An Electron Spin Resonance Study of Mechanical Fracture of Poly(methyl methacrylate)

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ABSTRACT: In this article, initially, we designed a simple drilling apparatus to obtain the mechanoradicals of poly(methyl methacrylate) (PMMA). Using this apparatus, we prepared some PMMA samples at 77 K in vacuum. We observed some electron spin resonance (ESR) signal of these samples. It is found that the ESR spectrum of mechanically fractured PMMA strongly depends on the vacuum conditions. The spectrum observed from the mechanically fractured PMMA in 10^{-4} torr vacuum at 77 K coincides with the characteristic spectrum of the "nine-line" ESR spectrum of PMMA. Otherwise, because of the interaction between the polymer powders and air during the stage of preparing the sample, some of the mechanoradicals convert into the peroxy radicals. In this situation, spectrum is mainly nine-line and partially superposed with the spectrum of peroxy radicals. The peroxy line observed at low temperatures disappears rapidly from the mechanoradicals with increasing temperature. It vanishes completely at $\sim$ 300 K and the spectrum turns into the nine-line spectrum of PMMA. Changes in the nine-line spectrum of mechanoradicals were investigated in the 100–350 K temperature interval. The line intensities were measured at each temperature. It was shown that the line intensities of both A and B do not change with time at constant temperature, and decrease with increasing temperature. The PMMA samples in vacuum were opened to air and the ESR spectrum was followed with time. It was observed that the nine-line spectrum converted into a line asymmetric spectrum in $<$ 1 min at room temperature. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 1161–1167, 1997

Key words: ESR; PMMA; mechanical fracture; mechanoradical; drilling apparatus

INTRODUCTION

If there exist a sufficient number ($>10^{15}$) of either free radicals or trapped electrons in a system, an electron spin resonance (ESR) signal originating from these unpaired electrons is observed from the system. This is the reason why ESR signals are selectively observed from free radicals and observation of an ESR signal is positive evidence for the presence of free radicals in a system.

The concentration of free radicals in a system is estimated from spectral intensity. Relative concentration of free radicals can be easily determined simply by comparing the intensities of the sample and standard spectra. A radical species can be identified by an appropriate analysis of its ESR spectrum. By observing changes in ESR spectra, one can follow changes in radical species. If the total intensity of an ESR spectrum stays constant through a spectral change, this means that a radical is being converted into other radical species without any decay. If the total intensity decreases, radicals are decaying (being converted into nonradical species). A very rapid mode of molecular motion of free radicals is detected by an analysis of changes in an observed ESR spectrum.

Mechanoradicals are defined as free radicals

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produced by mechanical action. Any method causing mechanical breakdown of polymers may produce mechanoradicals. Several types of apparatus, which were convenient for ESR observation, were designed by various researchers.[1–3] Use of a ball-milling method for this purpose was at first reported by Butyagin and Abagjan; Backman and DeVries designed an apparatus for slicing a polymer sample.[1,4] A slicing technique was also reported by Zhurkov, Tomashevskii, and Zakrevskii.[5] Lazar and Szöcs designed a drilling apparatus to produce a mechanoradical from a polymer in vacuum and at low temperature.[6]

There are large number of studies of mechanical fracture of poly(methyl methacrylate) (PMMA) and other polymers.[2–19] Many of these report the observation of a nine-line ESR spectrum for PMMA fractured at 77 K in vacuum.[8,10,11,13] It has also been demonstrated by several researchers that PMMA had a nine-line ESR spectrum when it was radiated by γ, X, and UV-irradiation.[20–29] Some researchers believe that the complete spectrum can be attributed to a single radical, the propagating radical in the polymerization of methyl methacrylate. Other researchers believe that two radicals are present, a five-line and four-line spectrum, the superposition of which produces the observed nine-line spectrum. It has been shown that there are many suggestions on the origin of these ESR spectra or on the type of the mechanoradicals. However, a number of physical models can be seen in the literature, and new experimental and theoretical studies have been carried out.[7,11,13,30,31]

EXPERIMENTAL

Methods of Producing Mechanoradicals

Any methods causing mechanical breakdown of polymers may produce mechanoradicals. For this subject, many studies have been done and different methods have been devised to produce mechanoradicals.[2,7,10,13,32] The common characteristics of all these methods are that the sample is prepared at low temperature and under anaerobic conditions. In this article, a simple drilling apparatus has been developed for these purposes, as shown in Figure 1.

