{(A^{\alpha})}^{1/\alpha}$ and $\bar{A}^{(0)} = \exp\overline{(\log A)}$ is sometimes defined. For $\alpha > 0$, we obtain

$$\bar{A}^{(\alpha)} = A_0 \left(\Gamma\left(\frac{p+\alpha}{n}\right)\Big/\Gamma(p/n)\right)^{1/\alpha} \quad \text{for} \quad p < -\alpha \quad \text{or} \quad p > 0 \,, \qquad (6a)$$

$$\bar{A}^{(\alpha)} = A_0(p/(p+\alpha))^{1/\alpha} \quad \text{for} \quad \text{n} = \pm\infty \quad \text{and} \quad (p < -\alpha \text{ or } p > 0) \,, \quad (6b)$$

$$\bar{A}^{(\alpha)} = \infty \qquad\qquad \text{for} \quad -\alpha \leqq p < 0 \,. \qquad (6c)$$

For $\alpha = 0$, $\bar{A}^{(0)} = A_0 \exp(\psi(p/n)/n)$, and $\bar{A}^{(0)} = A_0 \exp(-1/p)$ for $n = \pm\infty$. Here, $\psi(x) = \mathrm{d}(\log\Gamma(x))/\mathrm{d}x$. For negative α, $\bar{A}^{(\alpha)}$ is obtained from Eqs (6) by interchanging the signs $<$ and $>$ (and also $\leqq$ and $\geqq$) in conditions determining the operation of either of the three right sides in Eqs (6). From Eqs (5) and (6), $\sigma = ((\bar{A}^{(2)})^2 - \bar{A}^2)^{1/2}$.

Several special cases of distribution (4) are interesting. For $p = 1$ and $n = 2$, we obtain a normal Gaussian distribution with the maximum at $A = 0$. Note that the integration of the distribution proceeds only from zero to $+\infty$, which leads to a multiplication by a factor of two compared to a normalized Gaussian spectral function, where normalization integration proceeds from $-\infty$ to $+\infty$. For $p = 1$ and $n = \infty$, we obtain a rectangular distribution. The distribution of Gaussian functions described by Eq. (4) for $p = -1$ and $n = -2$ leads to a Lorentzian function[3]. If we assume that at each crosslink point, A assumes the value A_0 and in each intercrosslink chain, the value of A decreases in a geometric series with the quotient q in going from the crosslink point to the center of the intercrosslink chain, and if further the population of units decreases in a geometric series with the quotient q_0 with the distance from the crosslink point, then distribution (4) with $p = \log(q_0)/\log(q)$ and $n = \infty$ is obtained for $w(A)$, provided summation over A may be replaced by integration. In the subsequent analysis, the values of $n = 1$ (the χ^2 distribution), $n = 2$ (the χ^2 distribution applied to A^2), $n = \infty$ (called later p-distribution), and $n = 2$, $p = 1$ (the Gaussian distribution) were used, in all cases with an adjustable A_0 and in the first three cases also with an adjustable p.

The Form of Function S

The function S (Eq. (1)) was assumed in the Lorentzian form

$$S(x) = B/(\pi(x^2 + B^2)) \,. \qquad (7)$$

The lower limit of the parameter B may be obtained from NMR spectra measured with rotation about the "magic" axis[2] (MAR-NMR); in the spectra measured

without sample rotation, the value of B may be increased by physical heterogeneity of the sample[7,8]. The heterogeneity broadening is expected to be essentially independent of temperature. Indeed, in a simultaneous refinement of all the spectra of poly(oxyethylene) gels in the $CDCl_3$ swelling agent at various temperatures, assuming exponential dependence of both A and B on temperature, the difference $B - B_{MAR}$ turned out to be nearly constant. Thus, the refinement was repeated with B taken as its MAR value plus an adjustable constant independent of temperature: $B = B_{MAR} + B_{HET}$. The refined value of B_{HET} was 1·5 to three times higher than the B_{MAR} values.

