

Study on the interaction of diarylbutadiynes with free radicals: Interaction with propagating radicals of some vinyl monomers

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Abstract

In order to study the nature of interaction of arylbutadiynes with transient free radicals, polymerization and copolymerization of some vinyl monomers such as methyl methacrylate (MMA), styrene (ST), methacrylonitrile (MAN), vinylidene chloride (VCl₂), ethyl acrylate (EA) and acrylonitrile (AN), were carried out in the presence of diphenylbutadiyne (DPB), 4,4'-butadiynylene-N,N,N',N'-tetra-*n*-butyl-dibenzamide (BBA), and 4,4'-dibromodiphenylbutadiyne (BPB). MMA gave an intense ESR signal at the polymerization temperature when the polymerization system became viscous, and the number of radicals increased with polymerization time. Strong signals of polyEA and polyMAN radicals were also observed in the presence of DPB when the polymerization system became almost solid. This is a unique case where active transient propagating radicals such as that of polyEA can be detected at polymerization temperature. The rates of polymerization decreased by the presence of the diacetylenes, but the molecular weights did not change with the diacetylene concentrations. UV spectroscopy revealed that there was no diacetylene unit bonded to the obtained polymers, indicating that degradative chain transfer is not the case. The monomer reactivity ratios for MMA-ST and MMA-AN systems did not vary significantly in the presence of the diacetylenes, although some difference was observed. It seems that some arylbutadiynes interact with free radicals but do not form bonds.

Introduction.

The solid state polymerization of diacetylenes (DAs) is a well known process first proposed by Wegner (1), and its mechanism has been extensively studied (2) and currently established. Since then, there are numerous studies reported on this subject including nonlinear optical properties of topochemically polymerized polyDAs (3), and many studies on polyDAs are continuously being published. However, little has been investigated on the solution or molten state polymerization of DAs. Wiley and Lee have reported thermal polymerization of DPB in benzene and dimethylformamide, and analyzed the polymerization product by mass spectroscopy (4). Paley reported photopolymerization of a DA monomer in solution where the polyDA formed deposited in the form of thin film on a quartz substrate (5), and Hathaway also mentioned polymerization of some DAs but without details (6). The present authors have found previously that an intense ESR signal of propagating polyMMA radicals is observed at polymerization temperature of 70°C when the polymerization system contains DPB (7). It is needless to say that ESR signal of such transient radicals cannot be observed in the absence of DPB. It was also found that some aromatic DAs such as DPB and its derivatives contained small amounts of radicals and they

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interacted reversibly with diphenylpicrylhydrazil (DPPH) decoloring its yellow color solution (8). Furthermore, the ESR signal of polyMMA radical does not disappear for weeks after polymerization indicating the radical is living (9). These unique interactions of aromatic DAs with various types of radicals are intriguing, and therefore, more ESR studies were carried out for some aromatic DAs using different propagating radicals of vinyl monomers, and the results are reported in this paper.

Experimental

Materials: Diphenylbutadiyne (DPB), colorless needles mp. 80°C, was prepared by the oxidative coupling reaction of phenylacetylene (Aldrich) in acetone using purified copper(I) chloride and N,N,N',N'-tetramethylethylenediamine gently bubbling oxygen for several hours. *p,p'*-Bromodiphenylbutadiyne (BPB), yellow powder with mp. 224-225°C was synthesized by the oxidative coupling reaction of *p*-bromophenylacetylene, which was prepared by the reaction of *p*-bromoacetophenone with phosphorus pentachloride, followed by treating with potassium hydroxide powder in dimethylsulfoxide. N,N,N',N'-tetra-*n*-butyl-*p,p'*-butadiynylenedibenzamide (BBA), pale yellow crystals mp. 109-110°C, was synthesized by the reaction of N,N-di-*n*-butyl-*p*-bromobenzamide with trimethylsilylacetylene in pyridine and triethylamine using dichlorobis(triphenylphosphine) palladium(II) as a catalyst, followed by oxidative coupling reaction using copper(I) chloride and tetramethylethylene diamine. All of these diacetylenes (DAs) were purified by repeated recrystallization, and identified by elemental analysis, FTIR and NMR spectra. The vinyl monomers used were supplied by Aldrich Chemical Co, and they were distilled once before use. They include methyl methacrylate (MMA), methacrylonitrile (MAN), acrylonitrile (AN), styrene (ST), vinylidene chloride (VCl₂), ethyl acrylate (EA) and vinyl acetate (VOAc). The initiator, azobisisobutyronitrile (AIBN) was purified by recrystallization from ethanol.