A slap 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 sample polymer were transferred into a Pyrex ESR sample tube cooled at 77 K. This tube, containing polymer powder and liquid nitrogen, was connected to the vacuum system and evacuated by keeping the sample tube in the dewar flask containing liquid nitrogen. This sample was kept at the value of 10^{-4} torr vacuum for half an hour. After this procedure the sample tube was sealed off and preserved at the same temperature until experiments.

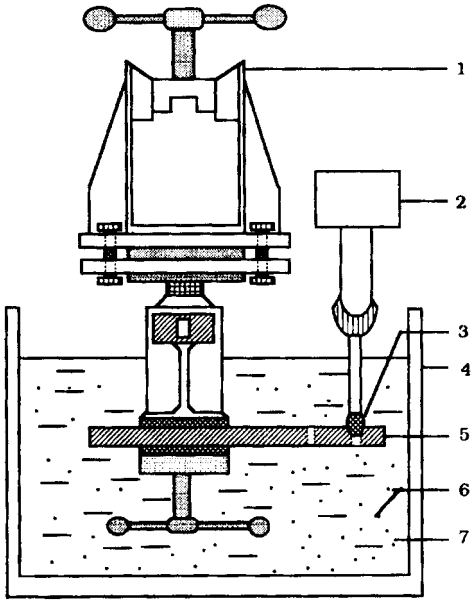


Figure 1 Schematic diagram of drilling apparatus. (1) Sample holder, (2) drilling, (3) dentist drilling tip, (4) dewar flask, (5) slap PMMA sample, (6) powder PMMA, (7) liquid nitrogen.

ESR Measurements

The ESR spectra were recorded by a Varian E-line type X-band spectrometer with 100 kHz modulation. The microwave power level was kept at 1.5 mW and the modulation amplitude was kept at 5 G during the experiments. During this study, rectangle double cavities were used. One of these cavities was equipped with a temperature control system. PMMA and Strong Pitch were used as a polymer sample and as a standard sample, respectively, for all experiments. There is a data-collecting system linked to the spectrometer. While the spectrum was being recorded, it was also converted to digital data and hampered to a computer.

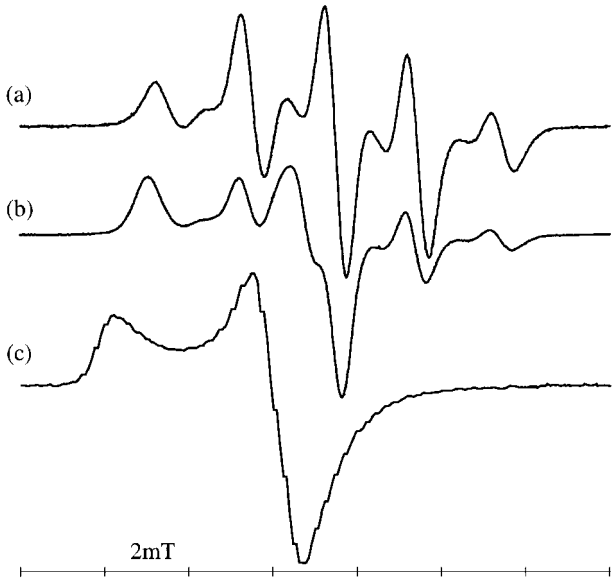


Figure 2 Observed ESR spectra of PMMA fractured in a drilling apparatus at 77 K. (a) The sample in vacuum at 10^{-4} torr; (b) preparing the sample interacting with air; (c) the sample was not vacuumed.

