

## ESR studies of the interaction of propagating radicals with diacetylenes

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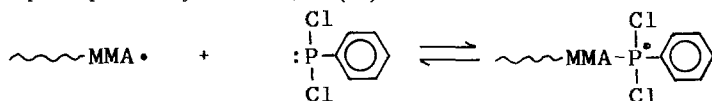
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### ABSTRACT

ESR studies were carried out for the polymerization systems of some vinyl monomers in the presence of diacetylenic compounds in order to determine the nature of interaction between the propagating radicals with the diacetylenes. The systems used in this study were methylmethacrylate, styrene and methylacrylate with diphenylbutadiyne and phenyl-4'-vinylphenylbutadiyne using 2,2'-azobisisobutyronitrile as an initiator. ESR spectra showed a broad triplet for the styrene system, which became exchange narrowed for the methylmethacrylate system. This is explained in terms of increased interaction between the propagating radicals and the diacetylene for methylmethacrylate than styrene. The propagating radicals are considered to be trapped temporarily by the diacetylenes during polymerization, but they do not react until the polymerization system becomes extremely viscous.

### INTRODUCTION

In the free radical polymerization of vinyl monomers, when the rate and degree of polymerization decreases by the addition of a compound, the compound is generally considered to be a degradative chain transfer agent, and the degradative chain transfer constants for such compounds have been determined(1). However, there are cases where the propagating radicals do not react with the added compound, neither addition nor abstraction, but the rate and degree of polymerization is considerably decreased. For example, the free radical polymerization of methylmethacrylate(MMA) is drastically retarded by the addition of dichlorophenylphosphine, but the phosphorus unit is never incorporated in the polymer, and the degree of polymerization increases with the polymerization time, the system becoming non-steady state, and ESR spectra of the system shows the existence of a phosphoranyl radical(2):

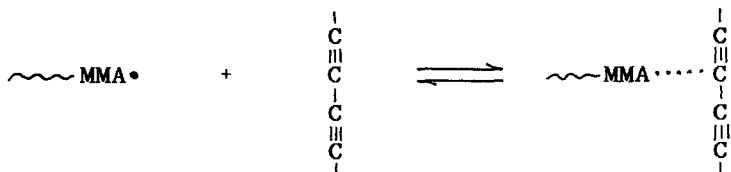


The reaction therefore must be reversible.

Phenyl-4'-vinylphenylbutadiyne(PVPB) does not undergo homopolymerization by free radicals in solution(3), because the propagating radical is trapped by the diacetylenic group. When PVPB is copolymerized with other monomers such as MMA(4),

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styrene(ST)(4) and maleic anhydride(5), copolymers are obtained, and the rate and degree of copolymerization increases with decrease in the PVPB concentration, and when the viscosity of the system increases, the gelation suddenly takes place. The free radical polymerization of vinyl monomers such as MMA, ST, acrylonitrile, etc, in the presence of diphenylbutadiyne(DPB) was studied(6). The rate and degree of polymerization decrease considerably with increase in the DPB concentration. However, the DPB unit is not found in the poly-MMA obtained, while it was found in the case of methylacrylate. These observations suggest that the poly-MMA propagating radicals are trapped temporarily by the diacetylenic groups:



The propagation reaction then competes with the trapping which increases with increase in the diyne concentration.

In order to study the nature of such an interaction between the propagating radicals and diynes, ESR spectra were taken under the polymerization conditions, and the results are reported in this article.

## EXPERIMENTAL

### Materials.

PVPB was prepared by the method reported previously from 2-chloroethylbenzene(3). DPB was prepared by the oxidative coupling reaction of phenylacetylene. They were purified by repeated recrystallization from methanol to obtain colorless crystals. MMA, ST and methylacrylate(MA) were supplied by Fluka and they were distilled before use. 2,2'-azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol.

### Instrumental Techniques.

Monomers containing required amounts of AIBN and diacetylenes were placed in a Pyrex tubes ( 1 mm i.d. x 2 mm o.d.) and the system was degassed by repeated freeze-pump-thaw cycles and sealed under vacuum. Variable ESR spectra were taken over a range of temperatures from room temperature to 85°C with a Bruker ER 200D-SRC spectrometer interfaced with an Aspect data system. The temperature was controlled by a Bruker ER 4111 VT temperature unit to 1°C. The magnetic field was calibrated with a Bruker ER 035M NMR gaussmeter with an accuracy of 2 mG. The frequency was measured with a Model 5342 A Hewlett-Packard frequency counter.

## RESULTS AND DISCUSSION

The system consisting of MMA and AIBN alone was used as a standard for the purpose of comparison with the diacetylene(DA) systems. Its spectrum is shown in Fig. 1. The spectrum appeared after more than 10 hours heating when the system became very viscous or almost solid. The five-line spec-

trum with a hyperfine splitting of 23.0 G and centered at  $g$ -value of 2.0025 confirms the presence of poly-MMA radical(7). Fig. 2 shows the spectrum of the system of MMA, DPB and AIBN. The ESR signals appeared much faster than in the system without the DA. It consists of a three-line spectrum with hyperfine splitting of 5.48 G and a  $g$ -value of 2.0030. This indicates that there exists an interaction with a rapid exchange of electron, the electron bouncing back and forward between the poly-MMA radical and DPB. After 2 hours at room temperature, the same spectrum was still observed.



