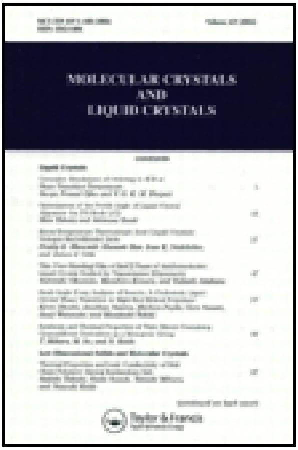

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The Polymerization of *p*-Vinylbenzamide in the Solid Phase

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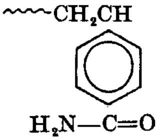
Abstract—A high degree of conversion can be obtained for the solid phase polymerization of *p*-vinylbenzamide when initiated thermally or by a post-irradiation technique. The Arrhenius activation energy for the radiation-induced polmerization is 20.3 kcal/mole while the value for the thermally initiated polymerization is 25.8 kcal/mole. EPR data of the polycrystalline sample shows a broad line spectrum which changes shape as the sample is heated from −196° (the irradiation temperature) to 105° (the polymerization temperature). The latter spectrum is consistent with a radical of the type:



The system has an initial radical concentration of 5.9×10^{17} radicals/g and this concentration decreases only by a factor of 2 after heating for 38 hours at 105°.

Introduction

The solid state polymerization of *p*-vinylbenzamide can be initiated either by cobalt 60 gamma radiation or thermally. Similar polymerization characteristics have been reported for solid syate polymerization of *p*-benzamidostyrene.[1] In this system thermal polymerization occurred well below the melting point of the monomer and although the polymerization appeared to occur in the crystalline

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[‡] This work was done in part at the Dow Chemical Company, Midland, Michigan.

regions of the monomer, the polymer produced was completely amorphous. This compound is a structural isomer of *p*-vinylbenzamide. It has been recently reported that *p*-vinylbenzamide can be polymerized in solution when initiated by benzoyl peroxide or potassium tertbutoxide to yield polymers with two different structures.[2] These workers show that two propagation steps are possible, one through the vinyl group to form the usual vinyl type polymer and the other by proton transfer from the nitrogen to the vinyl to yield a polyamide. Because of the structural analogy to *p*-benzamidostyrene it was decided to look at the polymerization of *p*-vinylbenzamide in the solid phase and to compare the observed thermal polymerization with the radiation-induced reactions and attempt to characterize the mechanism.

Experiment

The *p*-vinylbenzamide used in these investigations was prepared from *p*-chloroacetophenone. The *p*-chloroacetophenone was a commercial grade which was distilled and then reduced with lithium aluminum hydride in ether to *p*-choro-(α-methyl)-benzyl alcohol. The alcohol was dehydrated by mixing it with B_2O_3 and removing the resulting *p*-chlorostyrene by vacuum distillation. This crude *p*-chlorostyrene was redistilled and then converted to the corresponding Grignard reagent. This Grignard reagent was poured over solid carbon dioxide and the resulting complex hydrolyzed to yield *p*-vinylbenzoic acid. The *p*-vinylbenzoic acid was converted to the acid chloride by reacting it with thionyl chloride. The reaction mixture was allowed to stand at ambient conditions for 24 hours after which time the excess thionyl chloride was removed by distillation. In order to facilitate purification of the final product it was necessary to vacuum distill the acid chloride before addition to a mixture of ice and ammonium hydroxide. The crude *p*-vinylbenzamide was separated and purified by recrystallization from ethanol to yield a compound which melted at 171°C and had the following carbon, hydrogen, and nitrogen analysis of 73.4% C, 6.11% H, and 9.26% N as compared with calculated values of 73.4% C, 6.12% H, and 9.53% N.

Samples for polymerization were prepared by sealing powdered samples of the monomer in pyrex ampoules at 10^{-6} torr. Although air was found not to effect the rate of polymerization, all samples reported here were polymerized in vacuum.

