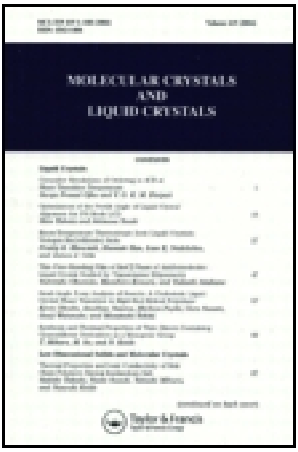

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A Novel Collision-Induced Solid State Radical Recombination

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A NOVEL COLLISION-INDUCED SOLID STATE RADICAL RECOMBINATION

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Abstract A novel mechanically-induced solid state radical recombination occurs in plasma-irradiated polycrystalline *myo*-inositol by its ball milling under anaerobic conditions.

INTRODUCTION

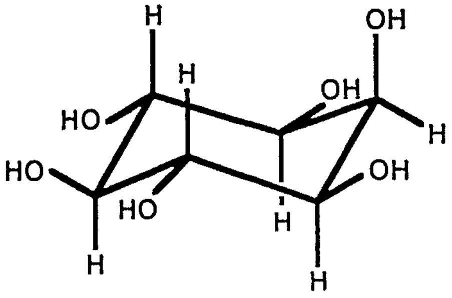
Polymers, synthetic and natural, in pulverized form are very often used for manufacturing a variety of solid materials in entire field of industry including pharmaceutical industry. Pulverization is conducted for various purposes due to the particle size reduction in metallic vessel in most cases, but without careful consideration for occurrence of mechanochemical reactions during the course of pulverization. For instance, mechanical fracture of amorphous and crystalline polymers at the temperature lower than the glass transition point (Tg) and/or the melting point is known to cause the mechanoradical formation due to polymer main-chain scission.[1] The nature of mechanoradical formation of several synthetic polymers at low temperature[2] and room temperature[3-5] has been well investigated. Furthermore, we have recently demonstrated the occurrence of solid state single electron transfer (SSET) reaction using dipyridinium dication when pulverization was conducted under anaerobic condictions in metallic vessel, but no reaction occurred when Teflon-made vessel is used.[6] Based on these findings, we were able to establish the total mechanism of mechanochemical polymerization and obtain the criteria for selecting effective monomers on polymer prodrug synthesis.[3,7,8] Nevertheless, the nature of polymer pulverization at molecular level is not well understood, because collision-induced mechanochemical reactions such as mechanoradical recombination can be considered to occur in the course of pulverization. No experimental attempt has yet been made to substantiate the occurrence of such reactions for any organic compound as well as organic polymers. We believe that pulverization can be best understood only after the nature of the mechanochemical reaction has been fully elucidated.

All kinds of organic radicals eventually undergo a termination reaction, producing stable molecules. The pathways available to a pair of radicals are recombination and disproportionation when β-hydrogen exists in the latter case. Unlike radicals in the liquid or gas phase, however, the recombination of solid state radicals is significantly suppressed due to the restriction of their mobilities. Interactions between radicals at solid-solid interfaces do not occur under a normal condition. This is the reason why mechanoradicals in many polymers can be easily observed by ESR spectra even at room temperature, so long as such radicals are kept under anaerobic conditions. In order to gain an insight into the nature of pulverization and provide criteria for such operations, we have explored to substantiate the possible occurrence of mechanically-induced free radical coupling.

We report the first experimental evidence for occurrence of solid-state free radical coupling of organic compound induced by application of mechanical energy based on the observation of electron spin resonance (ESR) spectra of plasma-irradiated *myo*-inositol containing the surface free radicals.

RESULTS AND DISCUSSION

We have selected for the initial study powdered (polycrystalline) *myo*-inositol, one of the polyhydric alcohols, containing plasma-induced surface radicals, because it is an organic compound of low molecular weight, so that it does not generate the mechanoradicals on its pulverization.



myo-inositol

We have recently reported the ESR study on elucidation of the surface radicals of Ar plasma-irradiated *myo*-inositol coupled with systematic computer simulations.[9] In order to discuss the mechanochemical reactions of the plasma-induced surface radicals of *myo*-inositol, it is appropriate to mention the sense of the results relevant to the present study.