Fig. 1. MMA + AIBN System. [AIBN] = 0.03 M.  
Spectrum was taken at 54.7°C after 13.5 hrs of heating.

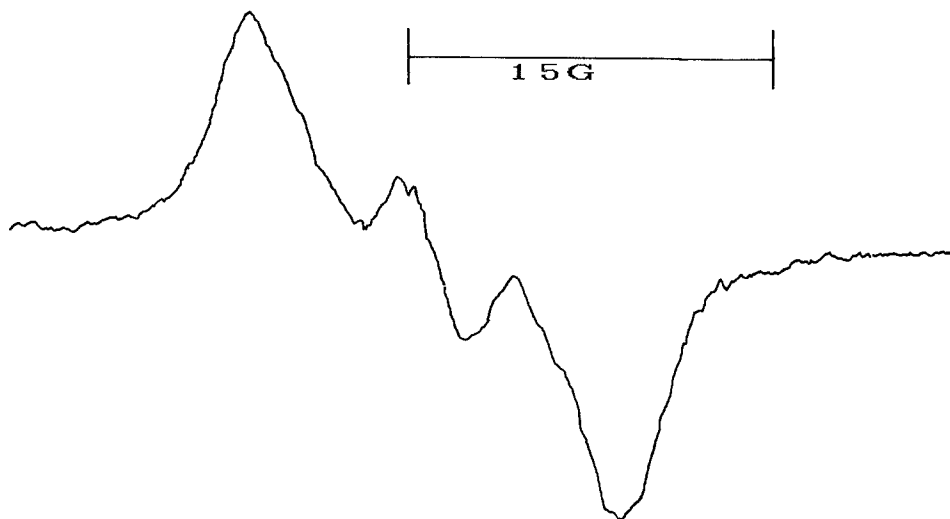


Fig. 2. MMA + DPB + AIBN System. After 30 minutes of heating at 68.5°C. [DPB] = 0.30 M [AIBN] = 0.03 M

Fig. 3 shows the spectrum of the system consisting of MMA, PVPB and AIBN. The spectrum is very similar to that of the DPB system, showing a three-line splitting with 5.88 G and a  $g$ -value of 2.0020. This system retained its signal when the spectrum was taken again after being left to stand at room temperature for 24 hours. Since little decomposition of AIBN takes place in

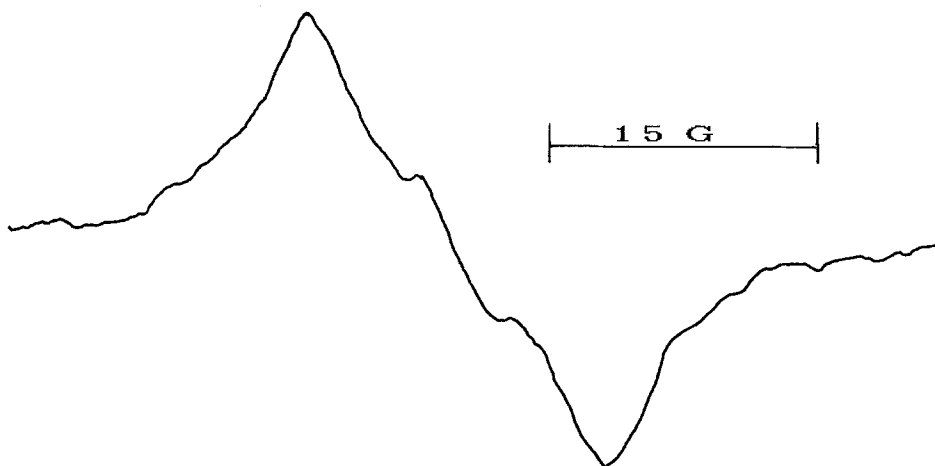


Fig. 3. MMA + PVPB + AIBN System. Spectrum taken at  $75.1^{\circ}\text{C}$  after 15 minutes of heating.  $[\text{PVPB}] = 0.40 \text{ M}$ ,  $[\text{AIBN}] = 0.02 \text{ M}$