A post-irradiation technique was used for the polymerization of the samples. All samples were irradiated by cobalt 60 gamma radiation at − 196 °C. At this temperature no detectable polymerization was observed even for samples that were stored after irradiation for one week at − 196 °C. The samples were polymerized after irradiation by placing them in a thermostated oil bath which was capable of maintaining the temperature constant to ± 0.05 °C.

The polymer was isolated by dissolving the monomer in the monomer-polymer mixture with ethanol and the polymer yield is reported in terms of the total ethanol insoluble fraction.

Discussion and Results

The conversion data for the radiation induced reaction are summarized in Fig. I. Here the percent conversion is plotted against

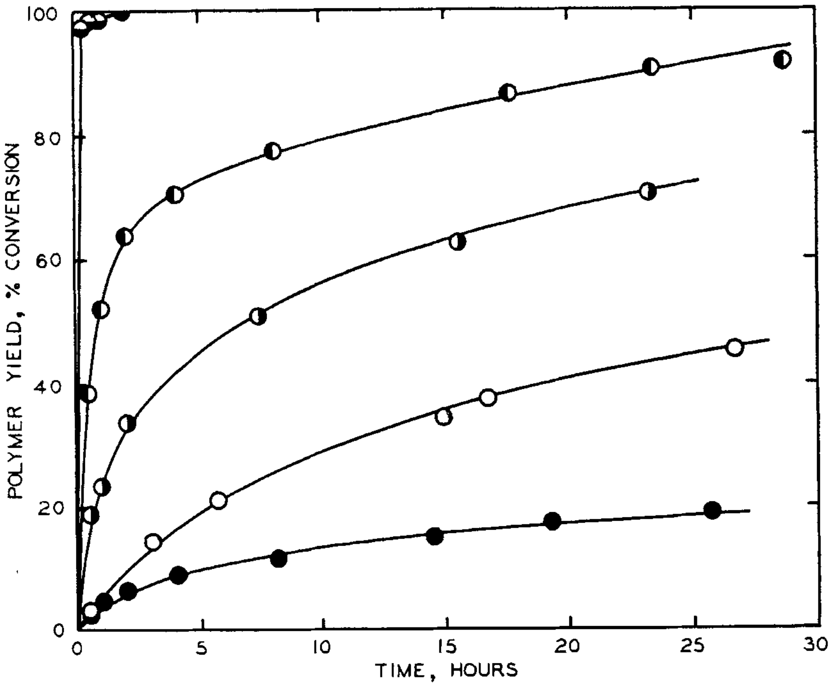


Figure 1. Post-irradiation of 4-vinylbenzamide. Dose rate 108 krads/hr, total dose 1.64 Mrads. ● 75 °C, ○ 89 °C, ◑ 105 °C, ◐ 120 °C, and ◒ 150 °C.

the polymerization time in hours. These samples received a total dose of 1.64 Mrads at an intensity of 108 krads/hr, and then were polymerized in a temperature range from 75 to 150 °C. It is interesting to note that the maximum polymerization temperature of 150 °C is 21°C below the melting point of the monomer. The polymer yield does not appear to be reaching a limiting conversion as has been observed for most of the monomers which polymerize in the solid phase. If the initial rates of polymerization for the data shown in Fig. 1 are plotted against the reciprocal of the absolute temperature an Arrhenius type diagram as shown in Fig. 2 is obtained. Here an activation energy of 20.3 kcal/mole is obtained for the radiation-induced polymerization.

In Fig. 3, the effect of radiation dose on the conversion is shown.