Polymerization: The bulk polymerization was carried out at 60°C in Pyrex sealed tubes with an inner diameter of 15 mm, in which 3 ml of monomer containing AIBN (0.004 M) and required amounts of DAs were placed, and the tube was sealed off in vacuum after repeated freeze and melt process. The polymers were precipitated in methanol and the yields were calculated from the weights of obtained polymers.

Copolymer composition and polymer analysis: The elemental analysis was performed for the DAs and the copolymers by Desert Analytics of Tucson, AZ, USA. The monomer reactivity ratios were obtained from the Fineman-Ross plotting, as the conversions were kept low (less than 5%). In order to see whether the diacetylenic unit is combined to polymer chains, UV spectra of polymers repeatedly purified by reprecipitation were taken using a UV/Visible spectrophotometer Perkin-Elmer Model 553 Fast Scan.

Molecular weight determination: The molecular weights were determined using a Waters GPC with columns of 500A and ultrastyrogel in chloroform.

ESR measurements: ESR spectra of the DAs and polymerization systems were taken using a JEOL ESR spectrometer Model JES-RE3X. The samples were placed in quartz tubes and sealed off in vacuum after repeated degassing. The numbers of radicals were estimated by the method reported previously (8,9).

Results and discussion.

The effects of the DPB on the rate of polymerization are shown in Fig. 1. Each rate was determined by time-conversion plotting of polymerization. It is clearly observed that the retardation effect is more enhanced for the systems with less stable propagating radicals. VOAc did not give polymer in the presence of DPB. The rates of polymerization decreased in the presence of these DAs, especially for EA whose propagating radicals are more reactive than the others. The less effect on VCl_2 is probably due to its steric effect being a tertiary radical. The molecular weights of polymers obtained were almost independent of the DPB concentration, and their distribution did not change either. In all the cases the polymers obtained with less than 20% conversion, did not contain any fragment of DAs (examined from UV absorption spectra of the polymers). This suggests that there is no bonding between DAs and propagating radicals, and therefore there is no chain transfer reaction of propagating radicals to the DAs, which is commonly assumed to take place. The effects of BBA and BPB on the polymerization of MMA were studied. The rate and degree of polymerization did not change appreciably over concentration ranges up to 0.02 M (BBA) and 8×10^{-4} M (BPB) which is the limit of concentration due to its poor solubility.