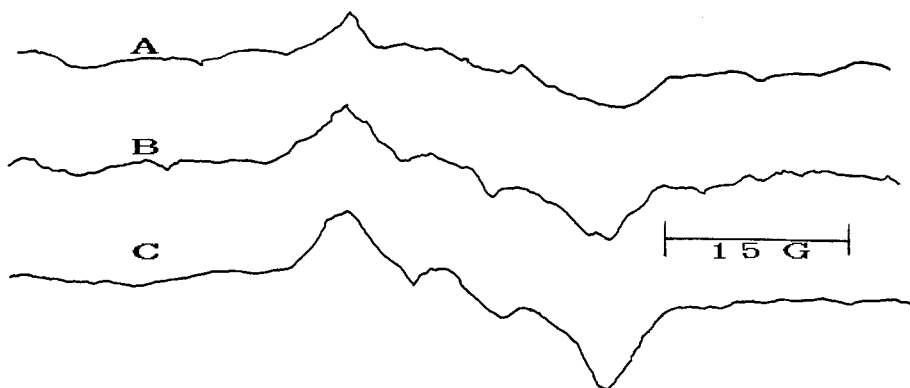


Fig. 4. Time dependence of ESR signal for the MMA + DPB + AIBN system.  $[\text{DPB}] = 0.30 \text{ M}$ ,  $[\text{AIBN}] = 0.03 \text{ M}$ . A: after 18 min. at  $65.8^{\circ}\text{C}$ ; B: after 22 min. at  $65.8^{\circ}\text{C}$ ; C: after 25 min. at  $68.4^{\circ}\text{C}$ .

dark at room temperature, it seems that the trapped poly-MMA radicals are alive. The high viscosity is also contributing to this stabilization, making the motion of macroradicals more

difficult.

Fig. 4 shows the changes in the radical concentration and the viscosity of the system with polymerization time, for the system of MMA, DPB and AIBN. It can be seen that the line width increases with time, i.e, the viscosity increases, and then the radical concentration increases with time. The line width,  $\Delta H$ , of the PVPB system is always greater than that for the DPB system. This is due to the crosslinking which takes place in the PVPB system(4,5).

In the case of ST and AIBN alone, after more than 50 hours of heating at 65 - 76°C, the ESR spectrum showed possible signals of ST radicals, but it was impossible to characterize the nature of the radical because the signals were not clear enough. In the case of the system of ST, DPB and AIBN, as shown in Fig. 5, an ESR spectrum with splitting of approximately 10.3 G was observed, which indicates that an interaction exists between the poly-ST radical and DPB. But it was difficult to estimate the g-value due to the ambiguity of the spectrum.



Fig. 5. ST + DPB + AIBN System. After 6 hours of heating at 78°C, and the spectrum was taken at 85°C.  
[DPB] = 0.30 M, [AIBN] = 0.03 M.

In the case of ST, PBPV and AIBN, a three line spectra with hyperfine splitting of 18.17 G and with a g-value of 2.0024 was observed as shown in Fig. 6. The line width was estimated to be approximately 9.28 G, which suggests the polymerization system is gelled when the spectrum appeared. The higher value of hyperfine splitting for the ST system, suggests that the exchange is slower in the ST-DA systems than the MMA-DA systems. This may be attributed to that the poly-MMA radical is more electron deficient than the poly-ST radical due to its carbonyl group, and the electrostatic attraction between the poly-MMA radical and DA, is greater than that for the ST-DA systems. The steric effect of the propagating radicals is also important. In the case of MMA, the tertiary radical is probably not able to get close enough to DA to form a bond. In the polymerization of

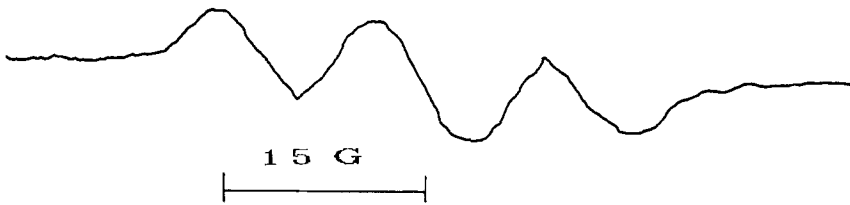
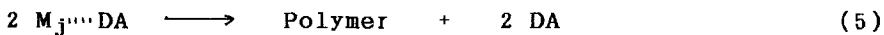
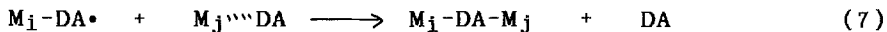
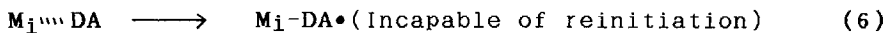


Fig. 6. ST + PVPB + AIBN System. After 30 minutes of heating at 79.3°C. [PVPB] = 0.40 M, [AIBN] = 0.02 M.

vinylidene chloride and methacrylonitrile, the decrease in the rate and degree of polymerization in the presence of DPB, is much less than the other monomers which give secondary radicals, such as methylacrylate, acrylonitrile and vinylacetate. The DPB units were found in the resulting polymethylacrylate(6). ESR spectrum for the MA, DPB and AIBN system could not be obtained under the conditions for the ST and MMA systems. Since the polymerization of MA is retarded by DA, the system never becomes viscous enough to increase the life of the trapped radical. From the results of this work and of the previous works(4,5,6), it can be concluded that DPB and DA of PVPB interacts with the propagating radicals Trapping them temporarily during the propagation. The polymerization mechanism is assumed to be as follows:



In the case of monomers which give reactive secondary radicals, the following termination termination is possible:



The reactions (6) and (7) are also involved in the cases of MMA and ST only when the polymerization system becomes very viscous, as insoluble polymers are formed in the copolymerization of PVPB with MMA. ST and Maleic anhydride when the yields increase(4,5).

#### ACKNOWLEDGEMENT

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