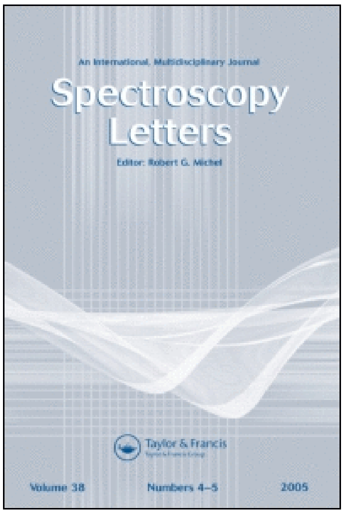

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Simulated Annealing Algorithm as Applied to the Resolution of Complex Spectra

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ABSTRACT

Simulated annealing algorithm (SAA) was applied to locate the global minimum of a non-linear least square function for spectra fitting. The resolution of methylene region of two ^{13}C-NMR spectra of polystyrene was implemented successfully with this method. Compared with the existing methods, this technique has important advantages in two respects: one is that the resulting resolution of spectra with this method have lesser dependence on the initial values of the parameters inputted to start the optimization of the least square function; the other is that it provides the possibility to determine the peaks which cannot be recognized by the observation. With this technique, some possible error arising from the observation can be avoided.

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INTRODUCTION

The resolution of spectra is one of essential techniques for quantitative analysis with modern analytical instruments. With the development of sensitivity and resolve power of the instruments, and increase in the complexity both in structure and in composition of samples analyzed, the spectra one encounters may be rather complex, and the resolution of the spectra may became very difficult.

Several methods such as factor analysis method [1,2], deconvolution method [3,4] and least square method[5], have been used for the digital data handling of the spectra. Among these techniques, the least square method is very effective if the contributing components are unknown or unobtainable. Unfortunately, with all the existing methods, spectra can only be resolved accurately only when the number and position of the contributing peaks are observable.

In fact, to resolve a spectrum with the least square method, for an example, one firstly has to construct a least square function for the spectrum simulating, then to find the minimum of the function in a reasonable range. On the supposition that the model for the simulating is correct, the minimum should be a global one. This is a problem of optimization. The variables are the parameters defining all the contributing peaks, and the reasonable range of the variables termed phase space is defined to be the set of points bounded by the minimum and maximum values of all variables.

Many algorithms, such as Gauss-Newton method, Marquardt[6] method and some other Newton's based methods[7,8], have been used to solve this problem. However, all these methods are local optimization algorithm. They can only find local minimum close to the values of the variables termed initial values of the variables assigned to start the optimization. The results of the resolution by local optimization algorithms are close to the initial values, and the number of the peaks has to be pre-decided. It means that, when local optimization is applied to resolve a spectrum, the initial values must be essentially close to the real ones of the respective variables.

In some cases, the contributing peaks are well dispersed and the determining the initial values close enough to the real values is possible. Nevertheless, in else cases that the contributing peaks are heavily overlapped, and even some peaks are covered by the others, the determination of such initial values will become very difficult.

Therefore, some algorithms, which can find the global minimum with lesser dependence on the initial values, are required. However, little or no progress has so far been reported in this respect.

As a global optimization algorithm, Simulated annealing algorithm[9] (SAA) has found broad application in the fields of physics and computational chemistry[10,11], and it can find the global minimum of the least square function for a spectrum fitting in the phase space. In this paper, the applicability of the SAA to the resolution of methylene region of ^{13}C-NMR of polystyrene is reported, and the procedure is described.

EXPERIMENTAL

The ^{13}C-NMR spectra were recorded at 60°C at 500MHz in 15% *O*-$C_6D_4Cl_2$ on a Bruker AM-125 spectrometer. Tetramethylsilane (TMS) was added as an internal. The spectra were ^{1}H noise decoupled and obtained after accumulation of 2000-7000 transients. The flip angle is set 90^0.

Sample 1 is ionic polymerized polystyrene provided by the Polymer Laboratory in the Chemistry Department of Nanjing University, China. The viscosity-average molecular weight is 260,000 measured with Size Exclusive Chromatograph (SEC). The distribution coefficient is 1.1.

