

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

The Chemical Dehydrochlorination of Polyvinyl Chloride. A New Method for Polyenic Sequences Evaluation

Emmanuelle Simon^a; Pierre Fraysse^a; Alain Perichaud^a

^a Laboratoire de Chimie Macromoléculaire, Université de Provence 3 P1. V. Hugo, Marseille Cedex 3, France

To cite this Article Simon, Emmanuelle , Fraysse, Pierre and Perichaud, Alain(1992) 'The Chemical Dehydrochlorination of Polyvinyl Chloride. A New Method for Polyenic Sequences Evaluation', *Journal of Macromolecular Science, Part A*, 29: 10, 893 – 903

To link to this Article: DOI: 10.1080/10601329208054126

URL: <http://dx.doi.org/10.1080/10601329208054126>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

THE CHEMICAL DEHYDROCHLORINATION OF POLYVINYL CHLORIDE. A NEW METHOD FOR POLYENIC SEQUENCES EVALUATION

EMMANUELLE SIMON, PIERRE FRAYSSE, and ALAIN PERICHAUD*

Laboratoire de Chimie Macromoléculaire
Université de Provence
3 Pl. V. Hugo, 13331 Marseille Cedex 3, France

ABSTRACT

The chemical dehydrochlorination of polyvinyl chloride was studied in solution in tetrahydrofuran. The dehydrochlorinated products were characterized by their chlorine contents and by UV/visible spectroscopy. The absorption spectra of dehydrochlorinated PVC consist of a series of absorption maxima between 200 and 600 nm due to the formation of conjugated polyenic sequences. In this article we describe a new method for polyenic sequences evaluation based on deconvolution of the experimental spectrum. A comparison with the former technique usually employed is presented.

INTRODUCTION

Polyvinyl chloride (PVC), widely used in industry, exhibits easily modifiable mechanical properties. However, it is very unstable. When processed, stored, or used under normal conditions, it undergoes degradation, principally through a dehydrochlorination reaction. This reaction causes deterioration of its thermal and mechanical properties, and a reduction in its chemical resistance which causes discoloration and increases the rigidity of its polymer chains.

The degradation of PVC exposed to heat [1–5] or light [4–7] leads to the formation of polyenic sequences through the elimination of hydrochloric acid. However, this dehydrochlorination (DHC) can also be caused by gamma irradiation

[4, 5, 8], electron bombardment [9], or by the presence of bases (chemical DHC) [4, 5, 10–24]. Among the numerous basic agents employed, potassium *tert*-butoxide (tBuOK) offers many advantages because of its solubility in THF, the basicity of the tBuO⁻ anion, and its large size, which minimize the risks of substitution [17, 18, 25–29]. Discoloration of the polymer is usually the first visible indication of dehydrochlorination. This is due to lengthening of polyenic sequences, the absorption of which changes from ultraviolet to visible [4, 5].

The modification of polyenic sequences formed during the reaction can be monitored by using UV/visible spectroscopy [5, 14] if the polymer is soluble in an organic solvent or by Raman spectroscopy once it has become insoluble, after major elimination [17, 18, 21, 30].

In this article we present a new method for determining the distribution of polyenic sequences from a solution of partially dehydrochlorinated PVC. This technique, based on deconvolution of the experimental spectrum into elementary spectra, is compared with the simplified method generally employed which uses the Beer–Lambert law [14].

EXPERIMENTAL

Materials

Polyvinyl chloride: Manufactured by Atochem at the St. Auban factory and called RB 8010. It is used without prior purification.

Potassium *tert*-butoxide: Product from FLUKA, purified by sublimation before use.

Methanol: Product from CARLO ERBA codex, redistilled.

Tetrahydrofuran: Pure SDS product for synthesis, distilled over potash and then over aluminum lithium hydride.

DHC Using Potassium *Tert*-butoxide

Sublimation of tBuOK

A concentrated solution of tBuOK (10 g/L) was prepared and stored under argon after having been purified as follows. A nonspecific quantity of untreated potassium *tert*-butoxide was placed in a sublimator. The apparatus was heated to about 80°C under vacuum. When sublimation was completed, the apparatus was brought back to atmospheric pressure and placed in an argon-filled glove-box. The purified powder was recuperated in a predegassed Schlenk tube (rapid vacuum and then degassing with argon several times) and weighed. A known volume of THF which had been recently distilled under nitrogen (over potash and then over LiAlH₄) was then added.

