

Experimental determination of conjugation lengths in long polyene chains

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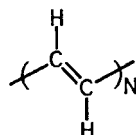
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Since the low energy absorption spectrum of a linear polyene is dominated by the strongly allowed $1^1A_g \rightarrow 1^1B_u$ transition (S_0 to S_2), it can be reconstructed for any chain length if the 0–0 band excitation energy, the band profile, and intensity are known. From this premise, this paper uses information developed in high resolution experiments on well-defined linear polyenes to extract the distribution of effective conjugation lengths from absorption spectra of solutions of long linear polyenes. These distributions are found to be dominated by short conjugation lengths. © 1995 American Institute of Physics.

I. INTRODUCTION

Linear polyenes may be specified by their chain length N , the number of conjugated double bonds (translational repeat units in the bond alternating polyene backbone) as indicated in the diagram below.



Knowledge of how the nonlinear optical response of a linear polyene depends on the number of conjugated double bonds is not only of fundamental importance, it is one of the key issues to be considered in designing new polymeric materials. While this dependence is open to experimental investigation, systematic studies have been inhibited by the lack of methods for synthesizing long polyene chains. This synthetic problem now appears to be well in hand¹ which has made possible the recent measurements of χ^3 for a series of model polyene oligomers with up to 240 conjugated double bonds by Samuel *et al.*² However, one problem remains. Even though chemical analysis leaves little doubt as to the number of repeat units in these long polyene chains, the conformations are not known and so neither is the distribution of effective conjugation lengths. This paper presents a method for estimating this distribution for a given polyene from the room temperature absorption spectrum. This method is then applied to the absorption spectra for polyenes with $N=28, 39, 68, 88, 152,$ and 240 as measured by Samuel *et al.*^{2,3} A model for the distribution of conjugation lengths in long polyene chains that accounts for the distributions derived in this paper is presented in a second paper.⁴

II. MODELING THE ABSORPTION SPECTRUM

Given a reference library of absorption spectra for planar *all-trans* linear polyenes, the decomposition of a measured absorption spectrum into an oligomer distribution would be straightforward, at least, in principle. Since the absorption spectrum of a linear polyene is dominated by the strongly

allowed $1^1A_g \rightarrow 1^1B_u$ absorption (S_0 to S_2), knowledge of the dependence of this excitation energy on the number of double bonds in a planar *all-trans* linear polyene together with the band profile and intensity for this transition would allow the generation of this library. Two of the three things that are needed, $1^1A_g \rightarrow 1^1B_u$ excitation energies as a function of the number of conjugated double bonds and the absorption band profile for the $1^1A_g \rightarrow 1^1B_u$ transition, are well known from experiment. There is less information on the third, the intensity of the $1^1A_g \rightarrow 1^1B_u$ transition as a function of the number of double bonds, but this may be reasonably estimated using molecular orbital theory.

A. $1^1A_g \rightarrow 1^1B_u$ transition energy

Excitation energies for the 0–0 bands of the $1^1A_g \rightarrow 1^1B_u$ transitions of unsubstituted linear polyenes with from 3 to 8 double bonds in conjugation have been measured for these molecules substituted in low temperature *n*-alkane crystals: Reference 5 summarizes these data and gives the citations to the original reports. The fully resolved vibrational structure of both the $1^1A_g \rightarrow 2^1A_g$ and $1^1A_g \rightarrow 1^1B_u$ transitions make it clear that the observed spectra are those of a mixed molecular crystal where the linear polyene simply replaces *n*-alkane molecules in a fully ordered *n*-alkane crystal. Since it is known from x-ray crystallography that in an *n*-alkane crystal the molecules pack as planar *all-trans* chains, this must also be the conformation of the substituted linear polyene.

We have previously shown that the 1^1B_u 0–0 excitation energies are accurately reproduced by a simple model (Hückel theory with alternating resonance integrals—the Hückel Spectrum Simulator or HSS model).⁵ Since there is an analytical solution for the energy levels in this model, it is easy to calculate the 0–0 excitation energy of a planar *all-trans* polyene chain of any length. The fact that such a calculation really amounts to extrapolating experimentally measured energies with a quantitatively accurate and physically reasonable model gives us confidence in the calculated values. Further assurance may be derived by looking at the behavior of the model in the long chain limit.

