# New Approach To Determine Orthopositronium Lifetime Distributions in Polymers: A Comparison between Maximum Entropy and the Numerical Laplace Inversion Methods

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*Received April 30, 1996; Revised Manuscript Received September 3, 1996*[⊗]

ABSTRACT: This work proposes to extract reliably the continuous distribution of orthopositronium (o-Ps) lifetimes in polymers from the positron annihilation lifetime spectra by solving a Fredholm integral equation using the maximum entropy method. The performance of the maximum entropy method (MELT) and the numerical Laplace inversion (CONTIN) methods for the reconstruction of the o-Ps annihilation lifetime distributions in polymers is compared using computer-simulated spectra. Both the MELT and CONTIN algorithms provide excellent estimates of the integrated intensities and the average lifetimes of o-Ps components in the simulated spectra. The width of the o-Ps lifetime distribution obtained by MELT is appreciably closer to the input value as compared with the result obtained by CONTIN, especially if the total number of counts in the data set is relatively low ($N_0 = 2-4$ million). The widths of o-Ps lifetime distributions obtained by MELT can be further modified and become even closer to the input value if we take into account the broadening of o-Ps lifetime distribution induced by some intrinsic factors in the simulation, for example, the finite statistics, range of lifetime grids, etc. MELT requires only relatively low statistics and does not need a reference spectrum with a single lifetime, which gives us the opportunity to reduce the measurement time and the possible negative influence of irradiation dose and the zero-time channel shift. The results in this work support the earlier conclusion based on the experimental evaluation that MELT is a powerful method for reconstruction of the o-Ps lifetime distribution in polymers (*Nucl. Instrum. Methods B* **1996**, *117*, 467−473).

## Introduction

The correlation between the free-volume properties and the viscoelasticity of polymers has been a topic of interest for several decades.[1] The average free-volume hole size, size distribution, and content influence the relaxation spectra, mobility of segments, and various transport phenomena in polymers.[1−3] Precise measurement of free-volume parameters, especially the free-volume distribution in polymers, becomes necessary to provide structural information which is related to the bulk properties of polymers. The positron annihilation lifetime spectroscopy (PALS) is a unique method to probe the free-volume properties of amorphous and semicrystalline polymers.[4] The effectiveness of PALS results from the formation of orthopositronium (o-Ps) atom and its localization in the free-volume space[5,6] and therefore the average hole size can be estimated from the average lifetime of the o-Ps atoms.[4,6,7] The correct determination of o-Ps lifetime distributions is thus a crucial point in providing the information about free-volume distributions in polymers. The relation between the mean o-Ps lifetime and the average free-volume size is established; however, the relation between the o-Ps lifetime distribution and the free-volume size distribution is still in debate.[6]

Due to the heterogeneity of local molecular structure in a polymer and the existence of different positron states, it has been proposed that the experimental positron lifetime spectrum should contain an integral of continuous decay functions[8]

$$y(t) = N_0 R(t) * \int_0^\infty \frac{f(\tau)}{\tau} \exp\left(-\frac{t}{\tau}\right) d\tau + B \qquad (1)$$

where $y(t)$ is the experimentally measured spectrum, $R(t)$ is the resolution function, * denotes the convolution, $f(\tau)$ is the continuous positron-lifetime probability distribution function (PDF), $N_0$ is the total number of counts, and $B$ is the noise and number of background counts. From the experimental data the $f(\tau)$ function may be extracted by inversion of the problem. The difficulty with such an inversion process is that it is ill-conditioned and the uniqueness of the solution is not assured.[9] There are several algorithms used to extract $f(\tau)$, i.e., the numerical Laplace inversion method[10,11] (or the constrained, regularized least-squares method[12]), the eigenfunction expansion of the Laplace integral,[9] and the maximum entropy methods.[13−15] However, there are also some limits to these methods, e.g., the convergence of the solution in the eigenfunction method is very slow,[9] and the CONTIN method needs a reference spectrum and high statistics and is not able to avoid the zero-time channel shift between the sample and reference spectra.[10,11] Recently, Shukla et al. have developed a program named the maximum entropy lifetime method (MELT), in which the maximum entropy method of solution is applied.[13−15] They have applied MELT to extract the PDFs of relatively shorter positron lifetimes in metals, superconductors, and semiconductors.[13−15] Recently, it has been shown that MELT is a promising method for finding a reliable o-Ps distribution of a PAL spectrum in polymers.[16] The purpose of this paper is to examine and compare the performance of both MELT and CONTIN routines in reconstruction of o-Ps lifetime distributions for polymers by using simulated spectra.