Action of Purified tBuOK—Description of a Standard Experiment

Purified THF (100 cm³, $C = 4.17$ g/dm³) was added with stirring in an oxygen-free atmosphere into a Schlenk tube containing powdered PVC (0.5 g). Degassing was carried out by repeated argon/vacuum cycles. The quantity of tBuOK necessary to achieve the required elimination rate in THF solution ($C =$

1.05 g/dm³) was then added to the reaction medium at room temperature for 2 h (PD73) or 40 min (PD313).

Magnetic stirring was fixed at 500 rpm. The progress of the reaction was determined by coulometric free chloride measurement. UV/visible analyses were performed directly on the samples without prior purification.

Analytical Methods

Coulometric Determinations

A constant intensity direct current generator enabled solubilization of a silver electrode and the generation of Ag⁺ ions which reacted with Cl⁻ ions to produce an AgCl precipitate. The equivalence point was determined by nil intensity potentiometry. Variations of the potential were monitored by using a combined silver electrode, AgCl/Ag, and a potentiometer equipped with a recorder. From the recorder speed and the applied current, it was possible to deduce the quantity of Ag⁺ ions released (using Faraday's law: one equivalent is released for 96,487 coulombs), and thus the quantity of chloride present in the medium. The "consumable" silver electrode was a TACUSSEL "AG12." The platinum counterelectrode was a TACUSSEL "PT16" with a 10% HNO₃ junction. The combined silver electrode, AgCl/Ag, was a METROHM, reference 60404.100.

UV/Visible Analysis in the Cell

UV/Visible spectra were taken in dehydrochlorinated PVC solutions using a UVIKON 930 spectrometer. Measurements were performed as rapidly as possible to avoid sample oxidation.

RESULTS

Description of the Deconvolution Calculation

The UV/visible spectrum of a dehydrochlorinated PVC solution consists of a series of absorption maxima due to the formation of conjugated polyenic sequences. As these sequences lengthen, the absorption maxima move toward longer wavelengths and thus become visible (bathochrome effect). However, this shift does not seem to go much beyond 600 nm, and for long polyenic sequences ($n > 15$) the absorption maxima are no longer discernible. It is thus impossible to estimate the limit length of polyenic sequences beyond 600 nm.

Using UV/visible spectroscopy, Sondheimer [31] studied a series of polyenes (H(CH=CH)_{*n*}H with $n \geq 3$) model compounds. He showed that all spectra of these compounds exhibited four main maxima. The sum of these spectra, modulated by several coefficients (sequence concentration, molar extinction coefficient, maximum absorption wavelength, half-height width) yielded the complete spectrum of the sample.

Usually, the simplified method for calculating the n -order polyene concentration (C_n) in a mixture (Shindo model) [14] is to apply the Beer-Lambert law $C_n = A/l\epsilon_n$ to the principal maximum wavelength λ_{mp} . However, the absorbance of this polyene at the λ_{mp} wavelength depends not only on the concentration of that very

polyene but also on those of the $n \pm 1$, $n \pm 2$, and $n \pm 3$ order polyenes. Consequently, by applying the Shindo model, the contributions of higher order polyenes are neglected, and thus the C_n concentration is overestimated.

We have tried to improve this method by taking into account four bands for the calculation of concentrations in each conjugated polyenic system. We have used an optimization program to adjust C_n concentrations so as to obtain the best possible agreement between the experimental spectrum and the curve calculated as the sum of component spectra of all the polyenes present [29, 32].

By varying the parameters in a data file, our computer program allowed deconvolution of the UV spectrum of a dehydrochlorinated PVC into a sum of component spectra, and led to the concentration of each polyenic sequence present in the starting sample. This program employed two types of data file: files containing the experimental points of the UV/visible spectra and parameter files containing the characteristics of the spectra studied by Sondheimer, thus making it possible to perform deconvolution cycles until the calculated and experimental curves coincided [33].