The $1^1A_g \rightarrow 1^1B_u$ excitation energy in the long chain limit calculated by this model is $16\,200\text{ cm}^{-1}$ or 2.0 eV. This

TABLE I. Representative $1^1A_g \rightarrow 1^1B_u$ excitation energies and transition dipoles obtained using the HSS model.

Double bonds	$E(1^1B_u)/hC$ (cm^{-1})	$\langle 1^1A_g \mu 1^1B_u \rangle$ (Debye)
2	47 630	5.160
3	37 740	6.876
4	32 180	8.381
6	26 240	10.873
8	23 190	12.819
10	21 380	14.351
15	19 080	16.957
20	18 040	18.509
50	16 580	21.336
100	16 300	22.022

is reasonably close to the value reported for the polyacetylene absorption band edge.

Since the simple HSS model not only accurately reproduces 1^1A_g to 1^1B_u transition energies in n -alkane solution for planar all-*trans* linear polyenes with 3–8 double bonds in conjugation, but appears to behave reasonably in the long chain limit, it provides the library of 0–0 band excitation energy versus chain length. Representative values are summarized in Table I and are plotted in Fig. 1.

B. 1^1A_g to 1^1B_u transition intensity

Unfortunately, the chain-length dependence of the intensity of the $1^1A_g \rightarrow 1^1B_u$ transition is not as thoroughly understood as is the transition energy. This is primarily due to the difficulties of making quantitative measurements on the low temperature mixed crystals for which the geometry of

the polyene chains is known to be *trans*-planar. Accordingly, we use theoretical values calculated with the simple model that accurately reproduces the excitation energies. It should be noted that although the $1^1A_g \rightarrow 1^1B_u$ transition dipole is proportional to the number of repeat units in the chain for the nonalternating chain, the increase of transition dipole with chain length is strongly suppressed by the alternation of resonance integrals that must be included to obtain the experimentally measured excitation energies. Representative values for the transition dipole moments calculated assuming a *trans*-planar geometry with all C=C bond lengths equal to 1.332 Å, all C–C bond lengths equal to 1.451 Å, and all C=C–C bond angles equal to 125° are given in Table I and plotted in Fig. 1.

C. 1^1A_g to 1^1B_u band profile

To simulate a spectrum, a delta function at the $1^1A_g \rightarrow 1^1B_u$ 0–0 excitation energy for a given chain length is convoluted with the appropriate absorption band profile weighted by the squared transition dipole times the probability of finding that chain length. Since the vibronic development of this transition is very similar for all chain lengths, any linear polyene $1^1A_g \rightarrow 1^1B_u$ absorption band shifted by its 0–0 excitation energy is a reasonable candidate for the band profile. The choice is an arbitrary one: we have elected to use the absorption spectrum for *trans* β -carotene in CS₂, shifted by 20 876 cm^{-1} to lower energy. This spectrum is shown in Fig. 2.

There is a recursive element in this analysis since the room temperature absorption spectrum of β -carotene may itself be the superposition of contributions from different