## The MELT and CONTIN Algorithms

**MELT Method.** Equation 1 has the form of Fredholm integral equation of the first kind. If we denote

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⊗ Abstract published in *Advance ACS Abstracts,* November 1, 1996.

S0024-9297(96)00639-0 CCC: $12.00 

the kernel $K(t,\tau) = R(t)^* \exp(-t/\tau)/\tau$ in eq 1, we can rewrite eq 1 as a system of linear algebraic equations, where $f_i$ represents the value of the unknown $f(\tau)$ at a certain reference grids,[13−15] i.e.

$$\sum_{\mu=1}^{n_\tau} K_{j\mu} f_\mu + B_j = y_j, \quad j = 1, 2, ..., n_{\text{data}} \tag{2}$$

Equation 2 can be denoted matricially as $F + B = Y$. There are, in general, a large number of solutions $f_i$ or $f(\tau)$ that can satisfy the experimental data.[9] In the case of a physical experiment, however, the existence of a solution (or the physical law) is usually guaranteed, and in some cases the uniqueness of the solution can be assured.[13] The maximum entropy method (MELT) utilizes Bayes' theorem as a framework for solving the inverse problem defined by an experiment described by the kernel $K$, the noise $B$, and the data $Y$. In order to make inference about the various possible results for the vector $F$, the maximum entropy method maximizes the posterior probability for the solution $F$ given by Bayes' theorem,[13−15] i.e.

$$p(F|Y) \propto \exp\left(\alpha S - \frac{1}{2}\chi^2\right) \tag{3}$$

where $S$ is the generalized Shannon−Jaynes entropy, $\alpha$ is the entropy weight, and $\chi^2$ is the weighted square deviation between the experimental data and the model spectrum constructed from the solution. Equation 3 amounts to maximizing $\alpha S - 0.5\chi^2$. A transfer matrix, **T**, gives a linear relation between the model decay curve $F_M$ and the distribution spectrum $F$ (i.e., $F_M = \mathbf{T}\cdot F$), in which the columns are constructed by the convolution between exponentials of the lifetimes on the analysis grid and the resolution function.[14] For convergence, MELT uses an approximation that the nonzero elements in **T** must be larger than a cutoff value $s$, preset by the user.[14] To obtain the optimized solution, two parameters, i.e., the entropy weight $\alpha$ and the cutoff value $s$, need to be optimized. The optimal $\alpha$ can be obtained by maximizing the probability $p(\alpha)$. The choice of $s$ is easy,[13] and some principles in determining the zero-time channel $t_0$ and the fwhm of the experimental resolution function have been discussed.[13−15]

**CONTIN Method.** The original constrained, regularized, least-square method, CONTIN, was developed by Provencher.[12] Gregory modified it to solve the integral equations with convoluted exponential as kernels, and a decay curve of a reference material with a well-known single lifetime was used to avoid the direct determination of the resolution function.[10,11] In the CONTIN method, the regularizer

$$S_1 = A^2 \int_0 [s''(\lambda)]^2 \, d\lambda \tag{4}$$

is added to the weighted sum of squared residuals for imposing the smoothness on the solutions $s(\lambda) = \lambda a(\lambda)$, where $\lambda = \tau^{-1}$ is the positron annihilation rate and $a(\lambda)$ is its PDF; $A$ is the regularized parameter. CONTIN gives a series of constrained, regularized least-squares solutions in which the size of the regularizer $A$ is progressively increased. The smoothest solution that is consistent with the experimental data and prior knowledge (e.g., there are usually three peaks in the positron annihilation rate profile in most polymers) is proposed as the optimal solution.[12]