In a crosslinked polymer, a distribution of B widths may also be assumed. Experimentally, it is manifested by the deviation of the MAR-NMR line shape from the Lorentzian shape. This effect is clearly seen in the poor swelling agent (CCl_4), where the B widths are considerably greater than in $CDCl_3$, and it is apparently responsible for the considerably worse agreement between the experimental and calculated spectra in the peak area in this case (Fig. 1). No such difficulty arose in the $CDCl_3$ swelling agent. As the heterogeneity broadening is dominating here, this situation indicates that the B_{HET} width has a narrow distribution in the $CDCl_3$ swelling agent. Note that in an analysis of the NMR spectra of crystalline polyethylene[1], it was also suspected that the most crystalline 6011L specimen with the largest B may be influenced by a distribution of the parameter B with no such indication in other, less crystalline specimens with smaller B values, although here the effect was not so apparent as in the present case.

Spectra Simulation

For spectra simulation, experimental data from ref.[2] were used. In obtaining them, radiofrequency field and modulation amplitude levels were adjusted so as to avoid shape distortion by saturation in the peak region; the noise level in the wings was about $1-2$ mm in the record, where the peak height was about 200 mm. The experimental curve was smoothed manually, and an average was taken from the upfield and downfield halves of the line, thus compensating for a possible small missetting of phase. For the refinement of the values $\bar{A}$, B, and p in Eq. (4), the same weighting scheme was used as in ref.[2]. This means that $\sum\limits_{i=0} \left(y_i^{exp} - y_i^{calc} \right)^2 / w_i^2$ was minimized with $w_i = \left(2y_i^{exp} + y_0^{exp} \right) / y_i^{exp}$ for $i > 0$ and $w_0 = 18^{1/2}$. The w_0 value was multiplied by $2^{1/2}$ compared to other w_i values to account for the fact that all the points except the central one were obtained as an average from two independent values. Due to the small influence of the truncation of the spectra, the truncation was omitted and the points for the refinement were taken in steps of 20 Hz in $v - v_0$ from zero to 600 Hz and in steps of 40 Hz from 600 Hz to 2 600 Hz; for spectra measured at 23°C and 29°C in CCl_4, where the peak was wider than in the other cases, the scale change was set at 800 Hz.

The results of the independent refinement of the spectra measured at various temperatures are shown in Table I. One or two more significant digits than necessary are shown here and in Table II to facilitate comparison of small differences between different ways of refinement. For the $CDCl_3$ swelling agent, the best agreement is found with the p-distribution $(n = \infty)$. Here, all the spectra are reproduced with experimental accuracy, and as the experimental spectra were already shown in ref.[2], no figure plots of these spectra are shown here. A maximum error of $7 \cdot 6$ mm appears in the steep slope of the sharp peak region, where errors in abscissa setting may become important. In the spectrum measured at $-13°C$ which is best reproduced by the calculation (Table I), the maximum error is $1 \cdot 8$ mm in a similar position. A maximum error in the wings is $1 \cdot 7$ mm. The other three distributions lead to slightly worse results, but still reproduce the experimental spectra with considerable accuracy. In all cases, the refined parameter $2B$ is considerably greater than the $2B_{MAR}$ value; keeping $2B = 2B_{MAR}$ leads to considerable worsening of the agreement between simulated and experimental spectra. In this case, the simulated spectra
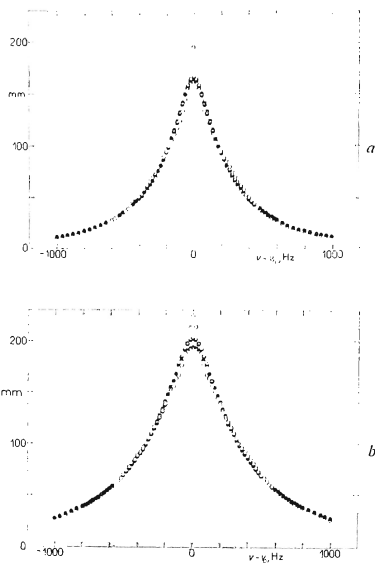

Fig. 1

Comparison between the experimental and simulated NMR spectra of crosslinked poly-(oxyethylene) swollen in CCl_4 (a measured at 50°C, b measured at 23°C): ○ experimental, ◐ simulated (χ^2 distribution of A, all temperatures independently), ◑ simulated (Gaussian distribution of A, all temperatures simultaneously, $B = B_{MAR} + const.$). Abscissa scale expanded twice compared to plots in ref.[2]. Far wings not shown as all curves match here within the accuracy of reproduction