For a given polyenic sequence, each i band was characterized by an apparent extinction coefficient ϵ (ϵa_i), by the n -order sequence concentration in the sample (C_n), by the midheight width ($h_{1/2}$) (identical for all bands in a sequence), and by the maximum absorption wavelength (λ_{\max}). Maximum wavelength absorptions were calculated by using the Beer-Lambert equation:

$$A_i = \epsilon a_i C_n \quad (1)$$

If the spectrum at a given n is decomposed into four component spectra, characteristics identical to the preceding are obtained, except for the apparent molar extinction coefficients which are replaced by the four true values ϵ (ϵv_j) and molar extinction coefficients of each peak j , with j varying from 1 to 4. Thus, as shown in Fig. 1, we obtain

$$\epsilon v_j < \epsilon a_i, \quad \text{for } i = j$$

Using these Gaussian peaks, we can recalculate the maximum wavelength absorptions for each of the four i bands of the n -order sequence as follows:

$$A_i = \sum_{j=1}^4 C_n \epsilon v_j \exp \left\{ (-\ln 2) \left[\frac{2}{\omega_j} \left(\frac{1}{\lambda_{\max_j}} - \frac{1}{\lambda_{\max_i}} \right) \right]^2 \right\} \quad (2)$$

with i , index calculated

j , index corresponding to the unit peaks constituting the component spectra

$$\omega_j = \frac{1}{\lambda_{\max_j} - \frac{h_{1/2}}{2}} - \frac{1}{\lambda_{\max_j} + \frac{h_{1/2}}{2}}$$

In fact, this expression gives the sum of the contributions of each unit peak, and it enables the maximum wavelength absorption of the i th band to be obtained. The exponential, expressed in wavenumbers to avoid a cessation of calculation by the computer because of a value which is too high, corresponds to the contribution of the j peak to the maximum wavelength. This contribution formula arises from the Gauss-shaped model peak at the λ wavelength according to

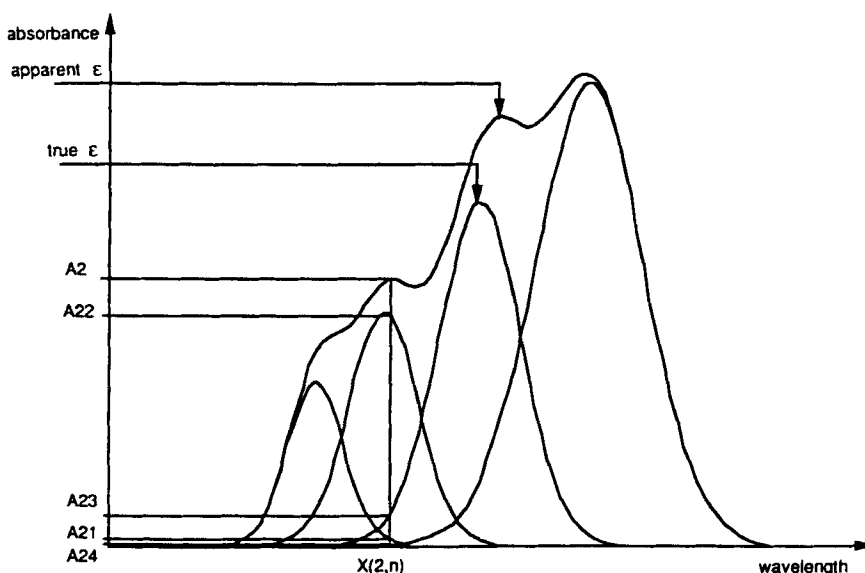


FIG. 1. Example of the calculation of true ϵ using apparent ϵ .

$$f(\lambda) = ae^{b\lambda^2} \tag{3}$$

The contribution of each j peak is calculated in turn according to its distance from the i band. We have illustrated the contributions A_{ij} of the j peaks for the i band in the case of an $n = 2$ order polyenic sequence.

$$A_2 = A_{21} + A_{22} + A_{23} + A_{24}$$

$$i = 2, j = 1: A_{21} = C_2\epsilon\nu_1 \exp \left[-\ln 2 \left(\frac{2}{\omega_1} \left(\frac{1}{\lambda\max_1} - \frac{1}{\lambda\max_2} \right) \right)^2 \right]$$

$$i = 2, j = 2: A_{22} = C_2\epsilon\nu_2 \exp \left[-\ln 2 \left(\frac{2}{\omega_2} \left(\frac{1}{\lambda\max_2} - \frac{1}{\lambda\max_2} \right) \right)^2 \right]$$

$$i = 2, j = 3: A_{23} = C_2\epsilon\nu_3 \exp \left[-\ln 2 \left(\frac{2}{\omega_3} \left(\frac{1}{\lambda\max_3} - \frac{1}{\lambda\max_2} \right) \right)^2 \right]$$

$$i = 2, j = 4: A_{24} = C_2\epsilon\nu_4 \exp \left[-\ln 2 \left(\frac{2}{\omega_4} \left(\frac{1}{\lambda\max_1} - \frac{1}{\lambda\max_2} \right) \right)^2 \right]$$

Consequently, we get Eq. (2).