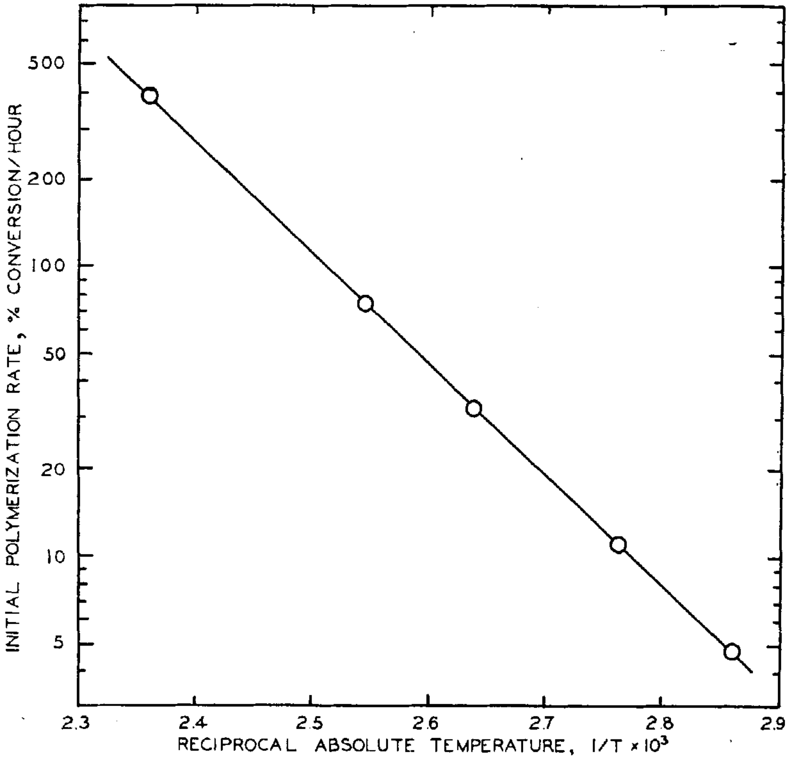


Figure 2. Arrhenius plot of the activation energy for the post-irradiation polymerization of 4-vinylbenzamide.

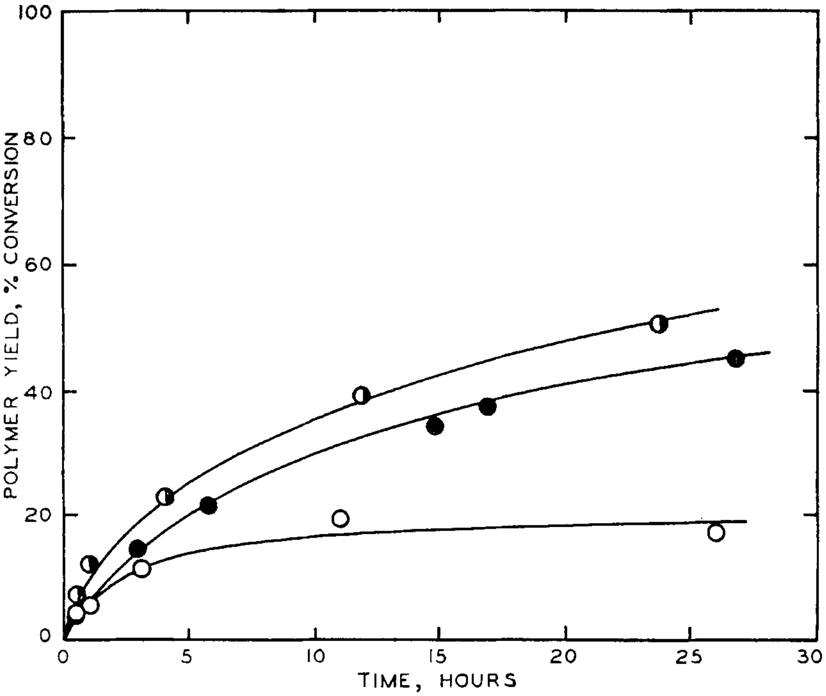


Figure 3. The effect of dose on the post-irradiation polymerization of 4-vinylbenzamide. ○ 0.82 Mrads, ● 1.64 Mrads, and ◑ 2.37 Mrads.