Figure 1 shows the progressive changes in three series of ESR spectra of Ar plasma-irradiated *myo*-inositol at various durations (A), and those on heating of the 15-s plasma-irradiated sample at 120℃ for 2 h (B), and followed by 155℃ for 1.5 h (C). The systematic computer simulations disclosed that there exist as many as six component spectra in the observed spectra and all the surface radicals formed were very stable for a long period of

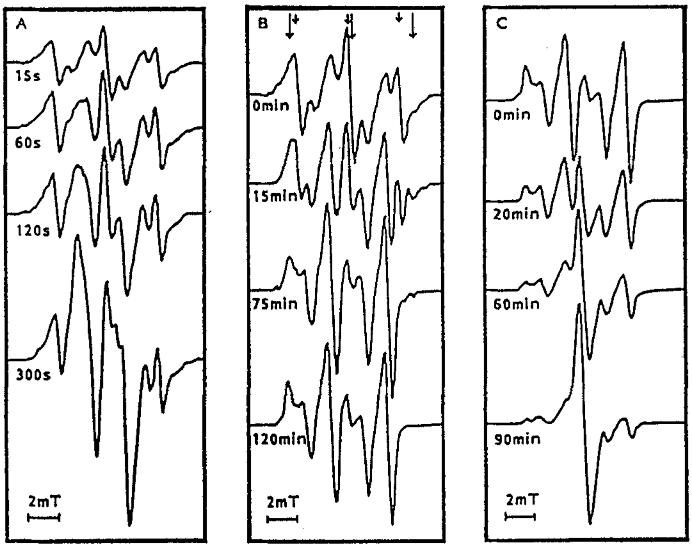


FIGURE 1 Progressive changes of observed ESR spectra of plasma-irradiated *myo*-inositol as a function of (A) plasma duration, (B) heating at 120°C of 15-s plasma-irradiated *myo*-inositol, and (C) heating at 155°C after heating at 120°C for 2 h.

time at room temperature. Figure 2 shows the representative spectral components of the simulated spectra: three isotropic spectra [doublets (I), triplets (II) and (III)] and three aniso-

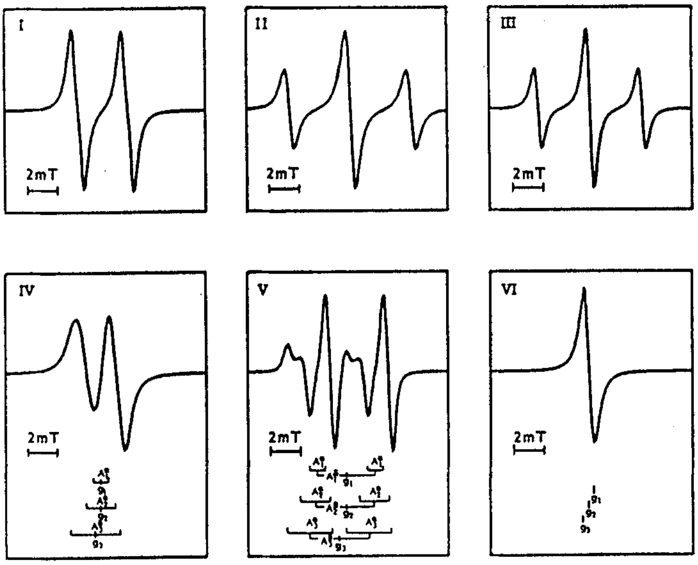


FIGURE 2 Six component spectra for the simulated ESR spectra of plasma-irradiated *myo*-inositol.

tropic spectra [doublet (IV), doublet of doublets (V), single broad line (VI)]. All simulated spectra were reproduced by these component with differing the ratio.

Although the ESR spectra were rather complicated due to the solid state radicals, the radical formation can be simply depicted in chemical structural terms as shown in Fig. 3: three kinds of hydroxyl alkyl radicals [three isotropic spectra (I) (II) and (III)], two kinds of acylalkyl radicals [two anisotropic spectra (IV) and (V)] and dangling bond sites (DBS) (VI) present at the surface crosslinked parts.

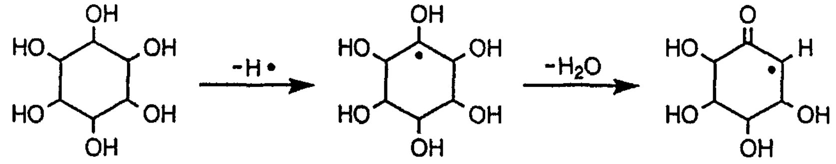


FIGURE 3 Reaction scheme for formation of hydroxyl alkyl radicals followed by dehydration to give acylalkyl radicals.