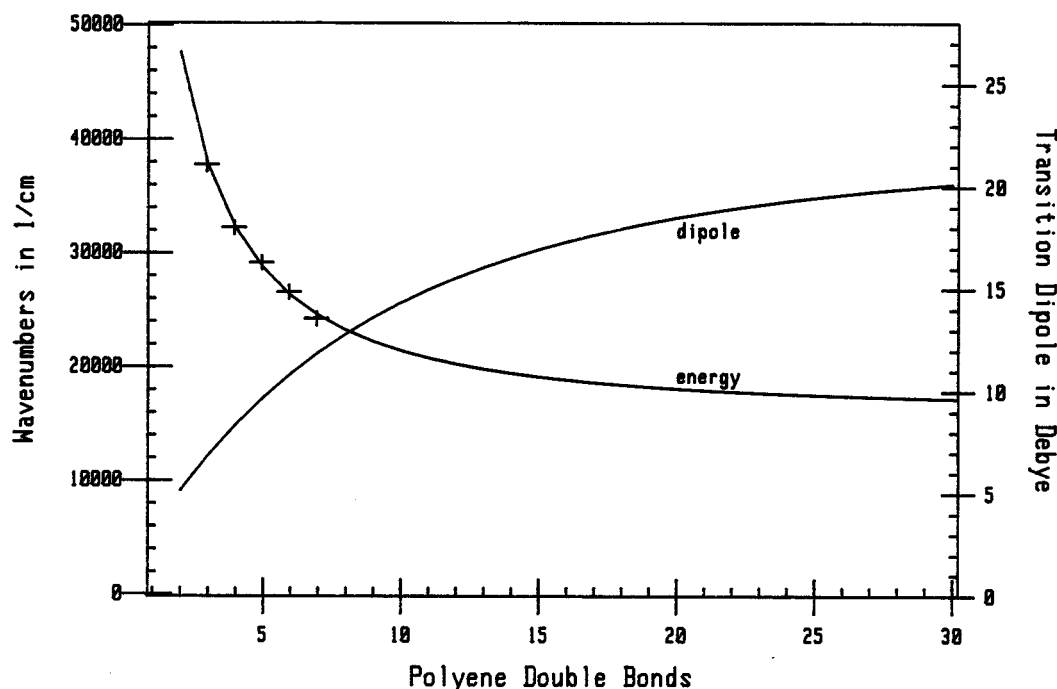


FIG. 1. Chain-length dependence of $1^1A_g \rightarrow 1^1B_u$ excitation energy and transition dipole. The smooth curves are drawn through values calculated with the HSS model. The $1^1A_g \rightarrow 1^1B_u$ 0–0 band excitation energies measured for linear polyenes substituted in low temperature n -alkane crystals are plotted as '+'s.

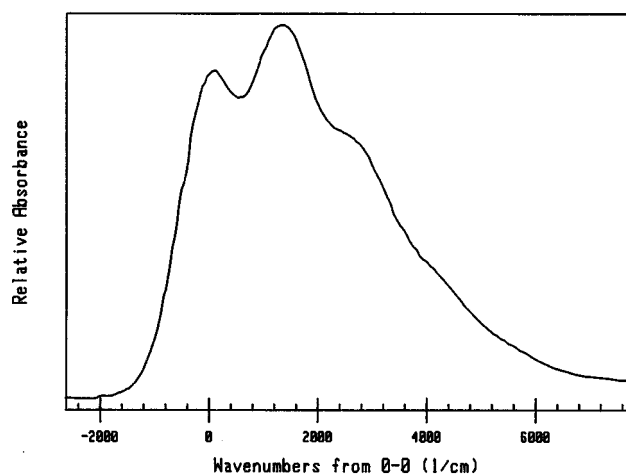


FIG. 2. Linear polyene absorption profile (absorption spectrum of β -carotene in room temperature CS_2 solution shifted $20\,876\text{ cm}^{-1}$ to lower wave number).

conjugation lengths, especially given the nonbonded interactions between the β -ionylidene ring and the polyene chain. This issue has been addressed in a previous paper where it was found that the β -ionylidene ring generates a range of conjugation lengths that is only 0.25 double bonds wide;⁶ this may be safely neglected. Further reassurance is provided by the fact that the model that accounts for the distributions derived in this paper predicts that the conjugation length distribution for chains of the length of β -carotene are dominated by the molecular chain length.⁴

III. ANALYSIS OF THE MEASURED SPECTRA

The algorithm for determining the chain length distribution from a measured absorption spectrum is straightforward. To calculate the absorption spectrum that corresponds to a given distribution, the band profile shown in Fig. 2 is shifted to the 1^1A_g to 1^1B_u transition energy for a chain with N double bonds in conjugation, weighted by the probability for that chain length times the squared transition dipole, and accumulated. The probability amplitudes are adjusted to minimize the rms deviation between the calculated and measured spectra. To demonstrate this decomposition we have analyzed six absorption spectra measured for the samples for which Samuel *et al.*^{2,3} reported χ^3 values. Three representative spectra are shown in Fig. 3.

It is informative to compare these measured absorption spectra to the absorption band profile shown in Fig. 2 shifted to the 0-0 energy obtained from the HSS model (ideal oligomer spectra). These ideal oligomer spectra are the spectra calculated by the means described in Sec. II when the distribution of conjugation lengths is taken to be a delta function at the molecular chain length. There are substantial differences: as is seen in Fig. 4 the measured spectra exhibit substantially less absorption to low energy and more absorption to high energy than is expected. This suggests that the distribution of conjugated chain lengths differs from the ideal situation where most of the molecules exist as fully conjugated chains. There must be significant contributions to the absorption spectrum from conjugation lengths that are shorter than the molecular chain lengths.