Determination of $\epsilon\nu_j$

From Eqs. (1) and (2) one obtains

$$\epsilon a_i = \sum_{j=1}^4 \epsilon\nu_j \exp \left\{ \left(-\ln 2 \right) \left[\frac{2}{\omega_j} \left(\frac{1}{\lambda\max_j} - \frac{1}{\lambda\max_i} \right) \right]^2 \right\}$$

Setting

$$Z(i,j) = \exp \left\{ (-\ln 2) \left[\frac{2}{\omega_j} \left(\frac{1}{\lambda_{\max_j}} - \frac{1}{\lambda_{\max_i}} \right) \right]^2 \right\}$$

$$\epsilon a_i = \sum_{j=1}^4 \epsilon v_j Z(i,j) \quad (4)$$

This system of four equations with four unknowns can be resolved by using a matrix method, and this allows calculation of the ϵv_j .

Calculation of Unit Peak Points

To calculate the absorption at any wavelength of the unit peaks defined by the above characteristics, we can apply the formula or

$$A(j,n,k) = C_n \epsilon v(j,n) \exp \left\{ (-\ln 2) \left[\frac{2}{\omega_j} \left(\frac{1}{\lambda_k} - \frac{1}{\lambda_{\max_{j,n}}} \right) \right]^2 \right\} \quad (5)$$

This equation is necessary to calculate absorption at a point k of the unit peak j in an n -order component sequence. For each Gaussian unit peak, and for each sequence, one has to define the absorption calculation range and the step required. An optimum calculation range is defined as a function of the precision of the calculation for a sufficiently short time (4×4 peaks, to be defined peak by peak) such that

$$\lambda_{\max_j} - \frac{3}{2} h_{1/2} < \lambda_k < \lambda_{\max_j} + \frac{3}{2} h_{1/2}$$

This can be expressed graphically as shown in Fig. 2. The choice of the calculation step, within the range, is left to the user.

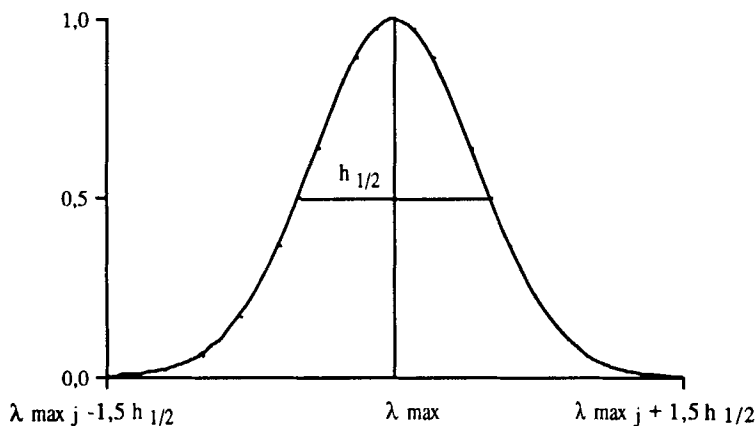


FIG. 2. Modeling of a j peak for a given n -order sequence and i band.