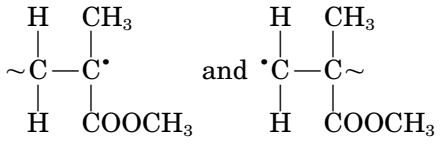
RESULTS AND DISCUSSION

Spectra and Identification of the Radical Spectra

Figure 2(a) gives the nine-line ESR spectrum of mechanically fractured PMMA in 10^{-4} torr vacuum at 77 K. It was found that the ESR spectrum of mechanically fractured PMMA changed with vacuum conditions. The signal based on the peroxy radical were observed in the ESR spectrum of any powder PMMA prepared at 77 K without vacuum, as shown in Figure 2(c).

In relatively weak vacuums, the ESR spectrum was a mixture of peroxy and the PMMA mechanoradical. This is shown in Figure 2(b). This spectrum is mainly nine-line but still partially superposed with the peroxy radical spectrum.

From the simulation of the nine-line ESR spectrum observed from the mechanically fractured PMMA, it was concluded that the radicals produced by the fracture of PMMA are the radicals from the scission of the carbon chain:



(R1) (R2)

Here radical R1 is the propagating radical for PMMA and is characterized by a nine-line spectrum. The R1 radical has two different conformations. These two conformations give a superposition of a five-line with a hyperfine splitting constant of 20.5 G and a four-line spectrum hyperfine splitting constant of 19.8 G. The spectrum for the R2 radical is a triplet with a hyperfine splitting constant of 23.8 G. In order to avoid the confusion the detailed studies that were carried out on PMMA mechanoradicals are not given here, but were submitted for publication in the *Journal of Polymer Science.*

ESR Spectra of Irradiated PMMA

Ionization radiation studies were done to compare the ESR spectrum of PMMA mechanoradicals with the ESR spectra of PMMA irradiated by UV- and γ-irradiation. These spectra are shown in Figure 3 and 4.

It was seen that these spectra conform both with the spectra of PMMA given in the literature and the spectra of mechanoradicals obtained in this study.

Change of the ESR Spectra of PMMA in Vacuum Variation of Temperature and Time

As stated previously, Figure 2(b) is a mixture of the ESR spectrum of peroxy radical and mechanoradicals at 77 K. The change in this spectrum was followed by increasing the temperature by 10 K steps in the 100–350 K interval to investigate

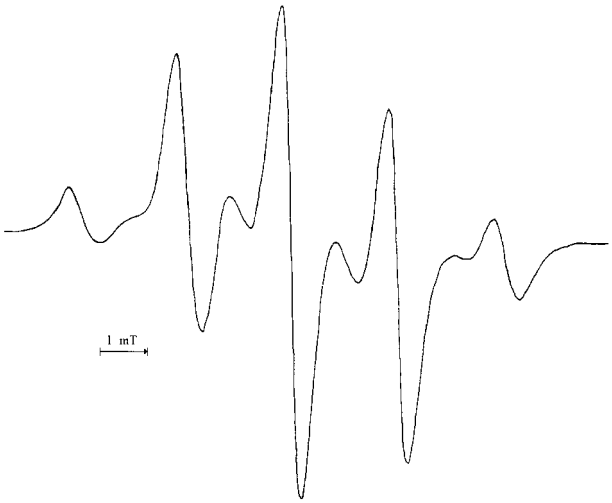


Figure 3 ESR spectrum of PMMA irradiated by γ-rays in vacuum for 40 h (23.6 kGy) at room temperature.