**Table 1. o-Ps Parameters in Simulated Spectra As Resolved by PATFIT, CONTIN, and MELT Programs[a]**

| | PATFIT | | CONTIN | | | MELT | | |
|---|---|---|---|---|---|---|---|---|
| spectra | $\tau_3$[b] (ns) | $I_3$[c] (%) | $\tau_3$ (ns) | $\sigma(\tau_3)$ (ps) | $I_3$ (%) | $\tau_3$ (ns) | $\sigma(\tau_3)$ (ps) | $I_3$ (%) |
| | | | $\tau_3 = 1.5$ ns | | | | | |
| $N_0 =$ | | | | | | | | |
| 1 M | 1.4961 | 29.37 | 1.3864 | 456 | 29.16 | 1.4970 | 81.5 | 27.1 |
| 2.5 M | 1.4971 | 29.34 | 1.3863 | 394 | 31.40 | 1.4967 | 56.3 | 27.3 |
| 4 M | 1.4973 | 29.31 | 1.4173 | 367 | 31.16 | 1.4984 | 54.1 | 27.2 |
| 6 M | 1.4986 | 29.27 | 1.4558 | 325 | 30.29 | 1.5018 | 68.8 | 27.2 |
| 8 M | 1.4987 | 29.27 | 1.4616 | 355 | 30.29 | 1.5018 | 62.0 | 27.4 |
| 10 M | 1.4989 | 29.27 | 1.4649 | 296 | 30.28 | 1.5018 | 57.8 | 27.6 |
| | | | $\tau_3 = 2.0$ ns | | | | | |
| $N_0 =$ | | | | | | | | |
| 1 M | 1.9945 | 29.28 | 1.9963 | 541 | 25.31 | 1.9910 | 114.0 | 28.3 |
| 2.5 M | 1.9961 | 29.26 | 1.9549 | 467 | 28.26 | 1.9958 | 76.6 | 28.7 |
| 4 M | 1.9960 | 29.25 | 1.9590 | 457 | 29.12 | 1.9974 | 70.9 | 29.0 |
| 6 M | 1.9972 | 29.24 | 1.9790 | 435 | 29.33 | 2.0010 | 83.1 | 28.9 |
| 8 M | 1.9974 | 29.24 | 1.9832 | 394 | 29.34 | 2.0010 | 68.6 | 29.1 |
| 10 M | 1.9974 | 29.24 | 1.9850 | 381 | 29.45 | 2.0009 | 68.5 | 29.2 |
| | | | $\tau_3 = 2.5$ ns | | | | | |
| $N_0 =$ | | | | | | | | |
| 1 M | 2.4935 | 29.23 | 2.5776 | 713 | 23.79 | 2.4927 | 144.1 | 27.1 |
| 2.5 M | 2.4949 | 29.22 | 2.4915 | 571 | 27.29 | 2.4964 | 99.6 | 27.4 |
| 4 M | 2.4950 | 29.22 | 2.4921 | 531 | 28.18 | 2.4978 | 93.1 | 27.7 |
| 6 M | 2.4961 | 29.21 | 2.5045 | 537 | 28.77 | 2.5013 | 86.6 | 27.8 |
| 8 M | 2.4962 | 29.21 | 2.5077 | 491 | 28.90 | 2.5010 | 79.7 | 27.9 |
| 10 M | 2.4961 | 29.21 | 2.5038 | 477 | 29.15 | 2.5009 | 71.9 | 28.0 |

[a] The simulated spectra have the input standard deviation $\sigma(\tau_3) = 50$ ps. [b] The error range for $\tau_3$ is between 4.8 and 15.4 ps. [c] The error range for $I_3$ is between 0.08 and 0.28%.

**Simulated Positron Lifetime Spectra.** Since positrons injected into polymers usually annihilate in three states, i.e., parapositronium (p-Ps), "free" positron and orthopositronium, a positron lifetime spectrum in a typical polymer normally contains three major inherent lifetime components. In this work, we have generated spectra having three Gaussian profiles of the positron lifetime PDF with intensities $I_i$, average lifetimes $\tau_i$, and standard deviations $\sigma_i$, i.e.,

$$f(\tau) = \sum_{i=1}^{3} \frac{I_i}{\sqrt{2\pi}\sigma_i} \exp\left[-\frac{(\tau - \tau_i)^2}{2\sigma^2{}_i}\right] \tag{5}$$