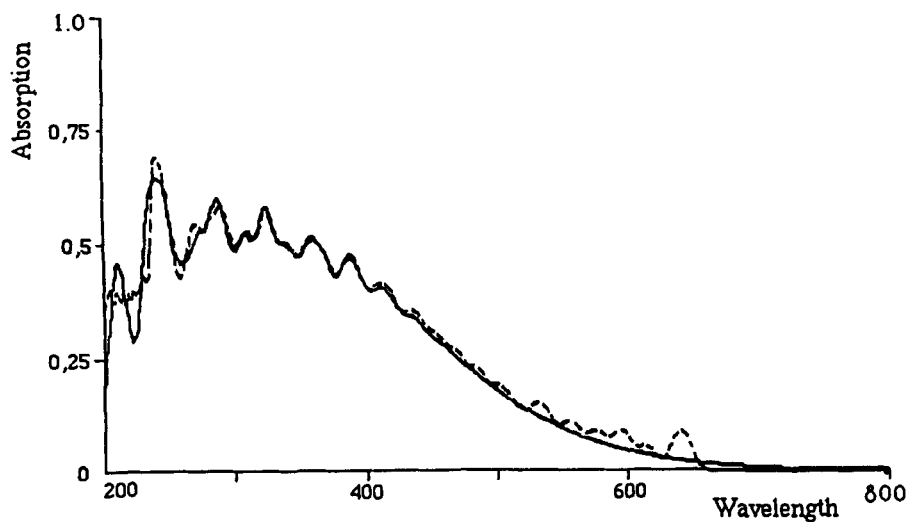


FIG. 3. Experimental (—) and calculated (- -) spectra given by the 4-band calculation. Sample PD313 (% DHC = 13).

Calculation of the Entire Spectrum

This is obtained by using

$$A_k = \sum_{n=2}^{15} \sum_{j=1}^4 A(j, n, k)$$

The difference existing between the experimental spectrum and the calculated spectrum is determined by using an SD indicator defined as follows:

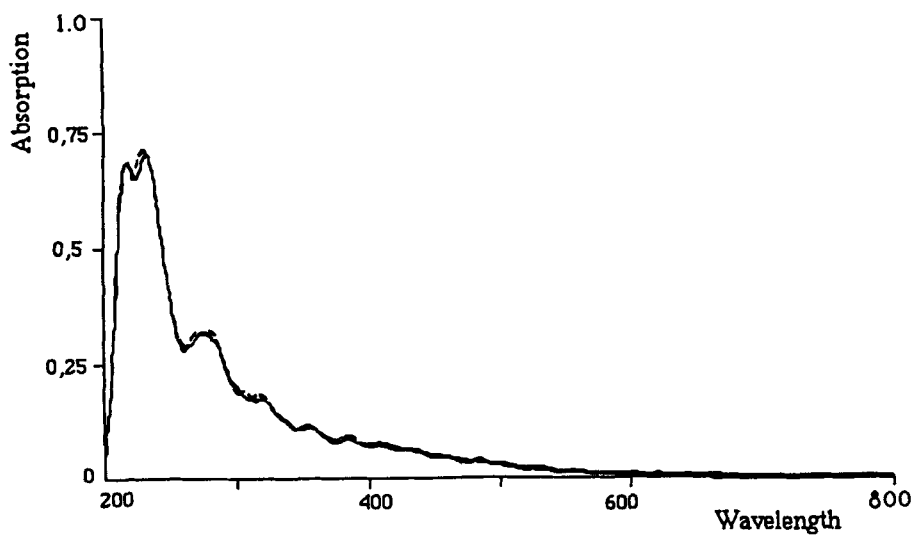


FIG. 4. Experimental (—) and calculated (- -) spectra given by the 4-band calculation. Sample PD73 (% DHC = 4).

$$SD = \sum_i \sqrt{(ED_i - CD_i)^2}$$

with ED = experimental data and CD = calculated data.

The iterative calculation ceases when the variation of the SD indicator between successive cycles is less than 0.1%, when at least 20 repeated cycles have been performed, or when the iteration diverges.

Results Obtained

At the end of the cycle, the information of Figs. 3 and 4 is obtained. The spectra of Figs. 3 and 4 correspond to two extreme levels of dehydrochlorination (13 and 4%, respectively). Beyond a DHC of about 15%, the polymer is no longer totally soluble in an organic solvent, and can thus no longer be analyzed in solution.