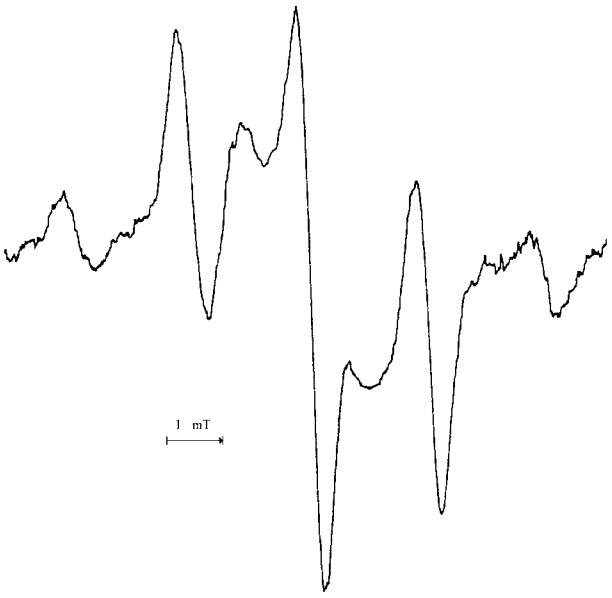


Figure 4 ESR spectrum of PMMA irradiated by UV-rays in vacuum for 13 h at room temperature.

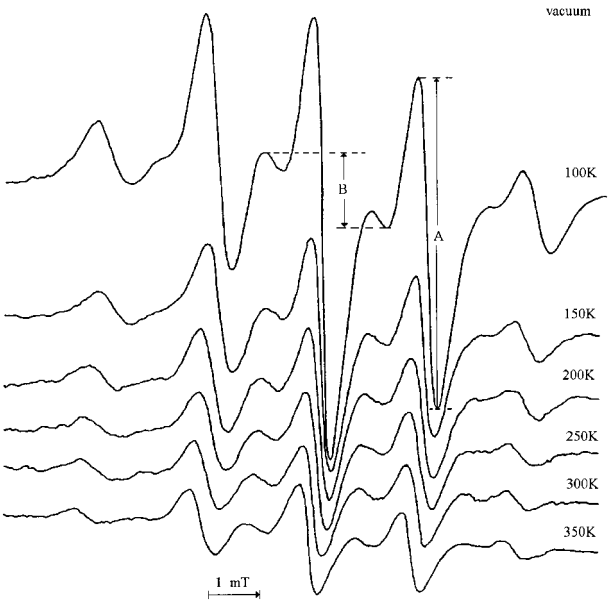


Figure 6 Variation of ESR spectrum of PMMA with respect to temperature, which was preparation in vacuum.

changes in the ESR spectrum as a function of the measured temperature. The peroxy line observed at low temperatures disappears rapidly from the mechanoradicals as the temperature increases. It vanishes completely at ~ 300 K and the spectrum turns into the nine-line spectrum of PMMA (Fig. 5). The temperature of this sample was decreased again to investigate whether the peroxy radicals observed at low temperature relay the decay or not. However, when the temperature was decreased from 350 to 100 K, the shape of the spectrum did not change; because of the decrease of the measurement temperature, the line intensities increased. Depending on this result, when the temperature increases from 100 to 350 K, these peroxy radicals decay rapidly from mechanoradicals by reacting with each other, and only mechanoradicals remain in the sample at 350 K. When the temperature is again decreased the peroxy radicals do not recur.

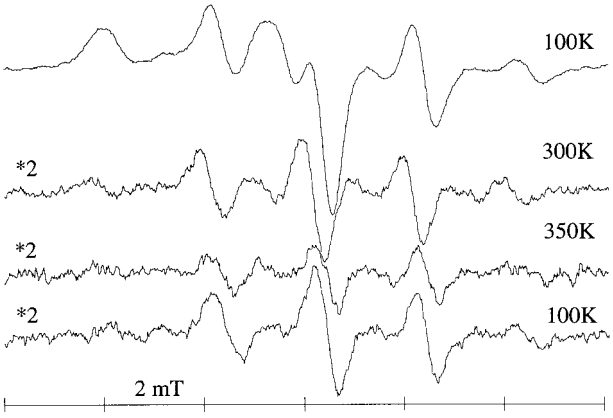


Figure 5 Variation of ESR spectrum of PMMA with respect to temperature, which was interacted with air during preparation.