Sample 2 is thermal polymerized polystyrene at 70 °C in our laboratory, it was purified by dissolution-reprecipitation with chloroform and methanol. The viscosity-average molecular weight was measured to be 780,000 with SEC, and the distribution coefficient is 1.32.

Theory

The least square function for a spectrum simulation can be constructed according to the least square principle.

$$S(P) = \sum_{i=1}^{n} (y_i^{cal} - y_i^{\exp})^2 = \sum_{i=1}^{n} (\sum_{j}^{m} f(p_j, x_i) - y_i^{\exp})^2 \qquad (1)$$

Where n is the number of data points of the scattered spectrum, m the number of the contributing peaks, x_i the values of abscissas (e.g. chemical shifts in ^{13}C-NMR spectra) of ith data point, y_i^{cal} and $y_i^{\exp}$ are the values of ordinate corresponding to x_i in simulated spectrum and experimental spectrum respectively, p_j the set of parameters defining jth contributing peak, P the set of the parameters defining all the contributing peaks. $f(p_j, x_i)$ the model function to fit the jth contributing peak, S the cost function.

When Lorentz's and Gauss' composite model function is used, $S(P)$ can be formulated as:

$$S(P) = \sum_{i=1}^{n}\{\sum_{j=1}^{m}\{a_{l,j}/[1+(x_i-b_j)^2/c_{l,j}^2]+a_{g,j}\exp[-(x_i-b_j)^2/c_{g,j}^2]\}-y_i^{\exp}\}^2 \qquad (2)$$

In equation (2), variables $a_{l,j}, c_{l,j}$ are defined to represent the height, the width of jth peak of Lorentz model respectively, variables $a_{g,j}, c_{g,j}$ are defined to be that of Gauss model, b_j is the position of jth peak.

The problem of the optimization can be written as

$$\begin{aligned} &\min S(P) = S(P^{opt}) \\ &P \in E \end{aligned} \tag{3}$$

In equation (3), E is the phase space, which is bounded by:

$x_{min} \le b_j \le x_{max}$ $\quad j=1,2,...m$

$a_{l,j}, a_{g,j} \ge 0$ $\quad j=1,2,...m$

$c_{l,j}, c_{g,j} > 0$ $\quad j=1,2,...m$

The phase space can also include the information of the spectra provided by observation and experimental results. Sequentially, with the initial values assigned, the optimization of the cost function proceeds.

A general procedure of the optimization by a local optimization algorithm or the SAA can be described below.

At the starting point of the optimization, all the variables are set at the initial values. Thereafter, the values of the variables are changed in each step, and the value of the cost function is evaluated. The new values of the variables are accepted or abandoned according to the change of the value of the cost function and certain criterion. The iteration is repeated many times until a given standard for the completion is conformed.

The main difference between the SAA and anyone of the local optimization algorithms is the difference in the criterion for the acceptation of new variables. The criterion of local optimization algorithms is that the new values of the variables are accepted only when the value of the cost function decreases. But in the SAA, the Metropolis[12] criterion is adopted, the possibility $p(\triangle E)$ for the acceptation of new values is determined by the equation $p(\triangle E)=exp(-\triangle E/kT)$.

RESULTS AND DISCUSSION

Two examples (sample 1 and sample 2) were selected to demonstrate the applicability of the SAA to the resolution of methylene region of ^{13}C-NMR spectra of polystyrene , the selected regions of the spectra are presented in Figure 1 and Figure 2 respectively.

The number of peaks in Figure 1, which can be picked out by observation, is no more than 20 and no less than 16, and in Figure 2 is between 17 and 13. However, if one Consider the position of the methylene carbon atoms in the polystyrene chain, the ^{13}C-NMR resolved number of repeating units in polystyrene chain can be inferred to be 6 and the number of the contributing peaks should be 20[13,14]. Therefore, the number of the contributing peaks, represented by n in equation (2), of the spectra (mehtylene regions in the ^{13}C-NMR spectra of sample 1 and sample 2) to be resolved was determined to be 20.