where we use $I_1 = 40\%$, $\tau_1 = 0.130$ ns, $\sigma_1 = 0.010$ ns; $I_2 = 30\%$, $\tau_2 = 0.350$ ns, $\sigma_2 = 0.010$ ns; and $I_3 = 30\%$, $\sigma_3 = 0.050$ ns and the average o-Ps lifetimes $\tau_3$ are given the values of 1.5, 2.0, and 2.5 ns, respectively. The total number of counts $N_0$ is chosen to be between 1 and 10 million. The simulated curves are convoluted with a Gaussian resolution function with a fwhm $= 2(2 \ln 2)^{1/2}\sigma = 250$ ps. A background and appropriate Poisson noise is added to each channel.[10,11,17,18] In a similar way, we also generated several reference curves with a single lifetime of 120 ps for the CONTIN performance. The channel width for all the simulated spectra is 23.6 ps. All the simulated spectra were also analyzed using the well-known PATFIT program,[19] which determines only single lifetime components. The PATFIT results are listed in Table 1 and are very close to the input ones for comparison. For all the PATFIT results, the $\chi^2 < 1.2$. An example of the simulated spectra is shown in Figure 1.

## Analysis of Simulated Data

First, the simulated spectra were analyzed by MELT. A total of 1200 channels were analyzed, and the solution

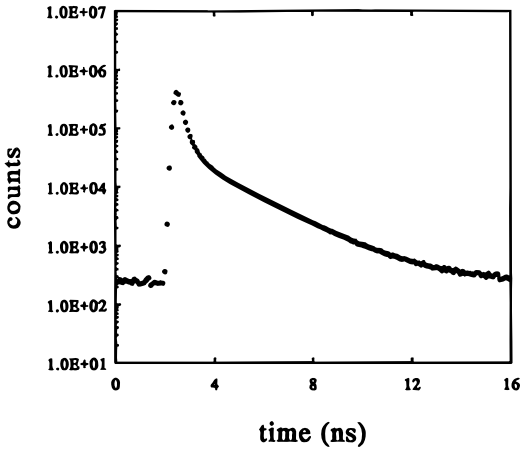


**Figure 1.** Simulated spectrum with $N_0 = 8$ M and an average o-Ps lifetime of 2.0 ns.

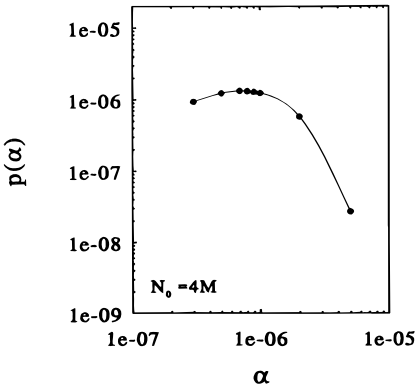


**Figure 2.** Variation of posterior probability p(α) vs the entropy weight α for a positron spectrum with $N_0 = 4$ million and an average o-Ps lifetime $\tau_3 = 1.5$ ns.

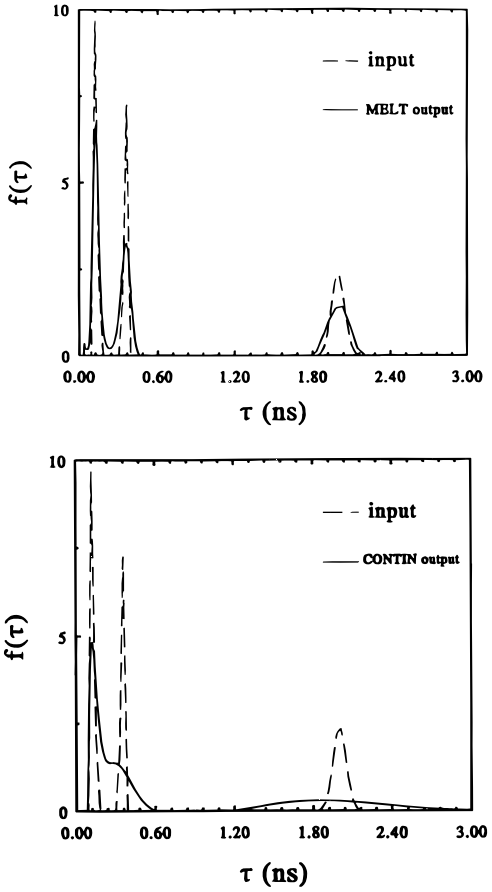


**Figure 3.** Solutions $f(\tau)$ for the simulated spectrum with $N_0 = 10$ million and the input o-Ps lifetime of 2.000 ± 0.050 ns obtained by (a) MELT and (b) CONTIN.