The ESR spectrum of PMMA at 77 K in 10^{-4} torr vacuum that does not have any interaction with the air is given in Figure 2(a). It was previously stated that the source of this spectrum is the sum of R1 and R2 radicals. Changes in this spectrum were investigated in the 100–350 K temperature interval. When the temperature was increased, the intensities of the lines decreased. The ESR spectra observed at several temperatures are shown in Figure 6.

The line intensities shown as A and B in Figure 6 were measured at each temperature, and the change of their normalized values plotted versus temperature are shown in Figure 7. The line intensity at B can be taken as an indicator of the development of peroxy radicals. The line intensity at A is a measure of the decay of mechanoradicals. The line intensities of both A and B equally decrease with increasing temperature.

The change of the shape and the intensity of the ESR spectrum was investigated at certain temperatures. If the sample temperature is kept

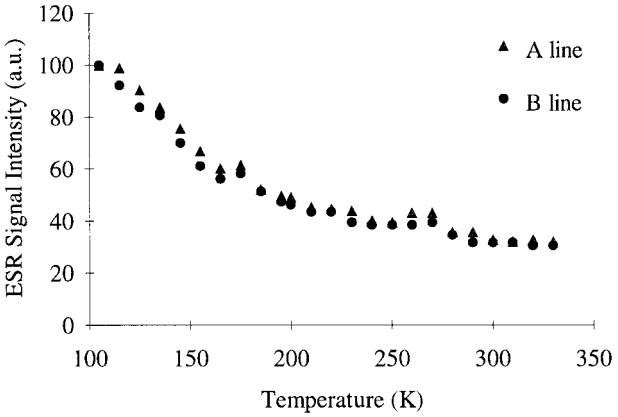


Figure 7 The variation of ESR signal intensities of lines marked as (A) and (B) in Figure 6 with respect to temperature.

constant within a range of 100–270 K, the radical concentration does not change with time.

It is concluded from these results that the changes shown in Figure 7 do not indicate the decay of radical concentration. If a decrease in the intensity existed as a result of decay of the radical rising temperature, the line intensities in Figure 8 would have to reduce as a function of time. Finally, we can conclude that there was no change in the radical concentration, since the ESR signal amplitude is inversely proportional to the absolute temperature (Curie's Law).[33]

Change of the ESR Spectra of PMMA in Oxygen Atmosphere Variation of Temperature and Time

The PMMA samples in vacuum were opened to air at room temperature and their ESR spectra

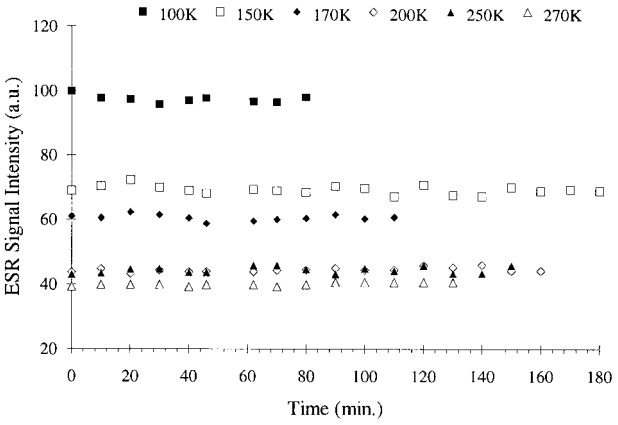


Figure 8 The variation of ESR signal intensities of PMMA that were kept at various temperatures as a function of time.