Here the samples were irradiated at 108 krads/hr to a total dose of 0.82, 1.64, or 2.37 Mrads and then polymerized at 89 °C. It can be seen that the degree of conversion increases with the dose. However, if the percent conversion at a given polymerization time is plotted against dose as shown in Fig. 4 the degree of conversion does not increase linearly with dose. This would suggest that saturation with respect to dose might result from very high doses.

Another interesting feature of the polymerization of *p*-vinylbenzamide in the solid state is the high degrees of conversion obtained for thermal polymerization in the absence or irradiation. These data are summarized in Fig. 5. Here the percent conversion is plotted against the time in hours for the polymerization in the temperature range from 100° to 145 °C. Again as in the case of the radiation induced polymerization the polymer yield does not appear to be approaching a limiting conversion. If the initial rates of polymeriza-

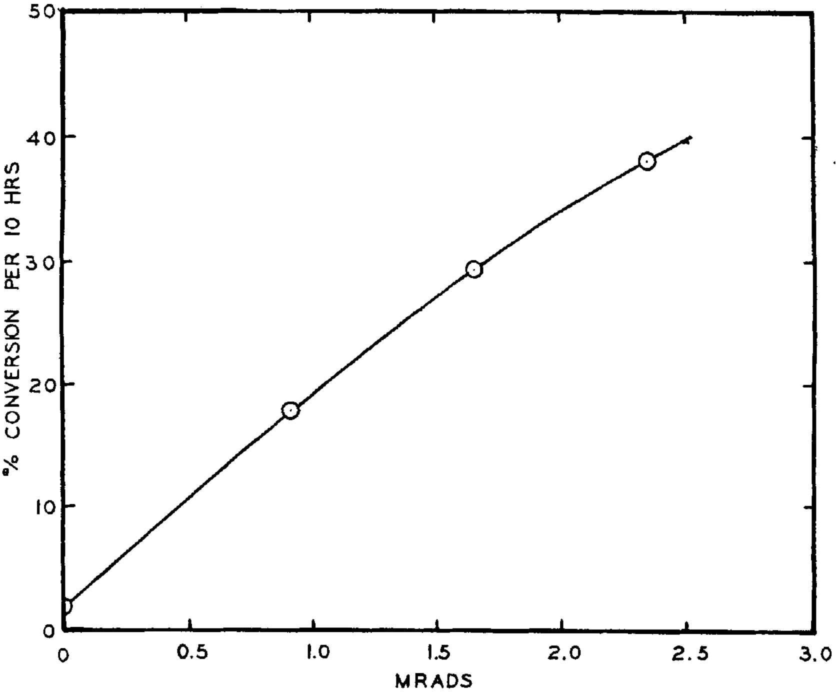


Figure 4. The effect of radiation dose on the degree of conversion after polymerization at 89 °C for 10 hours.

tion are plotted against $\frac{1}{T}$ an Arrhenius type diagram is obtained as shown in Fig. 6. Here an activation energy of 25.8 kcal/mole is calculated from the slope of the line. If the activation energy for the radiation induced and the thermally initiated polymerizations are compared, a difference of 5.5 kcal/mole is observed. This difference is probably an indication of the activation energies for the thermal initiation. This conclusion appears reasonable since the propagation and termination steps should be the same for both types of initiation. In Figs. 7, 8, and 9, the EPR signal for the radicals present in the polymerization mixture is shown. In Fig. 6, a single broad line is obtained from the monomer at − 196 °C approximately twenty minutes after irradiation. On warming this radical is slowly converted to a three line spectrum as shown in Fig. 7. On heating to 105 °C, the spectrum changes to the one shown in Fig. 8 and remains unchanged up to thirty hours. These spectra were taken at the same