Description of the Simplified Method (single band calculation)

This technique allows an estimate of the concentration of different polyenic sequences, knowing the absorbance A at each principal maximum wavelength λ_{mp} for each type of sequence observed experimentally in our spectra, by using the simplified equation

$$C_n = A/l\epsilon_n$$

where C_n = n -order concentration

A = absorbance at λ_{mp}

ϵ_n = molar absorption coefficient corresponding to λ_{mp}

l = path of the light beam in cm = 1 cm

TABLE 1. Values of Different Molar Extinction Coefficients for Each Principal Maximum Wavelength

n	Wavelength, nm	$\epsilon_n \times 10^3$ L/mol·cm
2	238	20.00
3	286	34.50
4	310	73.00
5	323	121.00
6	357	138.00
7	384	174.00
8	410	203.50
9	436	233.00
10	458	261.00
11	485	290.00
12	505	320.00
13	524	350.00
14	543	380.00
15	561	410.00

TABLE 2. Distribution of Polyenic Sequences in Dehydrochlorinated PVC at 13% (PD313) and 4% (PD73) Determined by Using the 4-Band Calculation (indicated by *) and the Simplified Method (indicated by **)

<i>n</i>	PD313					PD73				
	C4B.10 + 7		C1B.10 + 7		Absolute gap, %	C4B.10 + 7		C1B.10 + 7		Absolute gap %
	mol/ L*	%Pn 4B	mol/ L**	%Pn 1B		mol/ L*	%Pn 4B	mol/ L**	%Pn 1B	
2	186.48	42.63	340.90	45.37	45.3	265.44	72.95	357.40	69.34	25.7
3	103.06	23.45	161.30	21.47	36.1	60.07	16.40	92.58	17.96	35.1
4	61.03	13.84	72.35	9.63	15.7	19.26	5.29	25.70	4.98	25.0
5	31.08	7.01	46.75	6.22	33.5	8.38	2.30	14.63	2.84	42.7
6	19.05	4.31	36.90	4.91	48.4	4.10	1.07	8.25	1.60	51.2
7	11.33	2.59	26.93	3.58	57.9	2.06	0.54	5.15	1.00	60.0
8	7.06	1.57	19.96	2.66	64.6	2.06	0.54	3.72	0.72	44.6
9	6.01	1.33	14.86	1.98	59.6	0.30	0.08	2.68	0.52	—
10	6.09	1.35	10.61	1.41	42.6	1.37	0.38	1.92	0.37	28.7
11	4.08	0.84	7.16	0.95	43.0	0.71	0.20	1.29	0.25	20.0
12	2.61	0.60	5.29	0.70	50.7	0.43	0.12	0.98	0.19	36.8
13	0.03	0.01	3.73	0.50	—	—	—	0.71	0.14	—
14	1.22	0.28	2.83	0.38	56.9	0.26	0.07	0.49	0.10	30.0
15	2.00	0.21	1.88	0.25	6.0	0.23	0.06	0.30	0.06	23.3

The values of ϵ_n coefficients for each λ_{mp} were taken from the literature for $n = 2$ [34] and for $n = 3$ to 10 [14], and were extrapolated to values for $n = 11$ to 15 [29]. These values are shown in Table 1.

Comparison of the Two Methods

Table 2 shows the results of calculations performed by using the two techniques.

These values do not take into account isolated double bonds or sequences of orders higher than 15. We assumed that such sequences were negligible because the higher the n -order increases, the lower the concentration. The concentration of a 15-order polyene is already very low (about 10^{-7} mol/L).

CONCLUSION

We can observe the size of the variations obtained by using one or another method. The higher the dehydrochlorination of the PVC, the wider the variation corresponding to the concentration of second-order sequences. This was due to an overestimation of concentrations in the single band calculation because the method took into account the nonnegligible contribution of higher order bands. In the

same way, when the polymer was weakly dehydrochlorinated, and thus had short sequences of conjugated double bonds, the variations in the concentrations of high n -order sequences were much smaller than those for a more conjugated polymer.

If only percentage values are considered, one could be led to think that the two methods gave similar results and that the simplified method, which does not require a computer, would be the best method to determine the distribution of conjugated polyenic sequences. However, in view of the considerable differences in concentrations, we conclude that the four-band calculation is much more significant for use in any rigorous study.

ACKNOWLEDGMENT

The authors thank Georges Sauvet, Laboratoire de Recherches sur les Macromolécules, Université Paris-XIII, for his very helpful assistance in computer program development.