was sampled at 100 grid points in the region between 0.027 and 5.0 ns. By changing the value of the entropy weight α (or the regularized factor),[13−15] MELT gives a series of solutions, from which an optimized solution should be chosen. MELT also provides the probability $p(\alpha)$ of the entropy weight for each solution. The solution with the highest value of $p(\alpha)$ probability is the optimal one.[13,16] In Figure 2, the posterior probability $p(\alpha)$ vs α is shown for a spectrum with $N_0 = 4$ million and $\tau_3 = 1.5$ ns. The probability function $p(\alpha)$ vs α reaches the maximum value at $\alpha = 7 \times 10^{-7}$, and the corresponding solution is the optimized one. In our test with the simulated spectra, the cutoff value for determining the number of nonzero diagonal matrix elements in the construction of the transfer matrix is in the region of $(1-3) \times 10^{-6}$ and has no critical influence on the width of the o-Ps lifetime PDF. The $\chi^2$ for the optimized solutions given by MELT approach 1.0. The results are listed in Table 1.

An example of the solutions obtained by MELT is shown in Figure 3 a for a spectrum with $N_0 = 10$ million. The first and the second peaks have the average lifetimes $\tau_1 = 0.129 \pm 0.028$ ns, $\tau_2 = 0.350 \pm 0.038$ ns and the integral intensities are $I_1 = 40.2\%$ and $I_2 = 30.6\%$. The third peak has an average lifetime $\tau_3 = 2.010 \pm 0.069$ ns ($I_3 = 29.2\%$). The good agreement between the input values and the MELT results confirms that the maximum entropy method is a powerful tool for the reconstruction of typical positron lifetime distribution in polymers. The widths of three peaks in the MELT solution are somewhat broadened from the input profiles, which is probably due to the following reasons. Firstly, the practical lifetime spectrum is not a continuous curve but is sampled by a set of discrete numbers separated by a finite channel width. The finite channel width can contribute to the errors in the solution of the inversion process.[20] Secondly, the total number of counts is finite and a Poisson noise is added to the spectrum, which determines the information content and can also contribute to the final error in the solution.[7,20] Thirdly, because the lifetime range in the solution grid is limited, some truncation error can be introduced into the solution.[20] Fourthly, for the sake of fast convergence of the solution in the MELT algorithm, a cutoff for the diagonal matrix element is preset.[13−15] Therefore, some contribution from the matrix elements in the transfer matrix **T,** which are smaller than the cutoff value *s*, has been neglected.

The simulated sample spectrum is also analyzed by using the CONTIN program, where we used the simulated reference spectrum which has approximately the same total number of counts as the sample spectrum. The solutions are constrained to be positive in the range of annihilation rate of $\lambda = 0.2-12$ ns$^{-1}$ and sampled at 50 grids. Each solution set was sampled at 15 values of the regularizer parameter *A*. At low regularizer *A*, four or five peaks may appear in the solution, or, the integrated o-Ps intensities corresponding to one of main peaks do not agree with the input values. As the regularizer *A* increases, spurious peaks are suppressed and several solutions with three peaks are obtained. If the regularizer *A* increases further, one or two peaks may appear in the solution. We choose the solution recommended by CONTIN, which is considered to be

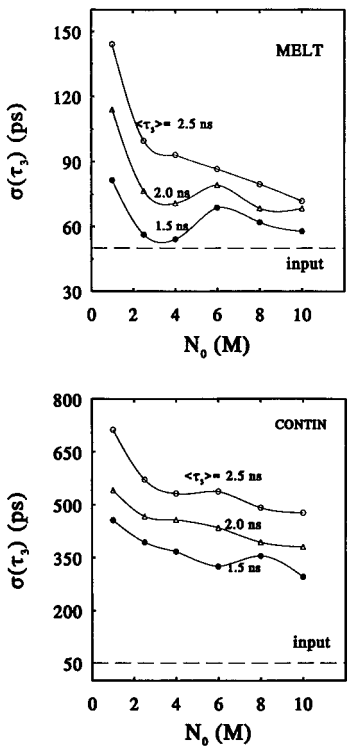


**Figure 4.** Standard deviation $\sigma(\tau_3)$ in the simulated spectra as a function of the total number of counts and the average lifetime $\tau_3$, obtained by (a) MELT and (b) CONTIN.