Table I

Simulation of NMR spectra of crosslinked poly(oxyethylene) (all temperatures independently). Root weighted mean square error, [rwmse], $(\sum_{i=0} ((y_i^{exp} - y_i^{calc})/w_i)^2 / \sum_{i=0} w_i^{-2})^{1/2}$; $w_0 = 18^{1/2}$, $w_i = (2y_i^{exp} + y_0^{exp})/y_0^{exp}$ for $i > 0$

T °C	$2B$ Hz	$2\overline{A}$ Hz	p	[rwmse] mm
		CDCl$_3$, χ^2 ($n = 1$)		
−13	32·93	4 171	1·47	0·4234
17	30·10	3 745	1·40	1·0320
23	32·17	3 956	1·34	1·1583
29	34·49	3 976	1·30	1·1620
42	28·96	3 975	1·33	1·1531
50	28·16	3 289	1·56	0·6333
		CCl$_4$, χ^2 ($n = 1$)		
23	252·72	2 273	2·42	1·6974
29	225·94	2 050	2·64	1·3212
50	158·36	1 422	4·21	1·5835
		CDCl$_3$, χ^2/A^2 ($n = 2$)		
−13	38·35	3 717	1·17	0·3687
17	34·93	3 325	1·12	0·8948
23	37·29	3 489	1·08	1·0029
29	40·01	3 494	1·05	1·0345
42	33·41	3 490	1·08	1·0093
50	33·44	2 983	1·21	0·5263
		CCl$_4$, χ^2/A^2 ($n = 2$)		
23	283·47	2 129	1·46	1·7601
29	252·83	1 929	1·58	1·3734
50	166·22	1 376	2·59	1·6242
		CDCl$_3$, p ($n = \infty$)		
−13	43·63	3 320	1·03	0·4123
17	39·50	2 967	0·99	0·7708
23	42·00	3 101	0·96	0·8582
29	44·52	3 090	0·94	0·9231
42	37·05	3 085	0·97	0·8878
50	39·33	2 701	1·04	0·4679

TABLE I
(Continued)

T °C	$2B$ Hz	$2\overline{A}$ Hz	p	[rwmse] mm
	CCl$_4$, p ($n = \infty$)			
23	347·70	1 882	0·89	1·8510
29	316·48	1 697	0·93	1·4535
50	209·59	1 233	1·40	1·7022
	CDCl$_3$, Gauss ($n = 2$, $p = 1$)			
−13	52·39	4 047	1	0·6228
17	43·55	3 533	1	0·9656
23	43·32	3 642	1	1·0394
29	44·00	3 589	1	1·0474
42	38·87	3 653	1	1·0440
50	49·26	3 250	1	0·8419
	CCl$_4$, Gauss ($n = 2$, $p = 1$)			
23	358·52	2 003	1	1·8052
29	336·96	1 774	1	1·4221
50	292·76	1 107	1	1·7352

are apparently too narrow and too high in the peak area. During refinement, it was found that a change in one of the parameters may be largely compensated for by suitably changing the other parameters without any substantial worsening of agreement between the simulated and experimental spectra. This is manifested, *e.g.*, by the fact that keeping p at unity (Gaussian distribution) leads to only very slight worsening compared to the χ^2/A^2 distribution (*cf.* Table I). Another example may be found by following the width of the central sharp peak in the spectrum at −13°C in CDCl$_3$ solvent in comparing the experimental and calculated spectra (not shown here). The width of this peak is controlled almost exclusively by the parameter $2B$. If the distribution used provides a correct height of the central peak, the least squares refinement procedure finds the correct value of $2B$ and both height and sharpness of the peak are reproduced correctly. This is the case of the p-distribution. In the χ^2/A^2 and χ^2 distributions, the calculated sharp peak gets somewhat too low. The refinement procedure partially compensates for this error by lowering the value $2B$ which leads to a higher but narrower peak (*cf.* values of $2B$ in Table I). In the Gaus-