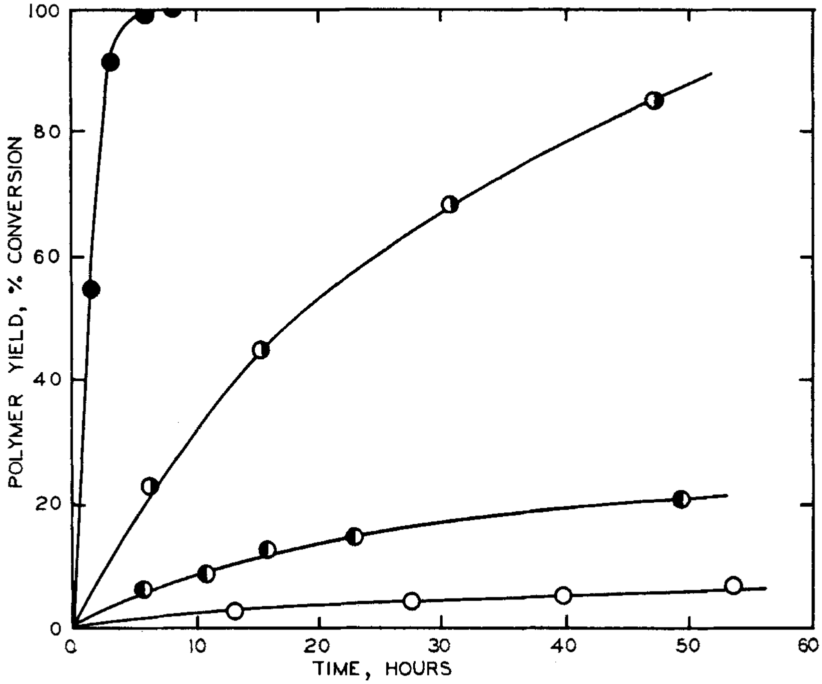
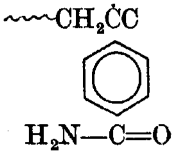


Figure 5. Thermal polymerization of 4-vinylbenzamide. ○ 100 °C, ◐ 115 °C, ◑ 130 °C, and ● 145 °C.

power levels and indicate that the total radical concentration of 5.9×10^{17} radicals/g only decreases by a factor of 2 when heated for thirty-eight hours at 105 °C.



A similar spectra has been observed in acrylamide when irradiated at − 196 °C with electrons.[3] Attempts to obtain a radical spectrum for the thermal polymerization have been unsuccessful. However, this probably indicates that the radical concentration, in this case, is below the level of detection.

The polymer produced from *p*-vinylbenzamide is very hard and has the exterior appearance of the monomer for samples polymerized to