The initial values of the variables $a_{g,j}, a_{l,j} (j=1,2,...20)$ in equation (2) were assigned to be 1, that of $c_{g,j}, c_{l,j}$ $(1,2,...20)$ to be 0.6. The initial values of b_j were assigned to be well distributed between $x_{\min}$ and $x_{\max}$. The constant k in Metropolis criterion was appointed 0.0042 and the constant T, which is named as temperature, from 3100 to 1.

In the procedure of the optimization, the values of the variables were changed at random in the phase space, and the new values of the variables were accepted or abandoned according to the Metropolis criterion. The iteration was repeated at a temperature for 10,000 times, then the temperature decreases to be 90% of the last one and the iteration proceeds at that new temperature again for same iterations. After the temperature decreases to 200, the temperature decreases by 20 after every 10,000 iterations until the temperature equals 20.

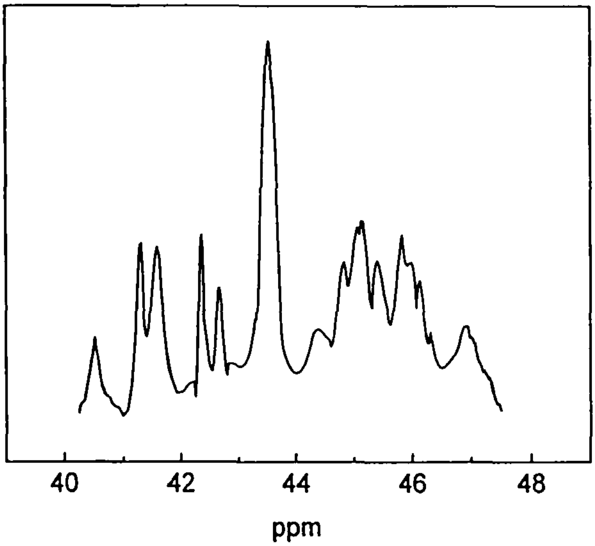


Figure 1 Methylene region in ^{13}C-NMR spectrum of polystyrene of sample 1

Finally, the temperature decreases by 40% after each of the same iterations and the procedure of the optimization ended when the temperature equals 1.

The initial values and constants k, T for the optimization relating to the spectrum in Figure 1 is the same as that in Figure 2. In order to make the procedure general, no further information about the spectra was used to shrink the phase space. It is clear that the initial values were not assigned according to observation.

Figure 3 and Figure 4 present the comparison between the simulated spectra and the experimental spectra (presented in Figure 1 and Figure) respectively. The curves of the value of the cost function versus computing

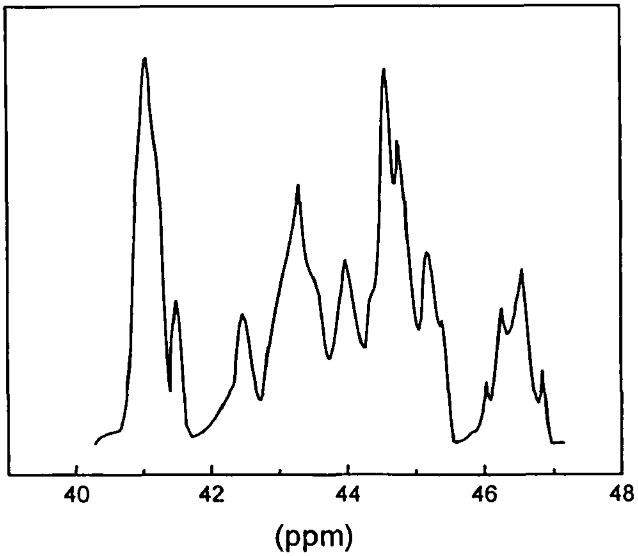
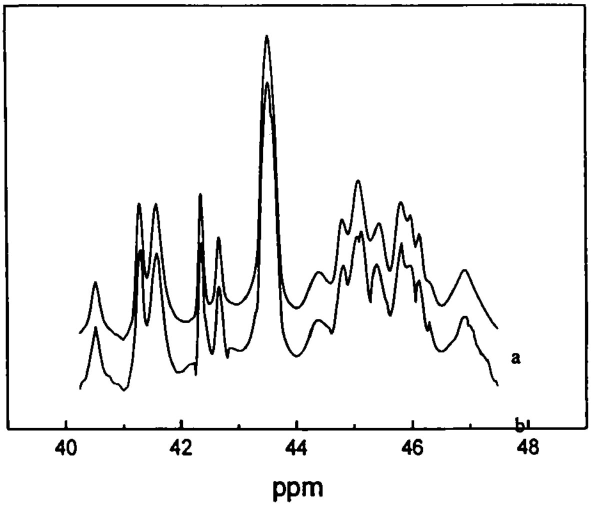


