Computer-Simulation Analysis of the ESR Spectra of Mechanoradicals in PMMA

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Received 1 March 1996; revised 22 April 1997; accepted 23 April 1997

ABSTRACT: In this study, initially, we tried to obtain the mechanoradicals of PMMA (poly(methyl methacrylate)). For this purpose, we designed a simple drilling apparatus. Using this apparatus, we prepared some PMMA samples at 77 K in vacuum. Later, by using an ESR (electron spin resonance spectrometer), we observed ESR signals for these samples at 77 K. This means that mechanoradicals have been successfully produced by mechanical fracture in PMMA using our drilling apparatus. Secondly, we tried to identify the radicals from these spectra through using theoretical analyses and, some computer simulations have been done by suggesting two different theoretical models for these ESR signals. Finally, by using experimental and theoretical data, we showed that our simple apparatus could be used to obtain mechanoradicals from polymers. Results were seen to be in very good agreement with the literature.

INTRODUCTION

Mechanochemistry is based on studies on mechanoradicals that are defined as free radicals produced by external mechanical action. ESR detects free radicals selectively. This is a big advantage of ESR compared to other methods. It has been established by several works that ESR is a useful experimental technique to study the molecular mechanisms of either mechanical fracture or large deformation by detecting free radicals produced by fracture or deformation. Also the formation of free radicals in polymers at low temperature (77 K) under strong mechanical action has been reported by several researchers on the basis of ESR experiments.

Several types of apparatus (ball-milling, drilling, slicing, large deformation), which were convenient for ESR observation, were designed by various researchers. There are large number of studies of mechanical fracture of PMMA and other polymers. Some workers observed a nine-line ESR spectrum of PMMA fractured at 77 K in vacuum. But there are many suggestions on the origin of these ESR spectra or on the type of mechanoradicals. However, a number of physical models can be found in the literature and new experimental and theoretical studies have been carried out.

In this study, we also used two models to explain the nine-line ESR spectrum of the mechanically fractured PMMA.

THEORY

ESR is a branch of spectroscopy that studies the interaction between electron magnetic moments and external magnetic fields. A net magnetic moment exists in atoms or molecules containing unpaired electrons and only then does the ESR technique become possible. An unpaired electron has
Table I. Properties of Gaussian Lines

<table>
<thead>
<tr>
<th>Line Shape</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equation for absorption line</td>
<td>$Y = Y_m \exp\left[-\ln \left(\frac{2(\Delta H_{1/2})^2}{(H - H_0)^2}\right)\right]$</td>
</tr>
<tr>
<td>Equation for first derivative of absorption line</td>
<td>$Y' = -Y_m \frac{2 \ln 2(H - H_0)}{(\Delta H_{1/2})^2} \exp\left[-\ln \left(\frac{2(\Delta H_{1/2})^2}{(H - H_0)^2}\right)\right]$</td>
</tr>
<tr>
<td>Peak to peak amplitude</td>
<td>$Y_{\max}^{\prime} = \left(\frac{2}{\pi e}\right)^{1/2} \ln 2(H - H_0) \left(\frac{2\Delta H_{1/2}}{(\Delta H_{1/2})^2}\right)$</td>
</tr>
<tr>
<td>Peak to peak width</td>
<td>$\Delta H_{pp} = \left(\frac{2}{\ln 2}\right)^{1/2} \Delta H_{1/2}$</td>
</tr>
</tbody>
</table>

no other electron as a partner in the same orbital, and for that reason it gives an ESR signal. The magnetic interactions between the electron and other nuclear spins in the same molecule give an ESR spectrum with a number of lines instead of one signal line.

It is usually possible to determine the type and number of nuclear spins that interact with the electron and the structure of the free radical by analyzing the number of lines, their separation, and their relative intensities.

The line separation depends on the interaction between the electron spin and each nuclear spin and on the magnetic moments of the involved nuclei. From the number of absorption lines in the hyperfine ESR spectrum and their relative intensities, it is possible to identify the number of equivalent nuclei in the molecule and to determine the structure. The maximum number of lines in the ESR spectrum is $(n+1)(m+1)$, if we have two nonequivalent sets of $n$ and $m$ protons. The position of the lines in the spectrum is a function of the hyperfine constants $a_n$ and $a_m$.

The $k$th line in the spectrum will be found at the field $H_k$ given by Equation 1.

$$H_k = H_c - \sum a_i M_i$$

where, $H_c$ is the magnetic field at the center of the spectrum, and $M_i$ is the sum of the $M_i$ values for the protons of the $i$th group.