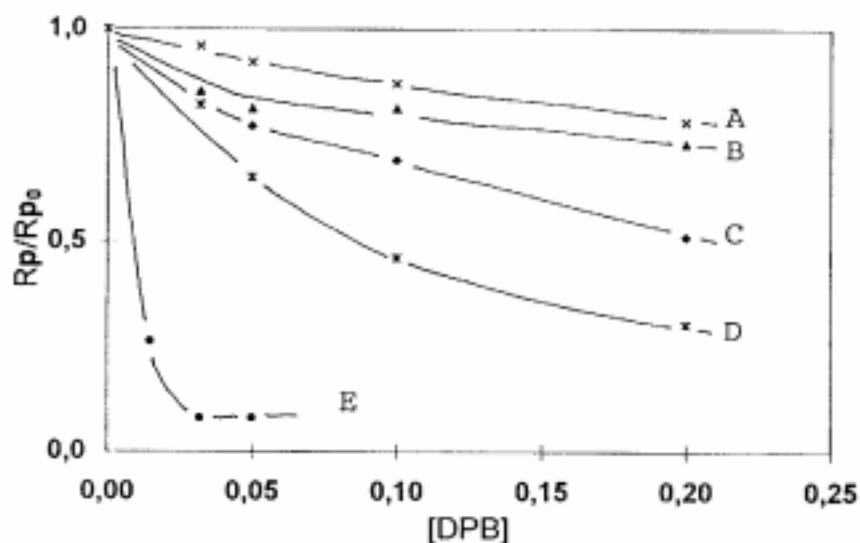


Fig.1. Effects of DPB on the rates of polymerization of vinyl monomers.

60°C.

[AIBN] = 4×10^{-3} M,
Bulk polymerization.
The rates were obtained by time-conversion plots of 5 points.

A: ST,
B: MAN,
C: MMA,
D: VCl_2 ,
E: EA

Time (min)	No. of radicals per Imole of MMA	No. of radicals per Imole of BBA
Starting at 70°C	4.1×10^{19}	1.2×10^{22}
20	7.4×10^{19}	2.1×10^{22}
40	9.6×10^{19}	2.8×10^{22}
60	9.9×10^{19}	2.9×10^{22}
80	9.7×10^{19}	2.8×10^{22}
100	9.7×10^{19}	2.8×10^{22}

Table 1. Number of radicals during polymerization of MMA in the presence of BBA in the ESR cavity at 70°C

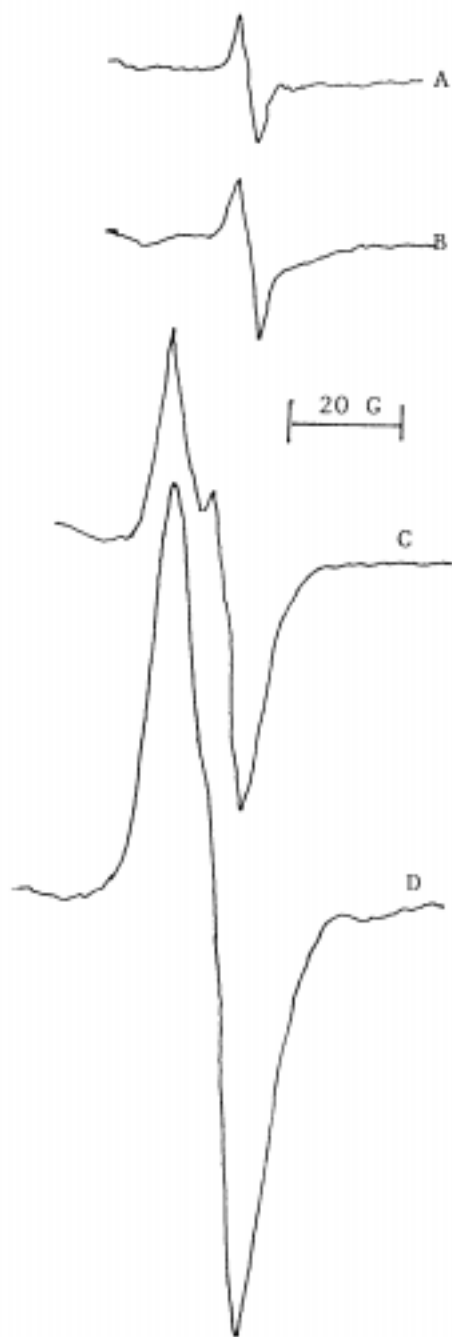
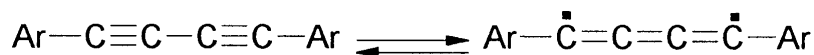


Fig. 2. ESR spectra of polymerization system of MMA in the presence of BBA. At 70°C. Bulk polymerization. [AIBN] = 0.02 M. [BBA] = 0.03 M. Modulation amplitude: 5 gauss, Modulation frequency: 100kHz, Microwave frequency: 9.166 GHz, Central field: 3250 ± 150 gauss, Receiver gain: 200(A,B,C) and 100(D). A: Before heating, B: at 70°C, C: 20 min. at 70°C, D: 100 min. at 70°C