the smoothest solution that is consistent with the data.[10−12] The regularizer values of the chosen solutions for all the simulation spectra are not equal but fall in the range of (3.3−5.4) × $10^{-4}$, suggesting that the modification of regularizer $A$ on the width of o-Ps annihilation rate PDF in the chosen solutions is similar[10] and therefore rationalizes the obtained width of o-Ps lifetime PDF from CONTIN decreases with $N_0$ (see Table 1). The average lifetime, standard deviation of lifetime, and integrated intensity for the o-Ps peaks in the chosen solution are calculated by the $M_{-2}/M_{-1}$, $M_{-3}/M_{-1} - (M_{-2}/M_{-1})^2$, and $M_{-1}$, respectively,[10] where the $j$th momentum $M_j$ for the o-Ps peak is defined by

$$M_j = \int \alpha(\lambda)\lambda^{j+1}\, d\lambda \qquad (6)$$

and the values of $M_j$ ($j = -3, -2, -1$) are directly given by the CONTIN output file. For the chosen solution, we observed that the average lifetime and integrated intensity of the o-Ps peak are in good agreement with the input data (see Table 1). An example of the lifetime distribution converted from the positron annihilation rate PDF is shown in Figure 3b. The two short-lifetime distributions cannot be discerned clearly, and the o-Ps peak has a considerable broadening as compared with the input profile. This observation is due to the fact that the recommended solution has been smoothed by the larger size of regularizer. In practice, even if one chooses the solutions fulfilling the demand of the three peaks and the minimum regularizer at the same time, the peaks in them are still much more broadened than the input profile.

In Figure 4a, the standard deviations $\sigma(\tau_3)$ of o-Ps lifetime distributions as a function of total number of counts at different average lifetime $\tau_3$ are given for the MELT solutions. In Figure 4b, a similar plot is shown for the CONTIN evaluation of the same simulated spectra. The following observations can be made: (1)

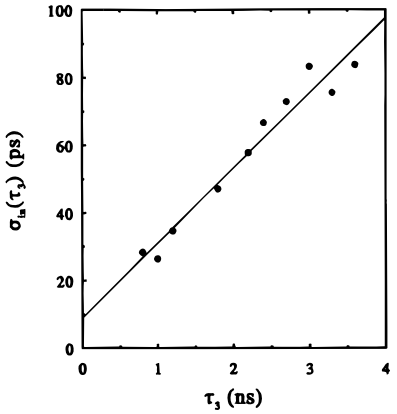


**Figure 5.** Intrinsic broadening of o-Ps component in the simulated spectra with $N_0 = 2.5$ million and a single o-Ps lifetime resolved by MELT.

The $\sigma(\tau_3)$ obtained by both MELT and CONTIN generally decrease with the increase of the total number of counts. This arises from the increasing content of information in the data.[8] (2) At the same $N_0$, the $\sigma(\tau_3)$ from both MELT and CONTIN increase with the average o-Ps lifetime $\tau_3$. The solution grids are not equally spaced and the interval between the neighboring grids increases with the lifetime and the truncation error in the solution due to the limited range of solution grids can be increased with the $\tau_3$,[20] which may lead to the increase of the error range of $\sigma(\tau_3)$. (3) The $\sigma(\tau_3)$ from MELT is in the range 54−148 ps and is much closer to the input value of 50 ps, as compared to the range 290−713 ps from the CONTIN program. Therefore, MELT can derive more reliable widths of o-Ps distributions than CONTIN. The reason for the larger broadening of o-Ps peaks in the solutions recommended by CONTIN is probably that the corresponding regularizer is large and tends to oversmooth the shape of solution and suppress the information. (4) The $\sigma(\tau_3)$ from MELT decreases with the total number of counts $N_0$ largely below $N_0 \approx 2.5-4$ M and then changes only slightly at $N_0 \geq 4$ M. Therefore, even at a relatively low total number of counts of 2.5−4 M, the resolution of MELT is excellent; and a further increase in the total number of counts is not greatly beneficial to the improvement of reconstruction of o-Ps lifetime distributions. The raw spectra for evaluation by MELT need only a limited acquisition time, and the possible negative effects of positron irradiation[21] and zero channel fluctuations on the solution can be avoided to a larger extent.[16] The conclusions from the simulated test agree well with earlier evaluation by MELT of the experimental spectra on poly(methyl methacrylate) (PMMA).[16]