TABLE II

Simulation of NMR spectra of crosslinked poly(oxyethylene) (all temperatures simultaneously). [rwmse], see Table I

Parameter	T, °C					
	− 13	17	23	29	42	50

CDCl$_3$, p, B exponentially

$2B$ (Hz)	45·07	41·41	40·80	40·22	39·07	38·42
$2\bar{A}$ (Hz)	3 366	3 082	3 035	2 990	2 901	2 851
rwmse (mm)	0·4684	0·8635	0·8737	0·9495	0·9769	0·6313

$p = 0.99$, overall [rwmse] = 0·8162 mm

CDCl$_3$, p, $B = B_{MAR}$ + const.

$2B$ (Hz)	46·74	41·49	40·72	40·00	38·68	37·99
$2\bar{A}$ (Hz)	3 350	3 079	3 034	2 991	2 906	2 858
rwmse (mm)	0·4507	0·8615	0·8732	0·9496	0·9707	0·6484

$2B - 2B_{MAR} = 28.48$ Hz, $p = 0.99$, overall [rwmse] = 0·8152 mm

CDCl$_3$, Gauss, B exponentially

$2B$ (Hz)	49·46	45·68	45·05	44·45	43·25	42·58
$2\bar{A}$ (Hz)	4 030	3 675	3 616	3 560	3 448	3 386
rwmse (mm)	0·6501	1·0412	1·0449	1·0491	1·1207	0·9298

overall [rwmse] = 0·9866 mm

CDCl$_3$, Gauss, $B = B_{MAR}$ + const.

$2B$ (Hz)	50·97	45·72	44·95	44·23	42·91	42·22
$2\bar{A}$ (Hz)	4 010	3 671	3 614	3 561	3 454	3 394
rwmse (mm)	0·6371	1·0391	1·0444	1·0491	1·1157	0·9397

$2B - 2B_{MAR} = 32.71$ Hz, overall [rwmse] = 0·9854 mm

CCl$_4$, Gauss, B exponentially

$2B$ (Hz)			357·04	340·23		291·47
$2\bar{A}$ (Hz)			2 014	1 750		1 114
rwmse (mm)			1·8055	1·4232		1·7353

overall [rwmse] = 1·6578 mm

TABLE II
(*Continued*)

Parameter	T, °C					
	−13	17	23	29	42	50
CCl_4, Gauss, $B = B_{MAR} + const.$						
$2B$ (Hz)			389·05	339·05		257·05
$2\overline{A}$ (Hz)			1 868	1 711		1 292
rwmse (mm)			1·8856	1·4469		1·8033

$2B - 2B_{MAR} = 209.05$ Hz, overall [rwmse] $= 1.7165$ mm

sian distribution, compensation proceeds in the opposite direction. The lower root weighted mean square error (rwmse) for the χ^2/A^2 distribution compared to the p-distribution in $CDCl_3$ at −13°C is occasionally caused by the fact that in the p-distribution calculated wings are 0·3 mm off (due to an error in base line setting far below the experimental inaccuracy) which is compensated for in the χ^2/A^2 distribution. In the CCl_4 swelling agent, an agreement in the peak region as good as in the $CDCl_3$ case was not obtained (Fig. 1). As has already been discussed in the preceding paragraph, this is apparently due to the distribution of the parameter B neglected in the calculation. Here, the χ^2 distribution works best with slightly worse results in other three distributions, but this finding is not very relevant, as a change in the parameter n may partially compensate for the error caused by the B parameter distribution. Even in this case, results are better than with the orientation-dependent Lorentzian G function in paper[2].