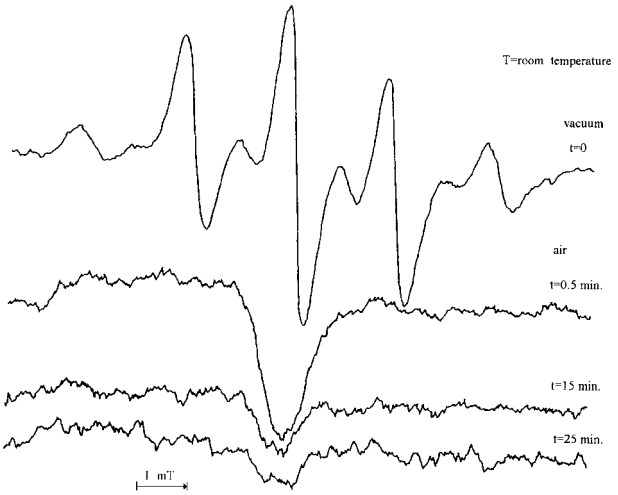


Figure 9 The variation of ESR spectra of PMMA that is open to air as a function of time at room temperature.

were followed with time. It was observed that the nine-line spectrum of the sample converted into a line-asymmetric spectrum in <1 min, as shown in Figure 9. Consequently, it was not possible to measure the period for the mechanoradicals in the sample to turn into peroxy radicals. These peroxy radicals also decay by interacting with each other as a function of time, as shown in Figure 9.

To investigate the formation of the peroxy radical at low temperatures, a study was undertaken of a PMMA sample prepared with the same conditions. Afterward, the sample was opened to the air at 100 K. Changes of the ESR spectrum with time are given in Figure 10.

After opening the sample to air at 100 K, no detectable change was observed. Even for runs lasting $\sim$ 25 min, we could not detect any im-

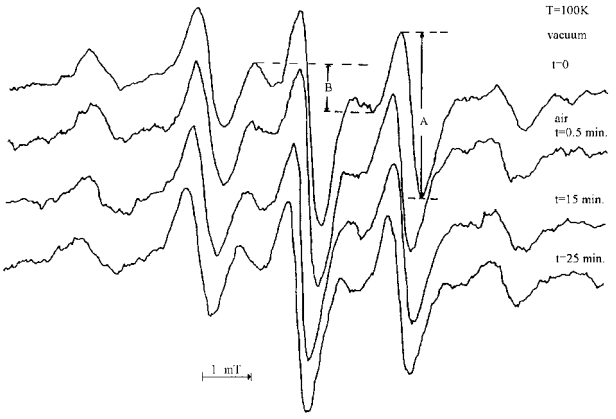


Figure 10 The variations of ESR spectra of PMMA open to air as a function of time at 100 K.

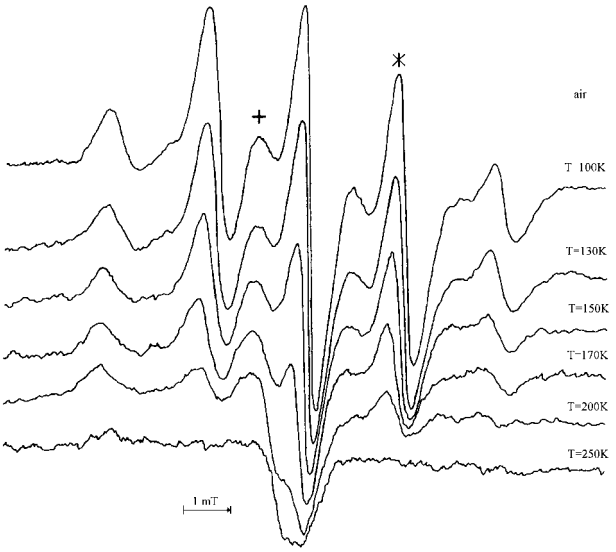


Figure 11 The decay of ESR spectra of PMMA in air as a function of temperature at 100 K.

portant changes in signal shape and intensity. To investigate the interaction between mechanoradicals and oxygen molecules, another experiment was performed at low temperatures. For this purpose, the sample was opened to air at 100 K and the temperature varied between 100 and 250 K (Fig. 11).