To model these absorption spectra we tried a number of forms for the conjugation length distribution: a single Gauss-

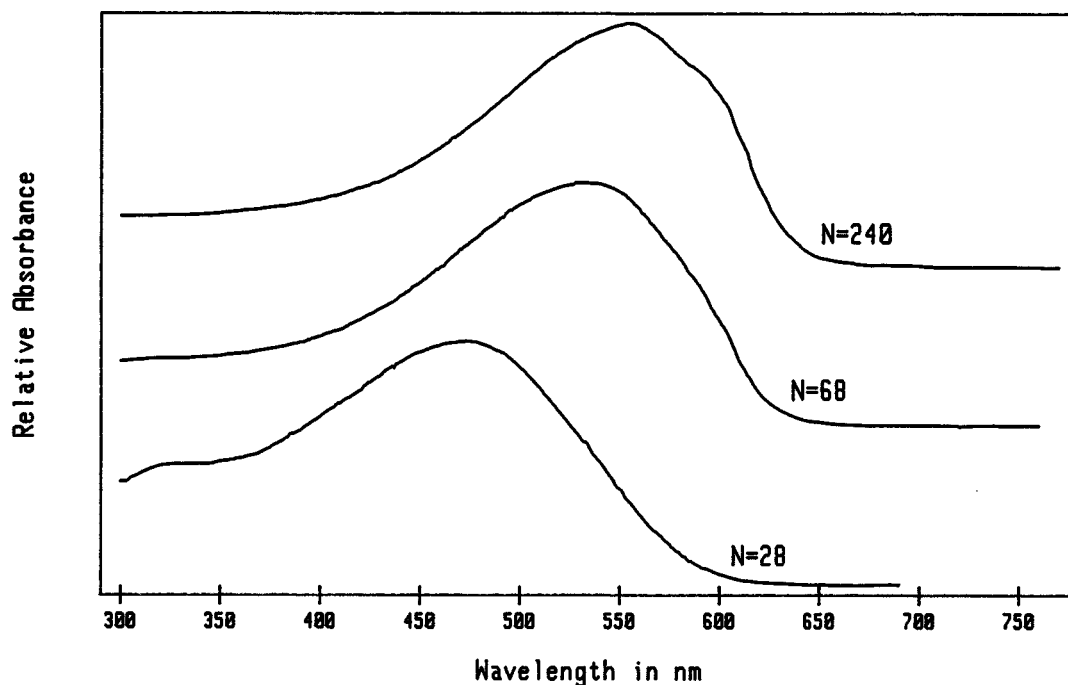


FIG. 3. Absorption spectra for long polyenes (28, 68, and 240 double bonds) in room temperature THF solution as measured by Samuel *et al.* (Ref. 3).