Due to the great mutual compensability of parameters, the fact that $\overline{A}$, B, and p do not change monotonically with temperature is not very surprising. In spite of this finding, a simultaneous refinement of all spectra at various temperatures was undertaken with the Gaussian distribution for both swelling agents and with the p-distribution for the $CDCl_3$ swelling agent only. First, the logarithms of both $\overline{A}$ and B were assumed to depend linearly on $1/T$, with a temperature-independent p (its approximate temperature independence may be seen in Table I). For the $CDCl_3$ swelling agent, the difference $2B - 2B_{MAR}$ was found to be approximately independent of temperature (Table II), in accord with what has been said about it in the preceding paragraph. Thus, the simultaneous refinement was repeated under the assumption that $2B$ was given by its $2B_{MAR}$ value plus an adjustable constant independent of temperature, with the other parameters refined as in the preceding case. Results of both

ways of simultaneous refinement are given in Table II. Comparison between Tables I and II shows that the simultaneous refinement simulates the experimental spectra with nearly the same accuracy as the independent refinement. In the case of the CCl_4 swelling agent, the assumption $2B = 2B_{MAR} +$ const. leads to considerable changes in refined $2B$, but these changes are compensated for by changes in $2\bar{A}$, and the increase in rwmse is only small. In spite of this finding, the assumption $2B = 2B_{MAR} +$ + const. is compatible with the experimental results even in the CCl_4 swelling agent.

DISCUSSION

Comparison between the results of the present adjustment procedure with the results of ref.[2] shows the largest differences in the peak area. With the orientation-dependent dipolar broadening function G of Lorentzian shape and $2B_{MAR}$ values, 15 to 25 mm errors appeared in the vicinity of the center of the sharp peak in the $CDCl_3$ swelling agent. These were apparently due to the fact that the calculated sharp peak was too narrow. Attempts to correct this by increasing $2B$ led to a peak which was too low. With an independent refinement of both $2A$ and $2B$, an even narrower and higher peak was obtained.

Although the orientation-dependent Lorentzian G function gave a good overall simulation of the spectra, and even errors in the peak region were not very large, the present results showed that for removing these errors a very broad distribution of the parameter A was necessary with a considerable or even maximum density at $A = 0$. This means that the spectra are not very sensitive to the distribution of the parameter A. No distribution $w(A)$ with negligible density around $A = 0$ could improve errors in the peak area; this was also the case of the orientation-dependent Lorentzian G function corresponding to the distribution (4) with $p = -1$, $n = -2$. The small sensitivity to the form of the distribution $w(A)$ is also seen from the fact that various values of n gave almost the same accuracy in simulating the spectra.

Due to the strong mutual compensation ability of the individual parameters, a refined set may only be considered as physically reliable if good fit in the whole spectrum is obtained. Parameters are sensitive to the accuracy in the wings, where an incorrect setting of the base line may cause much trouble. For this reason, the best way of simulating spectra is to use as few parameters as possible. This means that the one-parameter Gaussian distribution function should be preferred, with the parameters $\bar{A}$ and B constrained by temperature dependence and possibly with some parameters assumed or constrained from other sources (B from MAR). Some preliminary results on crosslinked polystyrene show that distribution (4) with $p = 1$, $n = 2$ (Gaussian distribution) works well in this case. Probably, this distribution will be sufficient for crosslinked polymer gels swollen in good swelling agents, where the distribution of the parameter B seems not to be important. If some systematic errors appear, variation of the parameter p may be tried. Increasing this parameter leads to a de-

crease in intensity in the peak region and in far wings and to an increase in intensity in the flanks (*i.e.* around $v - v_0 = 600$ Hz in the present case); this may serve as a hint whether variation of the parameter p could be effective in the improvement of spectra. Variation of the parameter n seems to be meaningful only if very accurate spectra, including far wings, could be measured with a very accurate setting of base line, which does not seem to be the case with the present measuring technique.

REFERENCES

1. Schneider B., Jakeš J., Pivcová H., Doskočilová D.: Polymer *20*, 939 (1979).
2. Doskočilová D., Schneider B., Jakeš J.: Polymer *21*, 1185 (1980).
3. Doskočilová D., Schneider B., Jakeš J.: J. Magn. Resonance *29*, 79 (1978).
4. Doskočilová D., Schneider B.: Pure Appl. Chem. *54*, 575 (1982).
5. Wennerström H.: Chem. Phys. Lett. *18*, 41 (1973).
6. Schaefer J.: Macromolecules *6*, 882 (1973).
7. Doskočilová D., Schneider B.: Macromolecules *5*, 125 (1972).
8. Doskočilová D., Tao D. D., Schneider B.: Czech. J. Phys. B*25*, 202 (1975).

Translated by L. Kopecká.