The intensity of the line shown as (*) in the spectrum provides an indication of the concentration of the mechanoradical. This line was chosen because it does not coincide with any part of peroxy spectrum. The line shown as (+) in the spectrum was chosen to investigate the change of the peroxy radicals as a function of temperature. The change of these line intensities as a function of temperature is shown in Figure 12.

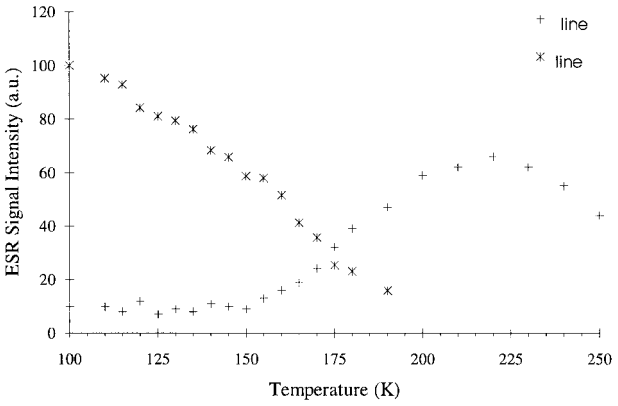


Figure 12 The variation of ESR signal intensities of (+) line and (*) line marked in Figure 11 as a function of temperature.

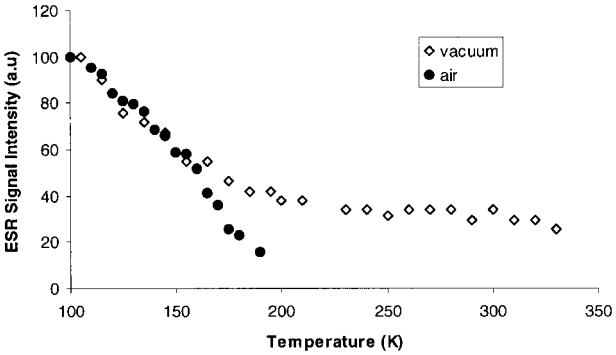


Figure 13 The comparison of ESR signal intensities of (A) line marked in Figure 6 (vacuum) and (*) line marked in Figure 11 (air) as a function of temperature.

In the spectra shown in Figure 11, the effect of a peroxy radical is first observed at ~ 150 K. The strongest line at the spectrum center was reduced by the peroxy spectrum and the spectrum symmetry began to decrease. This result was also confirmed by the curve shown in Figure 12. As seen in that figure, the line labeled (*) decreases more rapidly after 150 K, and this line vanishes completely at ~ 200 K. The line intensity shown as (+) remains constant up to 150 K and increases rapidly from this temperature to 220 K. If the temperature is further increased, the peroxy radicals being to decay by reactions with each other.

As seen in Figure 11, the peroxy radicals began to appear at 150 K. That is to say mechanoradicals interact with oxygen molecules starting at 150 K. As seen in Figure 13, the results presented above are also confirmed by the temperature studies done in the absence and the presence of air.

It was known that radicals generated and trapped in the polymers decayed stepwise. For PMMA radicals, we can say that one of these steps is ~ 110 K.[25] Some new molecular motions appear in the PMMA polymer at this temperature. Because of these molecular motions, all the radicals interact with each other, as seen in processes 1–3.

$$R^{\bullet} + R^{\bullet} \rightarrow 2R \quad (1)$$

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \quad (2)$$

$$RO_2^{\bullet} + RO_2^{\bullet} \rightarrow 2RO_2 \quad (3)$$

In the temperature range between 100 and 150 K, no change in ESR intensity occur. The peroxy radical $RO_2^{\bullet}$ is also stable in this temperature range, as no peroxy radicals actually decay. At temperatures > 150 K, the mechanoradicals begin to decay rapidly (process 1), and the peroxy

radicals begin to be generated more rapidly (process 2). At 220 K, the peroxy radicals begin to decay and the radical concentration decays monotonically (process 3).

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