Figure 2 Methylene region in ^{13}C-NMR spectrum of polystyrene of sample 2

times are shown in Figure 5 and Figure 6. The resolved contributing peaks of the spectra are shown in Figure 7 and Figure 8.

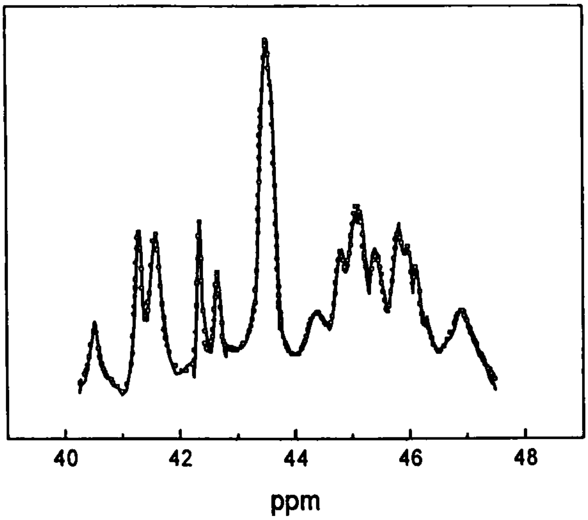
The values of the position and area of the contributing peaks resolved are presented in Table 1, in which each relative error is given as the ratio of the area between a simulated spectrum and the corresponding experimental spectrum to the total area of this experimental spectrum. From the Figure 3, Figure 4 and the values of the relative errors in Table 1 we can see that each of the simulated spectra is in good agreement with the experimental spectra respectively.

Each procedure of the optimization took about 13 hours with a Pentium 166 Personal Computer. The change of the initial values make no



a: Simulated spectrum b: Experimental spectrum

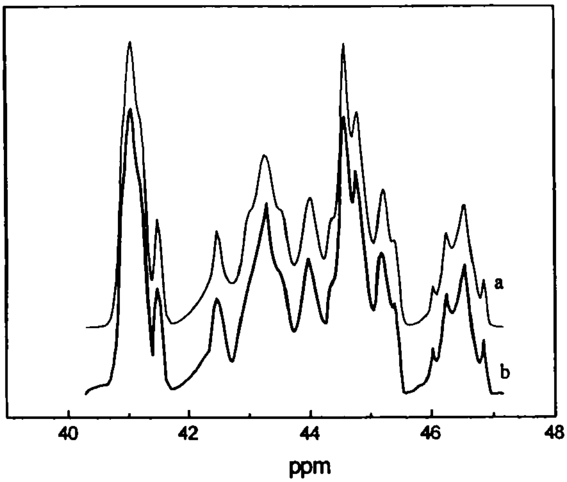
(A)



Scatter graph: Simulated spectrum
Line graph: Experimental spectrum

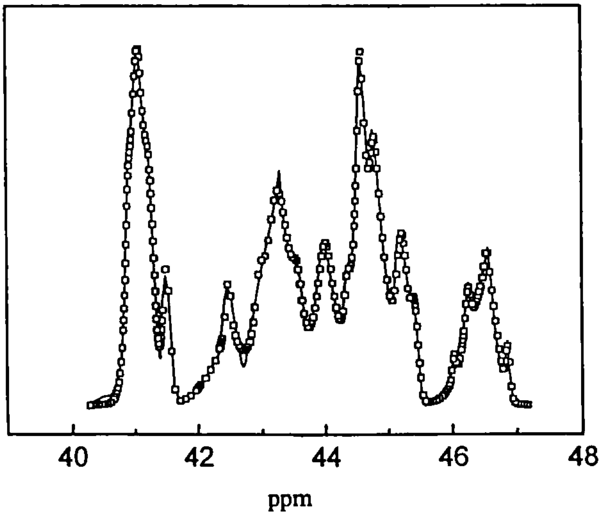
(B)