The shapes of ESR lines are described by Lorentzian or Gaussian line shapes. The main difference between the two types of line shape is that the outer wings of the Lorentzian line are much longer and drop more slowly then those of a Gaussian line. Some analytical expressions for characteristic Gaussian line is given in Table I.

Where, $Y$ is the intensity of the absorption line, $Y_m$ is the intensity of the absorption line at its center. $H$, is the magnetic field, $H_0$ is the field of resonance at the line center, $\Delta H_{1/2}$ is the half-width at half-height.

**Computer Simulations**

The observed ESR spectra were analyzed by using the method of nonlinear least-squares total curve fitting. The spectroscopic parameters [g-value, line width, hyperfine splitting constant and relative spectral intensity of component radicals] were obtained from the observed spectra digitized by an analog/digital (A/D) converter. Computer programs were run by using the Lorentzian and the Gaussian line-shape functions. But the Gaussian line-shape function was found to yield the best fit to the experimental spectra.

Some of the simulation studies on mechanoradicals are referred in the literature. In this study we tried two models and used a MINSQ (Least Squares Parameter Estimation) program.

**Model I**

Irradiated PMMA spectrum coincides with the characteristic spectrum referred to in the literature as the “$5 + 4$ line” spectrum most frequently attributed to a main-chain scission radical of PMMA (radical type R1).
In the first step of the calculation, a radical of the type R1 with eight equivalent protons have been considered. But it is seen that this model is not give good results. That's why we suppose that R1 radical has two different conformations. In one of the conformations, CH₂ protons can not interact with the unpaired electron and do not cause any hyperfine splitting. In that case, only CH₃ protons interact with the unpaired electron equivalently and give a 4-line (quartet) ESR spectra. In the other conformation, one of the CH₂ protons and the three CH₃ protons interact with the unpaired electron equivalently and it gives a 5-line (quintet) ESR spectra. Consequently the characteristic “5 + 4 line” spectra of PMMA is a result of the contribution of these two conformations.

**Model II**

In this model, it has been suggested that the C—C bond in the main-chain is broken by mechanical action and two different radicals (R1 and R2) produced.

![Structure of R1 and R2 radicals](image)

In the R2 radical, the unpaired electrons interact only with the CH₂ protons equivalently and cause hyperfine splitting. In that case, a 3-line (triplet) ESR spectrum is produced. In this model we suppose that the observed spectra depends on the relative concentrations of R1 and R2 radicals. The superposition of 9-line spectrum of R1 radical and 3-line spectrum of R2 radical gives still the observed 9-line spectrum, because the signal intensity of R2 radical is much smaller than that of R1.

The peak to peak amplitudes of the resonance lines in an ESR spectrum originating from radical R, are calculated by multiplying the $Y_{\text{max}}'$ values given in Table-1 with the binomial coefficients depending on the number of resonance line. The binomial coefficients for R1—4 lines, R1—5 lines and R2—3 lines spectra are given as $(1:3:3:1)$, $(1:4:6:4:1)$ and $(1:2:1)$ respectively. If the $Y'_{\text{max}}$ values given in Table-3 are multiplied with the corresponding binomial coefficients, one can easily conclude that the peak to peak amplitude of 3-lines resonance spectrum due to R2 radical are weaker than those of 9-lines resonance spectrum of R1 radical.

**EXPERIMENTAL TECHNIQUES**

**Methods to Produce Mechanoradicals**

Any method causing mechanical breakdown of polymers may produce mechanoradicals. In this respect, many studies have been done and different methods have been devised to produce mechanoradicals.

The common characteristics of all these methods are that the sample is prepared at low temperature and under anaerobic conditions. In our experiments a simple drilling apparatus improved for this purpose is shown in Figure 1.

A piece of polymer was fixed in a vessel filled with liquid nitrogen, and drilled with a hand-drill. The drilling tip used for drilling is a kind used by dentists. The small polymer particles (powder) from the polymer sample were transferred into a Pyrex ESR sample tube cooled down to 77 K. This tube, containing polymer powder and liquid nitrogen, was connected to a vacuum line and evacuated, keeping the sample tube in the dewar flask containing liquid nitrogen. This sample was kept at $10^{-4}$ torr vacuum for half an hour. After this...
As can be seen from Figure 2.a and Figure 2.b, it is possible to produce radicals by mechanical fracture of PMMA using our drilling apparatus. It is clear that the drilling apparatus is a quite proper system for mechanical degradation of bulk polymers.