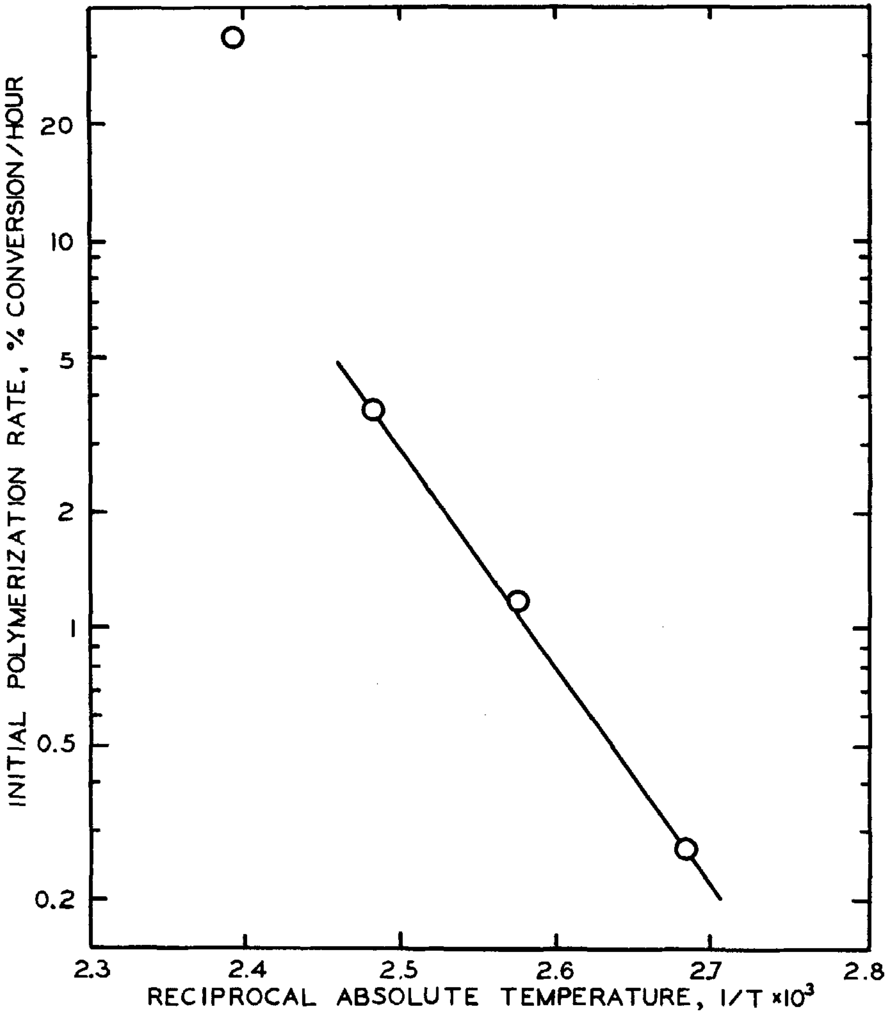


Figure 6. Arrhenius plot of the activation energy for the thermal polymerization of 4-vinylbenzamide.

a high degree of conversion. However, X-ray analysis shows the material to be completely amorphous. On heating the polymer to 320 °C the polymer softens but then rapidly decomposes as the temperature is increased to approximately 340 °C. Since the solution polymerization indicates that propagation can take place either through the vinyl group or through the amide linkage,[2] this offers the