Figure 3 Comparison of the simulated spectrum with the experimental spectrum in Figure 1



a: Simulated spectrum b: Experimental spectrum

(A)



Scatter graph: Simulated spectrum
Line graph: Experimental spectrum

(B)

Figure 4 Comparison of the simulated spectrum with the experimental spectrum in Figure 2

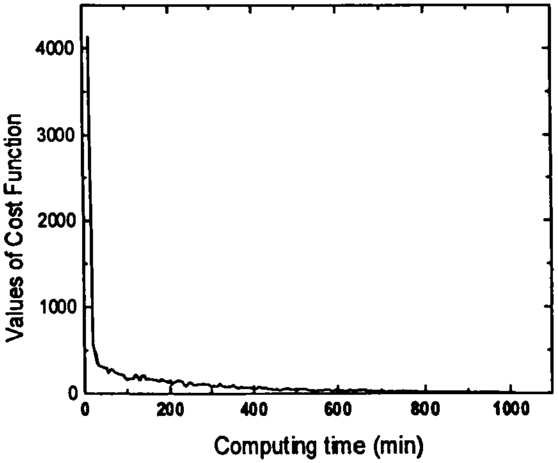


Figure 5 Decrease of the cost function with the times of the iteration in the resolution of the spectrum in Figure 1 the by SAA

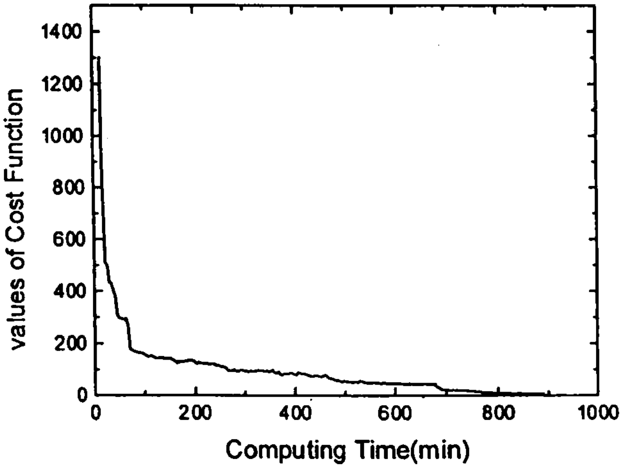


Figure 6 Decrease of the cost function with the times of the iteration in the resolution of the spectrum in Figure 2 the by SAA