The spectrum observed from the mechanically fractured PMMA in vacuum is shown in Figure 2.a. This nonet spectrum is the well-known spectrum of PMMA in the presence of oxygen. Figure 2.b shows the ESR spectrum of PMMA after the sample up opened to the air. This spectrum is the characteristic spectrum of peroxy radical. The ESR spectrum of another PMMA sample which has been prepared in a similar is shown in Figure 2.c. This spectrum is a mixture of the two spectra shown in Figure 2.a and Figure 2.b and may be viewed as an intermediate state between them. This spectrum is a composition of nine-lines and peroxy radical spectra of different weight percent. This is due to the fact that during the stages of sample preparation, because of the interaction between the polymer powder and air, some of the mechanoradicals produced by the mechanical fracture are converted to peroxy radicals.

The anisotropic singlet spectrum of peroxy rad-
The simulations of experimental spectra recorded in the temperature range of 77 K–230 K have been carried out using Model-I and Model-II. The experimental spectrum recorded at 77 K and corresponding calculated spectra with Model-I and Model-II are shown in Figure 4.

The values of some spectral parameters and corresponding standard deviation values calculated from simulations of the 77 K spectrum are given in Table-2, Table-3 and Table-4 for Model-I and Model-II, respectively.

To give the reader the opportunity of comparison, the ESR spectra of PMMA and that of the peroxy radical and their sum are given together in Figure 5.

From the results derived above, it can conclude that (1) The ESR spectrum of the radicals created in PMMA after γ, X and UV irradiation is very similar with the spectrum of mechanoradicals created at 77 K in vacuum.\(^9,^{21,22,23,24,25}\) (2) R1 (Model-I) or R1 + R2 (Model-II) radicals may be at the origin of this nonet spectrum. However, the results of Model-II are much better than that obtained from Model-I. This calculation indicates that R1 + R2 radicals are the origin of the nonet spectrum observed after irradiation or mechanical degradation of PMMA. (3) The general shape of the spectrum depends on the oxygen in the system. In that case, the origin of the antisymmetric spectrum stays content R3, R4, R5 (peroxy radicals) or superposition of R1, R2, R3, R4, R5 radicals.

### Table II. Parameter Obtained after the Simulation of 77 K Experimental Spectrum Using Model I

<table>
<thead>
<tr>
<th>Type of Radical</th>
<th>R1–5</th>
<th>R1–4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectroscopic splitting factor</td>
<td>2.0045</td>
<td>2.0040</td>
</tr>
<tr>
<td>Hyperfine splitting constant (mT)</td>
<td>1.98</td>
<td>2.02</td>
</tr>
<tr>
<td>Peak to peak width (mT)</td>
<td>0.52</td>
<td>1.77</td>
</tr>
<tr>
<td>Peak to peak amplitude</td>
<td>1.00</td>
<td>0.75</td>
</tr>
</tbody>
</table>

### Table III. Parameter Obtained after the Simulation of 77 K Experimental Spectrum Using Model II

<table>
<thead>
<tr>
<th>Type of Radical</th>
<th>R1–5</th>
<th>R1–4</th>
<th>R2–3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectroscopic splitting factor</td>
<td>2.0045</td>
<td>2.0039</td>
<td>2.0080</td>
</tr>
<tr>
<td>Hyperfine splitting constant (mT)</td>
<td>1.98</td>
<td>2.05</td>
<td>2.38</td>
</tr>
<tr>
<td>Peak to peak width (mT)</td>
<td>0.52</td>
<td>1.58</td>
<td>2.33</td>
</tr>
<tr>
<td>Peak to peak amplitude</td>
<td>1.00</td>
<td>0.51</td>
<td>0.43</td>
</tr>
</tbody>
</table>

### Table IV. Corresponding Standard Deviation Values Obtained after the Simulation of Experimental Spectrum Using Models I and II

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Model I</th>
<th>Model II</th>
</tr>
</thead>
<tbody>
<tr>
<td>77</td>
<td>0.023</td>
<td>0.013</td>
</tr>
<tr>
<td>88</td>
<td>0.023</td>
<td>0.018</td>
</tr>
<tr>
<td>100</td>
<td>0.028</td>
<td>0.019</td>
</tr>
<tr>
<td>140</td>
<td>0.031</td>
<td>0.023</td>
</tr>
<tr>
<td>230</td>
<td>0.044</td>
<td>0.034</td>
</tr>
</tbody>
</table>
In conclusion simple apparatus and techniques devised in the present work can be used to obtain mechanoradicals from polymers. Our observations and simulation results are in good agreement with those given in the literature.

REFERENCES AND NOTES