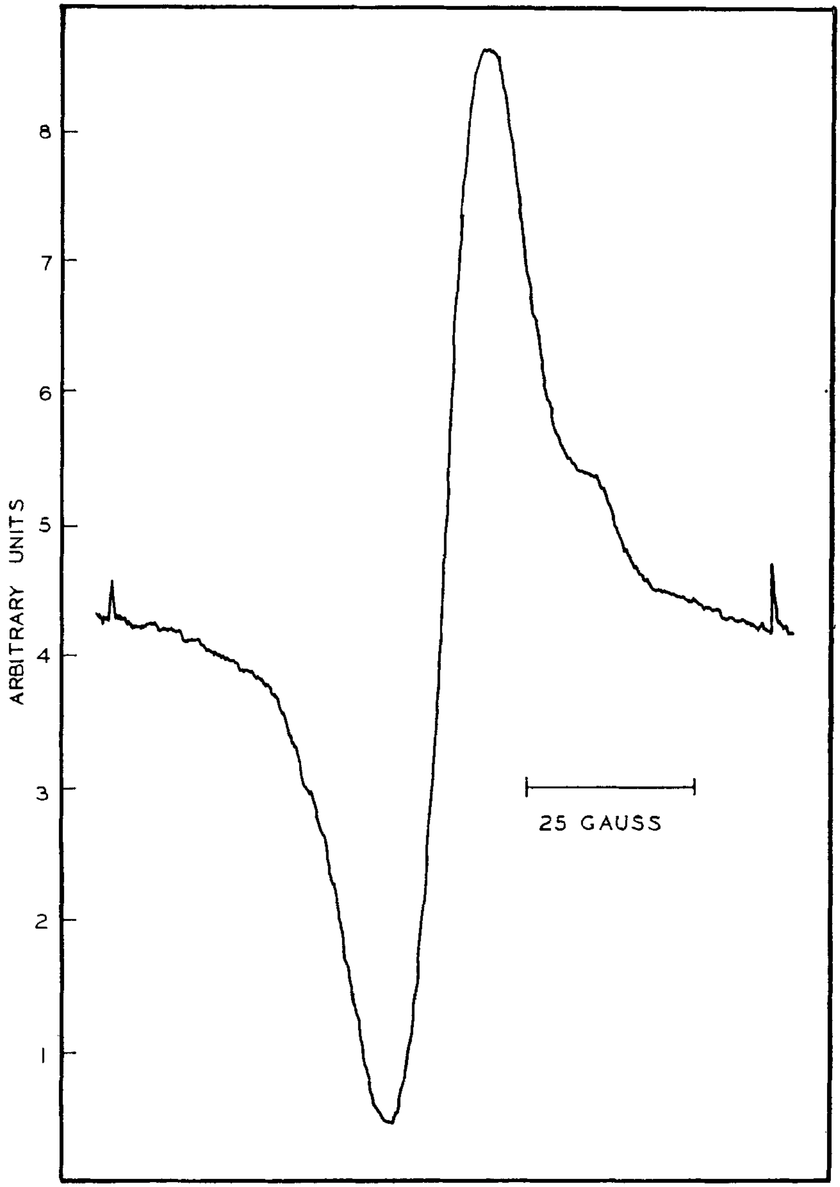


Figure 7. EPR spectrum of irradiated 4-vinylbenzamide measured at −196 °C.

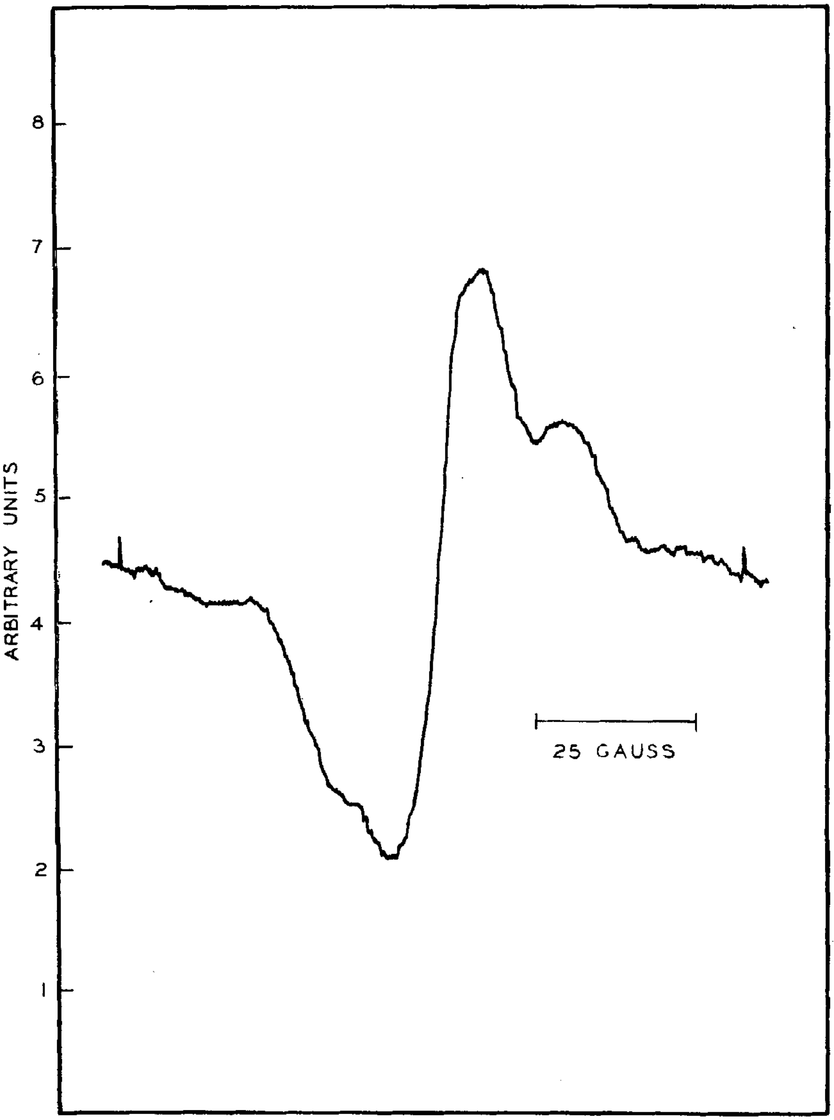


Figure 8. EPR spectrum of irradiated 4-vinylbenzamide measured after 30 minutes at 20 °C.