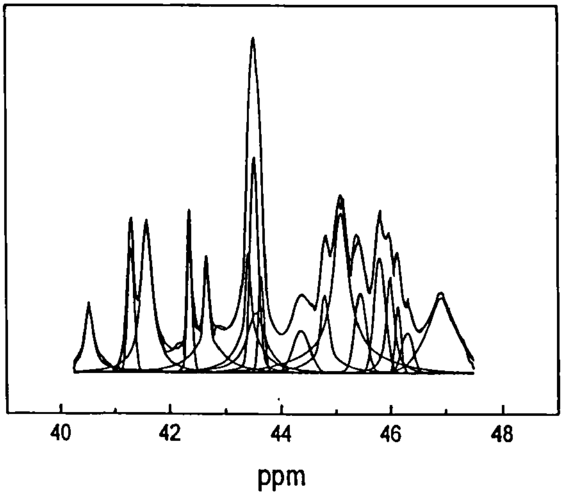


Figure 7 Contributing peaks resolved by SAA of the spectrum in Figure 1

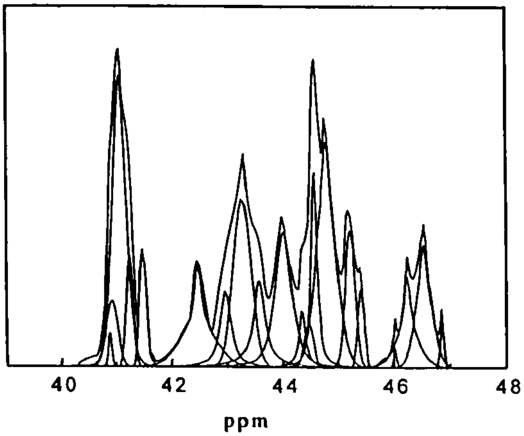


Figure 8 Contributing peaks resolved by SAA of the spectrum in Figure 2

Table 1. Resolution of the spectra by simulated annealing algorithm

Resolution of Figure 1.			Resolution of Figure 2.		
No.	CS[1] at peak	Area in percentage (%)	No.	CS[1] at peak	Area in percentage
1	40.52	3.65	1	40.89	0.41
2	41.30	3.09	2	40.94	2.63
3	41.60	9.39	3	41.07	14.31
4	42.36	2.64	4	41.25	2.67
5	42.67	6.68	5	41.49	2.76
6	43.42	7.40	6	42.47	7.07
7	43.53	7.70	7	42.95	3.99
8	43.55	6.24	8	43.26	10.24
9	43.66	2.26	9	43.56	5.21
10	44.35	2.84	10	44.00	9.37
11	44.80	5.07	11	44.33	1.93
12	45.11	17.90	12	44.46	1.45
13	45.46	4.07	13	44.57	5.86
14	45.81	5.13	14	45.78	14.24
15	46.01	4.09	15	45.23	4.71
16	46.13	1.49	16	45.42	1.81
17	46.30	1.83	17	46.02	0.21
18	46.93	8.53	18	46.26	4.62
			19	46.55	5.98
			20	46.85	0.53
Relative error: 3.96%			Relative error: 2.38%		

1)CS: Abbreviation of Chemical Shift

difference to the results of the resolution through adjusting the constants and step length of the iteration, but it will lead to the changes in the computing time.

Local minimization algorithms locate the minimum point either utilizing the numerical steepest approach or following the best path indicated by some derivative of the function. Therefore, it will be trapped in the local minimum near the initial values, and different initial values will lead to different minimum point. When local optimization algorithms are applied to the resolution of a spectrum, the results obtained will be varied with the change of initial values. Hence, to resolve a spectrum correctly with these methods, one has to find the initial values of the variables very close to the real ones.

Usually, the initial values are determined according to the maximum points and reflection points. As mentioned above, when some of the contributing peaks are heavily overlapped or even completely covered, only for a part of the peaks can the values of variables, decided by observation and used as the initial values, be considered close to the real values of these variables roughly. But for remains, the initial values have to be decided randomly. This will results in some error in the results of the resolution.

Nevertheless, in the procedure of the optimization by SAA, the Matropolis acceptation criterion is adopted, and the probe is moved and allowed to overcome small maxima in the beginning, thereby have the ability to move out of local minima. With this method, the results gotten are independent of initial values. Through one selecting the procedure properly, the resolution of spectra can be implemented correctly. This feature will be important when the spectra to be resolved are complex.

There may be some misleading in the thought that to make the results of the resolution close to initial values, which are decided according to observation, is a better way to make the results practical. In fact, a spectra can be thought to be a result of the accumulation of all the contributing components.

The situation of the accumulation may be quite different from what we observed.

In some cases, the real values of some variables can be determined by experiments, and that of some others can be decided close to the real values by observation. The SAA can also make use of this knowledge through changing the bound of the phase space and carry out better resolution for the values of the variables undecided. For example, if the position or the range of the position of *i*th peak can really be determined undoubtedly by an experiment, the value of the variable b_j will be fixed or bounded according to the range in phase space, which can save the computing time. As can be seen above, the phase space in this work are designed according the basic knowledge which can be acquired from most spectra.

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