REFERENCES

- [1] T. Van Hoang, A. Michel, C. Pichot, and A. Guyot, *Eur. Polym. J.*, **11**, 469 (1975).
- [2] T. Van Hoang and A. Guyot, *Polym. Degrad. Stab.*, **21**, 165 (1988).
- [3] W. C. Geddes, *Eur. Polym. J.*, **3**, 747 (1967).
- [4] A. K. Mukherjee and A. Gupta, *J. Macromol. Sci. — Rev. Macromol. Chem.*, **C20(2)**, 309 (1981).
- [5] T. Hjertberg and E. Sörvik, *Degradation and Stabilisation of PVC* (E. D. Owen, ed.), Elsevier Applied Science Publishers, London, 1984.
- [6] D. Druessedow and C. F. Gibbs, *Natl. Bur. Std. Circ.*, **525**, 69 (1953).
- [7] C. Decker and M. Balandier, *Eur. Polym. J.*, **18**, 1085 (1982).
- [8] C. Decker, *A.C.S. Symp. Ser.*, **364**, 201 (1988).
- [9] D. Vesely, D. S. Finch, and G. E. Cooley, *Polymer*, **29(8)**, 1402 (1988).
- [10] E. Tsuchida, C. N. Shih, I. Shinohara, and S. Kambara, *J. Polym. Sci.*, **2**, 3347 (1964).
- [11] J. P. Roth, P. Rempp, and J. Parrod, *J. Polym. Sci., Part C*, **4**, 1347 (1963).
- [12] T. Danno, H. Kondoh, K. I. Furuhashi, and K. Miyasaka, *J. Appl. Polym. Sci.*, **29**, 3171 (1984).
- [13] W. I. Bengough and I. K. Varma, *Eur. Polym. J.*, **2**, 61 (1966).
- [14] Y. Shindo and T. Hirai, *Makromol. Chem.*, **155**, 1 (1972).
- [15] A. Wirsen and P. Flodin, *J. Appl. Polym. Sci.*, **22**, 3039 (1978).
- [16] B. Ostensson and F. Flodin, *J. Macromol. Sci. — Chem.*, **A12(2)**, 249 (1978).
- [17] J. H. Bowley, D. L. Gerrard, and W. F. Maddams, *Makromol. Chem.*, **186**, 707 (1985).
- [18] J. H. Bowley, D. L. Gerrard, W. F. Maddams, and M. R. Paton, *Ibid.*, **186**, 695 (1985).
- [19] H. Kise, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 3189 (1982).
- [20] K. T. Howang, K. Iwamoto, M. Seno and H. Kise, *Makromol. Chem.*, **187**, 611 (1986).

- [21] A. Périchaud, S. Dhainaut, P. Bernier, and S. Lefrant, *Synth. Met.*, **24**, 7 (1988).
- [22] S. Dhainaut, Thèse 3ième cycle, Université d'Aix-Marseille I, 1989.
- [23] A. Périchaud, P. Bernier, M. Audenaert, S. Lefrant, and A. Le Méhauté, *Solid State Commun.*, **72**(5), 413 (1989).
- [24] A. Périchaud, P. Bernier, S. Lefrant, and A. Le Méhauté, Kluwer Academic Publishers (1989).
- [25] D. Dussoubs, A. Périchaud, and L. Savidan, *Eur. Polym. J.*, **17**, 1211 (1981).
- [26] B. Ivan, J. P. Kennedy, T. Kelen, and F. Tüdös, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 679 (1981).
- [27] B. Ivan, J. P. Kennedy, T. Kelen, and F. Tüdös, *J. Macromol. Sci.—Chem.*, **A17**(6), 1033 (1982).
- [28] D. Dussoubs, Thèse d'état, Université d'Aix-Marseille II, 1983.
- [29] A. Périchaud, Thèse d'état, Université d'Aix-Marseille II, 1983.
- [30] A. Baruya, D. L. Gerrard, and W. F. Maddams, *Macromolecules*, **16**, 578 (1983).
- [31] F. Sondheimer, D. A. Ben-Efraim, and R. Wolovsky, *J. Am. Chem. Soc.*, **83**, 1975 (1960).
- [32] E. Simon, Thèse en sciences, Université d'Aix-Marseille III, 1990.
- [33] C. Schuerch, J. R. Dombroski, and A. Sarko, *Macromolecules*, **4**(1), 93 (1971).
- [34] G. Lechermeier, A. Revillon, and C. Pillot, *J. Macromol. Sci.—Chem.*, **A12**(2), 285 (1978).

Received February 6, 1992

Revision received March 16, 1992