ESR spectra of the polymerization systems for MMA with BBA are shown in Fig.2. The signal A is probably due to the biradicals of BBA. DPB also showed the similar signal due to its biradicals (8). It seems that aromatic DAs contain their biradicals at room temperature. This is not observed for aliphatic DAs. As the polymerization proceeds the signal of interacted MMA radicals appears (B), and eventually the signal of BBA is covered and hidden in that of the MMA radicals. Such signal is not observed in the absence of the DAs. The numbers of radicals during the polymerization are shown in Table 1. They increase with time, but seem to become more or less constant after a certain time, probably due to consumption by the termination. The signal did not disappear after polymerization, and it continued to exist after several weeks when left to stand at room temperature until the system was exposed to air. This tendency was also observed for other aromatic DAs such as di(methoxycarbonyl)-4,4'-diphenylbutadiyne and DPB, but the DAs having electron donor groups such as amino and methoxy groups did not show this tendency, and the signals disappeared when the tubes were removed from ESR cavity (9). ESR spectra of BBA alone was taken over the temperature range from room temperature to 170°C, and it was found that the number of radicals calculated from their ESR spectra did not vary appreciably with temperature, showing that 1 molecule out of 3,400 molecules of BBA exists as biradical. A system of BBA in 1,2-dichlorobenzene containing 0.02 M of AIBN was studied, and it was found from ESR spectra that 1 out of 12,000 molecules existed as biradical at the temperature range of 60-100°C. In the case of solid state polymerization of topochemically polymerizable DAs, such biradicals formed by irradiation can rapidly propagate to the very adequately situated, adjacent molecules, but in the cases of DAs which are not topochemically polymerizable due to unfavorable crystal packing, the

radicals are isolated and can exist as the monomer radicals.



As can be seen from Table 1, the numbers of the radicals of the polymerization system are much greater than that of the case for BBA alone, and more than 1 % of total BBA are interacting with polyMMA radicals.

The oligomerization of some diarylbutadiynes in solution or in the molten state is considered to proceed via coupling reaction of the biradicals (10), which is being studied and will be reported in future.

It should be noted that the ESR signals of propagating radicals only appear when the viscosity of the polymerization increases thus the number of radicals increased. When the viscosity is low, the termination of propagating radicals seems to take place freely, and therefore their ESR signals are not observed. In the cases of monomers whose propagating radicals interact more strongly, such as acrylates, the polymerization is retarded and the systems do not become viscous and ESR signals cannot be observed. In the cases of MAN its polymerization is very slow, a highly viscous state could not be obtained under the polymerization conditions of this work, and its ESR signal was not observed during polymerization. Therefore, in order to prove this hypothesis, polyMAN was placed in the ESR tube, into which MAN containing DPB and AIBN was added, and after degassing the system, the tube was sealed off in vacuum, and left to stand for a few weeks so that the monomer penetrates into the polymer forming an extremely viscous mass. Fig. 3 shows ESR signal of polyMAN radical observed when this mixture was heated in the ESR cavity. In the case of EA, the polymerization is very much retarded and only low molecular weight polymers are obtained, and therefore, a viscous state can never be achieved during polymerization. Similarly to the case of MAN, polyEA, EA, AIBN and DPB were placed in an ESR tube, and after degassing the system, it was sealed off, left to stand for a week until homogeneous mixture was formed, and heated in the cavity. At the beginning of heating, a weak signal was observed and this is probably due to DPB itself, but with temperature rise the intensity increased, as can be seen in Fig. 4. These signals are due to the propagating polyEA radicals interacted with DPB and trapped in the viscous system, and not the tertiary polymer chain radicals which could have been formed by the abstraction of the tertiary hydrogen by the propagating radical. In the absence of DPB no such signal could be observed, and this is the only case so far that ESR signal of polyEA radicals are observed for a homogeneous system at temperatures as high as 100°C. The signal disappeared when left to stand at room temperature for several days, but on heating the signal reappeared. When the system was heated at above 170°C the signal started to fade and totally disappeared at 190°C. The system was completely colorless even at 190°C suggesting that the addition of the polyEA radical to the DA did not take place. If this had occurred, the system should have become colored due to formation of a highly conjugated radical. In the case of ST, (polyST added with ST containing DPB and AIBN) a broad ESR signals which is the same as reported previously (7), was observed. VOAc did not give any signal when treated similarly to the above cases, probably because they are too unstable. Other vinyl monomers probably will give ESR signals of their propagating radicals if highly viscous systems are created in the presence of diaryldiacetylenes.