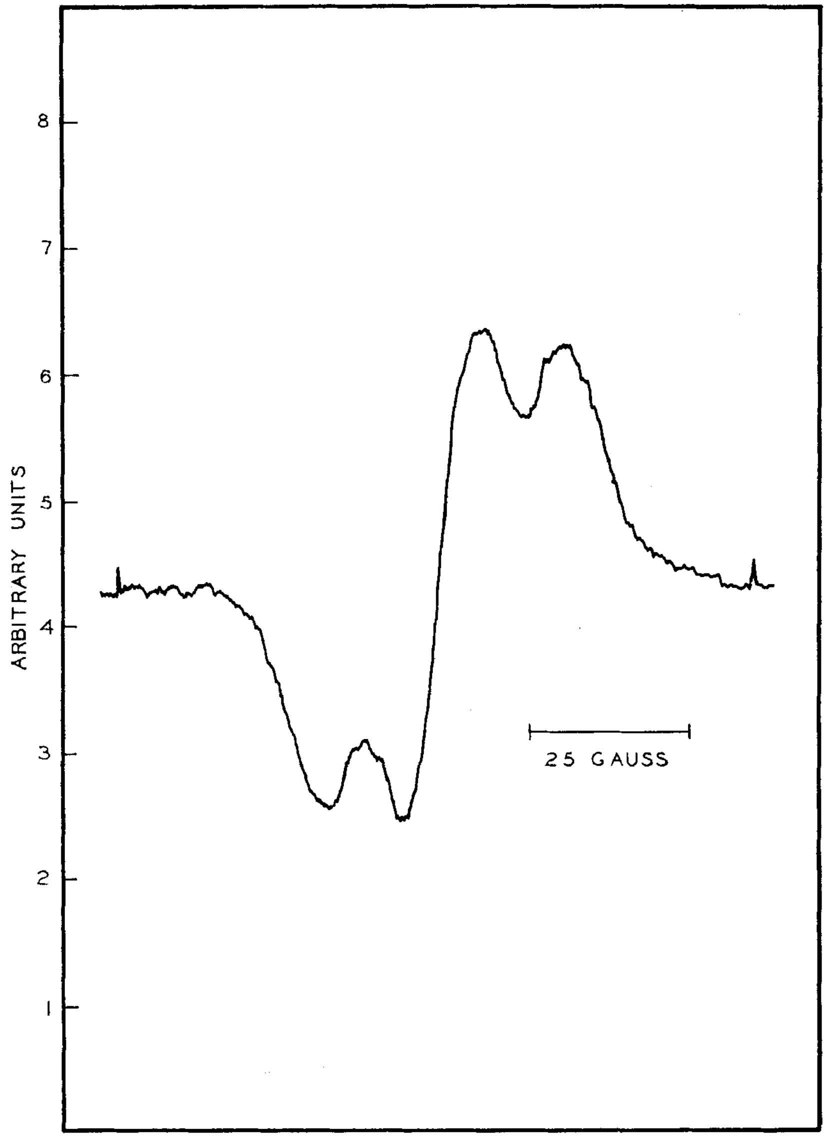


Figure 9. EPR spectrum of irradiated 4-vinylbenzamide measured after 30 hours at 105 °C.

possibility for cross linking which is supported by the insolubility of the polymer.

From the activation energy of approximately 20.5 kcal/mole and the fact that the material can be polymerized thermally it is believed that the reaction proceeds via a radical mechanism and that the propagating radical has the structure indicated above.

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