So, we have examined the possible occurrence of mechanically-induced solid state radical recombination reaction of polycrystalline *myo*-inositol containing plasma-induced surface radicals (2.8×10^{17} of spin numbers/g) by use of the ball milling apparatus (Fig. 4) which consists of Teflon-made twin-shell blender and Teflon-made ball to eliminate any undesired side reaction. After the pulverization for the prescribed period of time, the sample was directly transferred into the ESR tube and sealed for the spectral measurement. All operations were carried out under strictly anaerobic conditions.

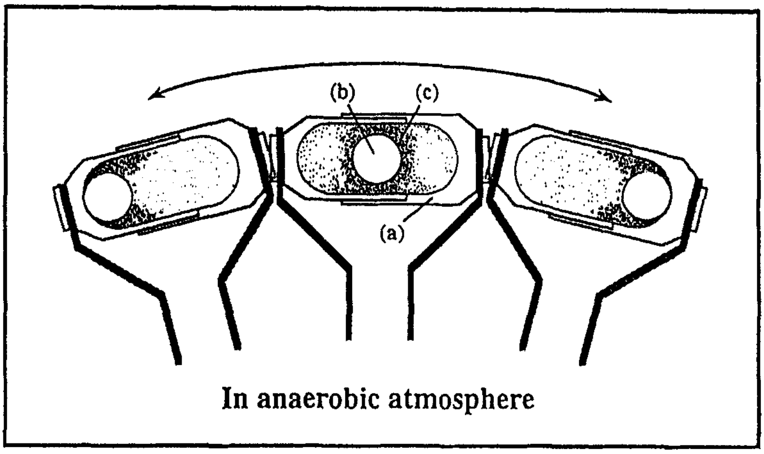


FIGURE 4 Experimental setup of vibratory ball milling.
(a) Teflon-made twin-shell blender (7.8 mmϕ, 24 mm long)
(b) Teflon-made ball (6.0 mmϕ, 290 mg)
(c) Powder sample

Figure 5 shows the progressive changes in the ESR spectra of *myo*-inositol radicals caused by ball milling at 57 Hz vibration as a representative example. It is seen that the application of vibratory pulverization caused the effective decay in the ESR spectral intensity of stable *myo*-inositol surface radicals in all cases without changing the spectral pattern. Therefore, it can be said that the spectral decay must have been caused by mechanical collision of each particle, not by local thermal effect. If it occurs by thermal effect in the course of pulverization, the spectral pattern should have been changed from spectra A to spectra B and/or C, figuring that the samples for spectra B and C were obtained by temperature annealing of spectra A. Another important feature derived from the spectral decay without changing the spectral pattern is that all the component radicals have more or less the same reactivities on its pulverization.

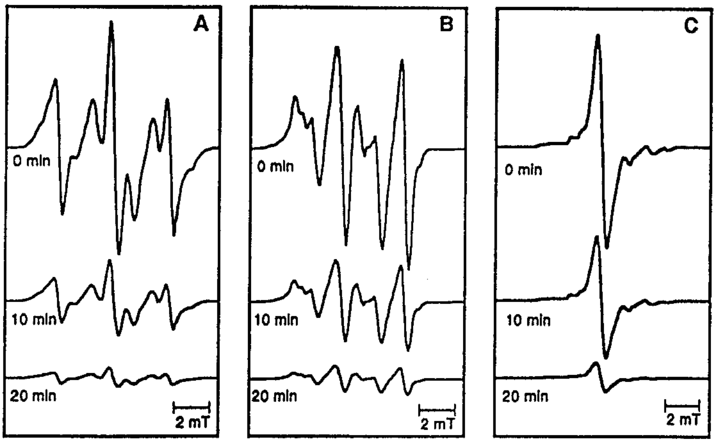


FIGURE 5 Progressive changes of ESR spectra by Teflon-made ball milling (57 Hz of milling ball frequency) of (A) 15-s plasma-irradiated *myo*-inositol, (B) after heating at 120℃ of 15-s plasma-irradiated *myo*-inositol, and (C) after heating at 155℃ for 1.5 h of the sample heated at 120℃ for 2 h.

The dependence of ball milling conditions on decay of ESR spectral intensity clearly indicated that the radicals decay with a faster rate as the applied vibration frequency increases, while the spectral intensity remains constant on its standing at room temperature. (Fig. 6) It is also seen that the spectral intensities tend to level off and reach the stational state, indicating that two types of radicals, reactive and non-reactive radical, exist in *myo*-inositol radicals under the present operational conditions. Figure 7 shows the nature of decrease in total spin concentration with various ball milling conditions. It can be seen that, since the decay rate of all the component radicals is more or less the same, the nature of radical decay can be exhibited by a single curve depending on the vibration frequency, regardless of its radical structure.