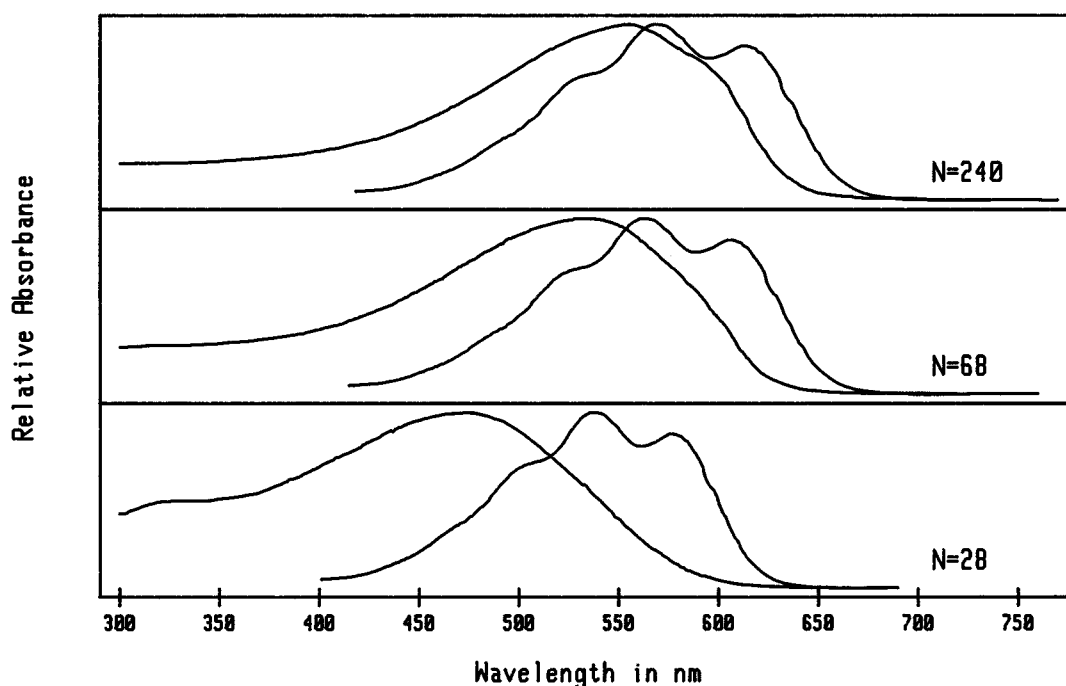


FIG. 4. Absorption spectra of solutions of long polyenes compared to the corresponding ideal oligomer spectra. The ideal oligomer spectra were generated by shifting the β -carotene absorption spectrum so that the 0–0 band energy is at the value predicted by the HSS model. The HSS model accurately reproduces all of the 0–0 excitation energies that have been measured for planar all-*trans* polyene chains in *n*-alkane crystals.

ian centered at the molecular chain length (that is, the maximum possible conjugation length), a single Gaussian centered at the chain length that minimized the squared deviations of the calculated and measured spectra, etc. We were somewhat surprised to find that distributions where probability increased with conjugation length gave spectra that differed qualitatively from the those measured, whereas distributions where probability *decreased* with conjugation length did much better. The best model by far contained two Gaussians centered at $N=2$, the shortest conjugation length considered

$$P(n) = \frac{e^{-(n-2)^2/\sigma_1^2} + A e^{-(n-2)^2/\sigma_2^2}}{\sum_{n=2}^N (e^{-(n-2)^2/\sigma_1^2} + A e^{-(n-2)^2/\sigma_2^2})}. \quad (1)$$

In this model three parameters (two widths and the relative amplitude for the broader of the two Gaussians) were varied to obtain a best fit to the measured spectra. The distributions that gave the best fit to the measured spectra for three representative cases are shown in Fig. 5. The measured and simulated spectra are compared in Fig. 6. As is seen in Fig. 6, the resulting fits are almost perfect. The only apparent deviations are at short wavelengths and these derive entirely from the partially resolved vibrational structure in the reference spectrum.

Similar analyses on solution spectra for other molecular chain lengths ($N=39$, $N=88$, $N=152$) were also carried out with exactly analogous results. The chain length distribution parameters for all six cases are summarized in Table II.

IV. CONCLUSIONS

Absorption spectra measured for solutions of long model polyenes show significantly less intensity at long wavelengths and significantly more intensity at short wavelengths than would be predicted from what is known about ideal oligomer spectra. The conjugation-length dependence of the

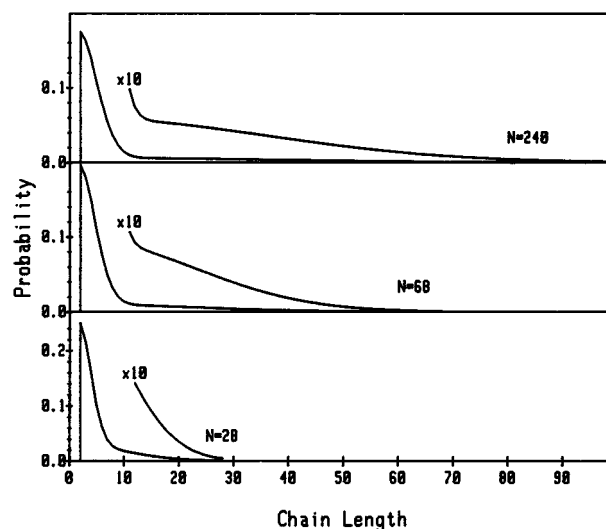


FIG. 5. Chain length distributions that reproduce the absorption spectra measured for THF solutions of long linear polyenes (28, 68, and 240 double bonds in conjugation in the lower, middle and upper panels, respectively).