**Further Modification of MELT Results.** As mentioned above and shown in Figure 4a, the broadening of o-Ps lifetime is inevitable, since an intrinsic broadening can be induced by the experimental setup or the initial conditions in the simulation (e.g., the total number of counts, finite channel width, and range of lifetime grids, etc.), as well as the MELT algorithm.[22] In order to further modify the width of o-Ps peaks resolved by MELT to approach the input value as close as possible, one needs to estimate the intrinsic broadening in $\sigma(\tau_3)$. We have simulated a series of positron lifetime spectra in which $N_0 = 2.5$ M and a single lifetime component without broadening, i.e., $f(\tau) = \delta(\tau-\tau_3)$ in eq 1, where $\tau_3 = 0.8-3.6$ ns. We use MELT program to calculate the intrinsic width of broadening, $\sigma_{in}(\tau_3)$. The result is shown in Figure 5. The $\sigma_{in}(\tau_3)$

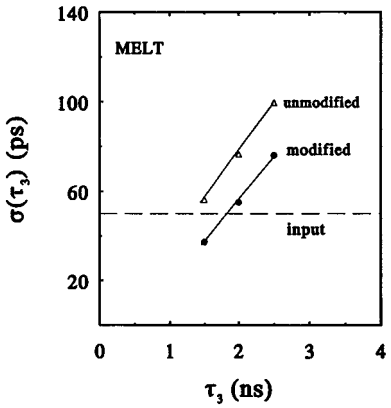


**Figure 6.** Modified and unmodified widths of o-Ps peaks at $N_0 = 2.5$ M as a function of the input average o-Ps lifetime $\tau_3$. The lines are drawn to guide the eyes.

increases with $\tau_3$ and can be fitted empirically into a linear equation:

$$\sigma_{in}(\tau_3) = 22.18\tau_3 + 8.86 \quad (7)$$

where the $\tau_3$ and $\sigma_{in}(\tau_3)$ are expressed in nanoseconds and picoseconds, respectively.

For the sake of simplicity, we assume the o-Ps distribution profile $f(\tau)$ in the solution from the MELT output to be Gaussian and be expressed as

$$f(\tau) = \int_0^\infty G(\tau - t_0, \sigma_{in}) f^0(\tau_0)\, d\tau_0 \quad (8)$$

where $G(\tau - \tau_0, \sigma_{in}) = (2\pi\sigma_{in}^2)^{-1/2} \exp[-(\tau-\tau_0)^2/2\sigma_{in}^2]$ is the broadening factor and $f^0(\tau)$ is the true distribution profile we want to resolve. Now we assume $f^0(\tau)$ also to have a Gaussian profile with a standard deviation of $\sigma_0$. It is easily proven that $\sigma_0^2 = \sigma^2 - \sigma_{in}^2$. Through this procedure we can estimate the discernible width $\sigma_0$ of the o-Ps lifetime distribution that MELT can give. An example is shown in Figure 6, where we plot the unmodified widths of o-Ps lifetime distribution in the simulated polymer spectra ($N_0 = 2.5$ M) from the original MELT output, and the modified widths where the value of $\sigma_{in}$ is based on eq 7. It is evident that the modified widths are closer to the input values than the unmodified ones.

## Conclusion

We have performed tests with simulated spectra using the maximum entropy lifetime method (MELT) and the constrained, least-squares regularized method (CONTIN) for the reconstruction of positron lifetime distributions in polymers. A series of simulated spectra having three Gaussian peaks were generated. The average lifetime and the integrated intensity of o-Ps component obtained by both MELT and CONTIN are in good agreement with the input data. However, CONTIN needs the total number of counts to be at least 10 M to reproduce reliable o-Ps lifetime distributions[18] while MELT only needs a relatively low number of counts and does not require a reference spectrum. Our numerical test proves that the MELT method is the preferred one for analyzing the positron lifetime spectra of polymers.

**Acknowledgment.** The authors wish to thank Dr. Abhay Shukla (Grenoble, France) and Dr. M. Eldrup (Risø, Denmark) for useful discussions and valuable comments. This work was supported partly by the Swedish Research Council for Engineering Sciences (TFR), and partly by Chalmers University of Technology.

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MA960639G