In this work BBA and BPB were chosen as DAs having steric hindrance, so that the termination between the two propagating radicals might be retarded, resulting in increase in the molecular weights and the rate of polymerization. However, there was no appreciable difference between these two DAs and DPB which has no substituted groups on the phenyl rings. No detailed study could be made with BPB due to its poor solubility in solvents. The steric effect by the bulky groups at the *para* positions do not seem to be important.

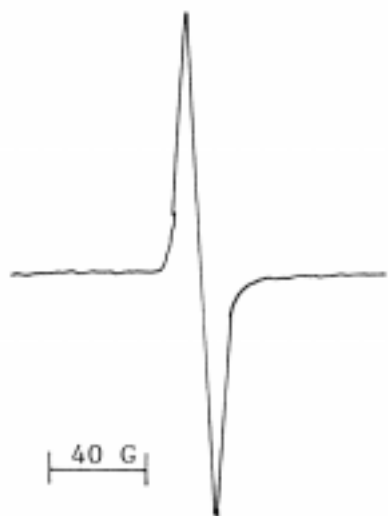


Fig. 3. ESR signal of polyMAN radicals in the presence of DPB at 90°C. Modulation amplitude: 0.5 gauss, Modulation frequency: 100kHz, Microwave frequency: 9.153 GHz, Central field: 3250 ± 150 gauss, Receiver gain: 50.

It seems when the viscosity of polymerization system is low the propagating radicals are only interacting by the rapid exchange of electron with the DAs, without adding to the triple bond. However, when the polymerization system becomes extremely viscous or solid, the addition of propagating radicals to the triple bond may take place. The polymerization of phenyl-4-ethenylphenyl-butadiyne was studied previously (11), and it was found that insoluble polymers were obtained when this monomer was copolymerized with MMA to high conversion.

The free radical reactivity of aromatic DAs in solution seems to be very unique. The DAs apparently do not combine with free radicals such as