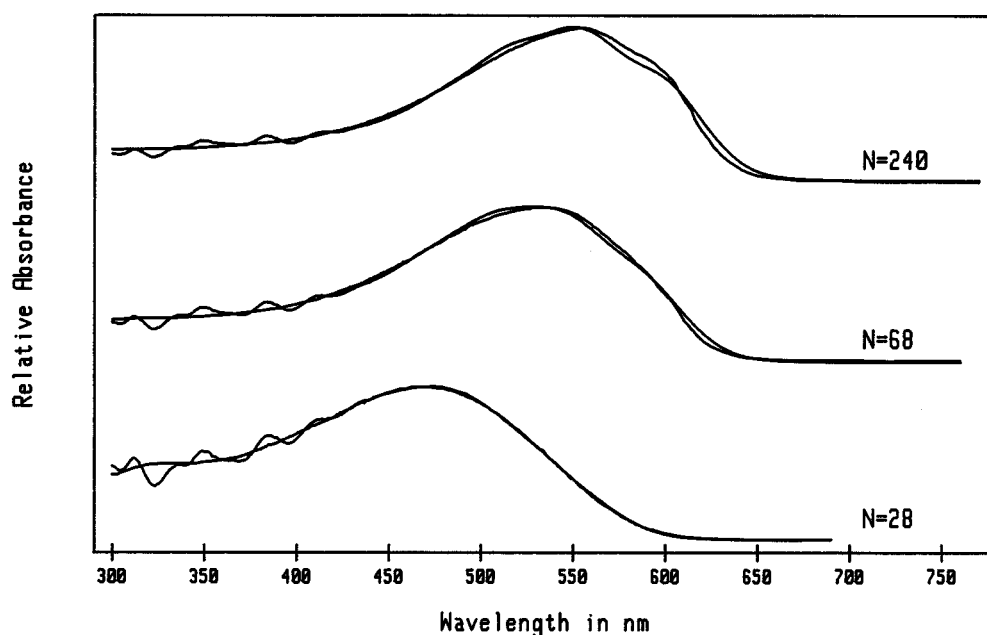


FIG. 6. Fit of absorption spectra measured for long polyenes by the convolution of the chain length distribution shown in Fig. 5 with the band shape shown in Fig. 2. For each molecular chain length the close correspondence between the two curves makes it impossible to distinguish the measured from the simulated spectrum except at short wavelengths where the simulated spectrum shows more structure.

energy and intensity of the 1^1A_g to 1^1B_u transition that has been developed in high resolution experiments on well-defined linear polyenes can be used to extract the distribution of effective conjugation lengths from the absorption spectra measured for solutions of long linear polyenes. These distributions are found to be dominated by short conjugation lengths, exactly as would be predicted if it is assumed that higher energy conformations where conjugation is broken—presumably by twisting about essential single bonds—exist.⁴ While a different extrapolation of the high resolution data on well-defined oligomers would change the distribution parameters, the qualitative form is dictated by the directly determined data on short chains. Of course, we have left open the question of the detailed structure and dynamics of these segmented conformers.

Given the fact that for $N \geq 4$ fluorescence yield increases with decreasing chain length, it might be imagined that ex-

citation on the blue edge of the absorption band would result in emission from the short segments that dominate the conjugation length distribution. This would only be expected if these segments were isolated. Because they are linked together we expect that the transfer of excitation energy from short to longer segments will effectively quench the emission from the short segments. While we do not feel that we know enough about the detailed structure and dynamics of the conjugation breaks to speculate further on the fate of excitation after photon absorption, this is an issue that deserves serious attention.

When samples contain a broad distribution of effective conjugation lengths, experimentally determining the conjugation-length dependence of nonlinear optical response is difficult, but, at least in principle, it should still be possible. The determination of these distributions that is presented here is a first step in this more extensive analysis.

ACKNOWLEDGMENTS

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TABLE II. Chain length distribution parameters. The probability of chain length n is given by Eq. (1) where $\sqrt{\ln(2)}\sigma_1$ is the half-width at half-maximum (HWHM) for the short chains, $\sqrt{\ln(2)}\sigma_2$ is the HWHM for the long chains, and A is the relative amplitude of the long chains.

Double bonds	HWHM short chains	HWHM long chains	Relative amplitude long chains
$N=28$	2.80	10.73	0.121
$N=39$	3.16	13.47	0.090
$N=68$	3.68	19.76	0.052
$N=88$	3.78	27.35	0.048
$N=152$	3.97	36.32	0.033
$N=240$	4.09	40.39	0.035

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