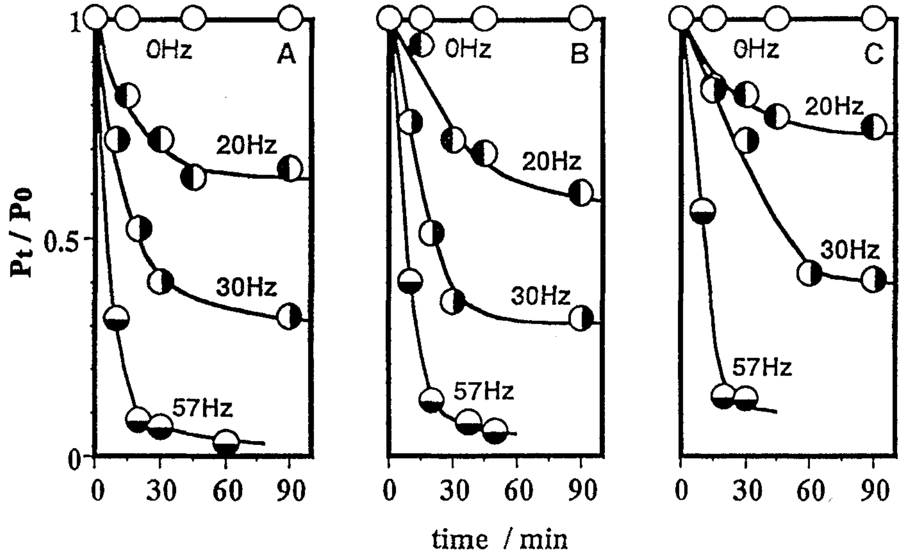


FIGURE 6 Decay of ESR spectral intensity of *myo*-inositol radicals under various ball-milling conditions.

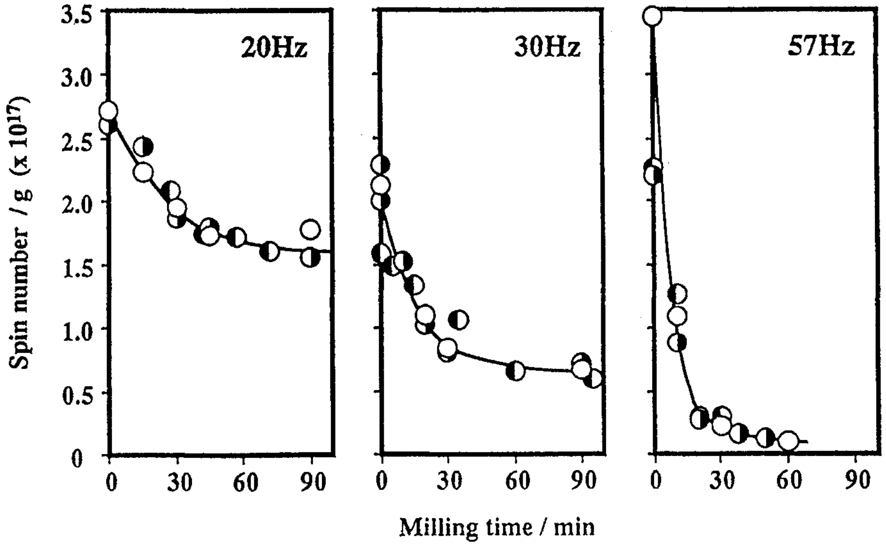


FIGURE 7 Dependence of ball milling conditions on decay of *myo*-inositol radicals.
○ : 15-s plasma-irradiated *myo*-inositol
◑ : after heating at 120℃ of 15-s plasma-irradiated *myo*-inositol
◐ : after heating at 155℃ for 1.5 h of the sample heated at 120℃ for 2 h

Based on these results as well as the fact that one of the characteristic of plasma irradiation is surface-limited, it is clear that plasma-induced *myo*-inositol surface radicals underwent the solid state radical recombination reaction on its vibratory pulverization. It seems otherwise difficult to interpret such results.

The present result is not only of interest on its own right but also of special significance in connection with understanding of the nature of polymer pulverization used for manufacturing a variety of solid materials in entire field of industry. We are now actively elaborating this initial study.

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