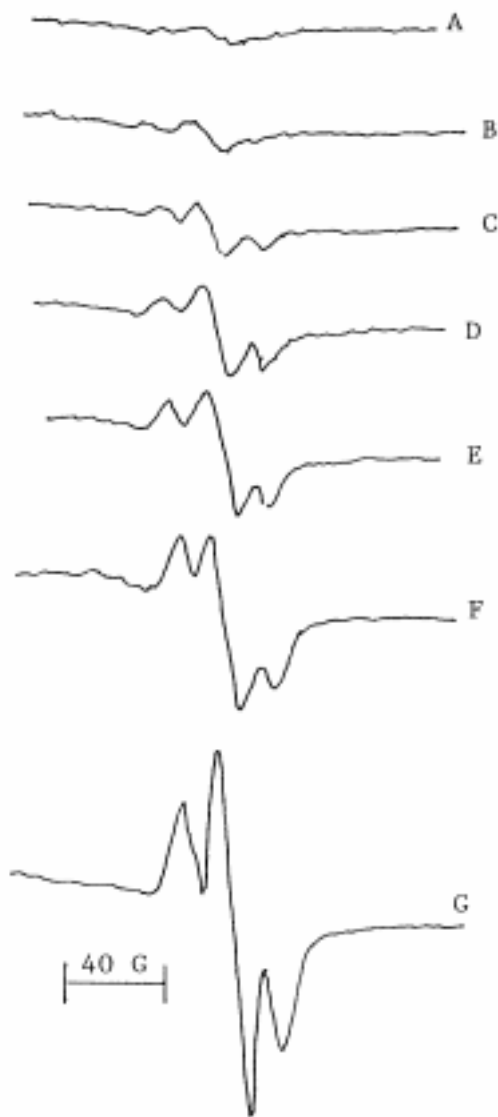


Fig. 4. ESR spectra of polymerization system of EA in the presence of DPB at polymerization temperatures. A: room temperature, B: heated to 70°C, C: after 1 hr at 70°C, D: temp. raised to 80°C, E: at 100°C, F: at 110°C, G: heated to 130°C. Modulation amplitude: 5 gauss, Modulation frequency: 100 kHz, Microwave frequency: 9.156 GHz, Central field: 3240 ± 400 gauss, Receiver gain: 200.

propagating polymer radicals, stable radicals such as DPPH, etc. When they are reacted with peroxides such as di-*tert*-butylperoxide in 1,2-dichlorobenzene, its oligomerization takes place, but very interestingly, the product does not contain the fragments of *t*-butyl group, and furthermore, the number of DA radicals increases significantly in the presence of peroxide at room temperature (10).

In order to see if the difference in the magnitude of interaction with DAs, between the different propagating radicals, copolymerization of MMA with ST and with AN were carried out. The conversion was kept below 5 % so that the monomer reactivity ratios can be estimated by the Fineman-Ross plotting of 5 concentrations, which were found to be: Absence of DPB ($r_{1(\text{MMA})} = 0.48$, $r_{2(\text{ST})} = 0.29$); Presence of DPB ($r_{1(\text{MMA})} = 0.47$, $r_{2(\text{ST})} = 0.45$); Absence of DPB ($r_{1(\text{MMA})} = 1.70$, $r_{2(\text{AN})} = 0.08$); Presence of DPB ($r_{1(\text{MMA})} = 2.38$, $r_{2(\text{AN})} = 0.09$). These values lie among the values reported by previous studies (12) and the differences between the values in the presence and absence of DAs were not significant to make discussion, but they may be attributed to the electronic effect at the transition state. By the interaction with the DA which interacts as electron acceptor, the electronic density of the interacted propagating radicals is lowered, and this facilitates the addition of the monomer having higher electronic density. In the cases of MMA/AN system, AN is the monomer with lower electronic density and therefore MMA adds to the interacted radicals, thus increasing $r_{1(\text{MMA})}$. In the case of MMA/ST the same can be said, as $r_{2(\text{ST})}$ increased in the presence of DAs.

It can be concluded that propagating polymer radicals of vinyl monomers interact with aromatic DAs through rapid exchange of electron, thus the radicals are stabilized enough to show their ESR signals at polymerization temperatures. The interaction is reversible and competes with propagation and termination. Because the polymers obtained from the monomers studied in this work, did not contained the DPB, it can be said that the DAs do not combine with the propagating radicals under the conditions of this work, and that no degradative chain transfer reaction of DAs is involved. It is intriguing but difficult to understand why transient radicals such as polyMMA radical do not add to DAs *in solution*, while the DA biradicals appear to combine each other.

ESR signals of the propagating radicals at polymerization temperature, are only observed when the polymerization system becomes extremely viscous, i.e. the content of the ESR tube does not move when inclined, where the mobility of polymer radicals is retarded and the termination becomes difficult, and the numbers of radicals increases.

From the results of this work and other studies in our laboratory, it can be said that aromatic DAs can be considered to be a unique, new type of radical scavengers, or stabilizers, as they interact with stable and transient radicals without forming bonds in solution.

The exact nature of such interaction should be clarified in future, but it seems that aromatic DAs possess peculiar behaviors toward free radicals.

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