

Diacetylenes Polymerize in Amorphous State? Free Radical Initiated Polymerization of Aromatic Diaryldiacetylenes.

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Introduction

Since Wegner reported more than 35 years ago the unique polymerization of some diacetylene crystals [1], a great number of papers were published on their polymerization mechanisms [2], their nonlinear optical properties [3] and their applications. However, because of their crystalline nature, the processing into thin films with acceptable optical quality, are not obtained, and the interest in the crystalline diacetylenes faded away.

In order to obtain films with high optical quality, it is essential to obtain amorphous polymers. Amorphous polymers are obtained by solution polymerization or molten state polymerization. It is known that aliphatic diacetylenes which undergo topochemical polymerization do not polymerize in solution or in molten state. At the temperature below their thermal decomposition temperatures, around 200°C, nothing happens, even irradiated with UV light.

Aromatic diacetylenes on the other hand, form 1,4-butatriene diradicals when irradiated with UV light, which then couple each other to form dimeric diradicals [4]. When they were heated at temperature above their melting point, but below their thermal decomposition temperature, they also form stable diradicals detectable by ESR at the reaction temperatures [5].

In this presentation, the formation of stable diradicals of aromatic diacetylenes is discussed, and their polymerization mechanism in solution systems will be discussed, as well as the possibility of obtaining amorphous polydiacetylenes.

Experimental

The aromatic diacetylenes were synthesized by the oxidative coupling reaction of the corresponding aryl acetylenes. The reactions of diacetylenes were carried out in 1,2-dichlorobenzene at 110°C using t-butylperoxide.

Results and Discussion

Fig 1. shows a typical ESR spectra of diphenylbutadiene (DPB) reacted with t-butylperoxide. The signals is that of free electron ($g = 2.003$) of highly conjugated carbon radicals. The radicals are stable and their decay with time is very slow. The numbers of radicals formed in the presence of peroxide were greater by one or two order than those in the absence of peroxide. (10^{17-19} radicals per mole of diacetylenes). The substituted diacetylene formed more radicals than the unsubstituted DPB. This is because the radicals of substituted diacetylenes are more stable by resonance effect, or they do not undergo coupling reactions due to the steric effect.

Fig 2 shows ^1H NMR spectra of oligoDPB ($M_n = 2000$). There is no proton that arises from t-butyl group. This indicates that the t-butoxy radicals do not add to the diacetylene. Previously the free radical polymerization of vinyl monomers were carried out in the presence of aromatic diacetylenes [6], and it was found that the propagating polymer radicals do not add to diacetylenes. The FT-IR spectra of the oligomers do not contain any peak due to the t-butyl and carbonyl groups or ether bonds.

The product oligo-DPB contained substantial amount of radicals even after the products were exposed to air, and subjected to extraction, washing, reprecipitation. This indicates that the these radicals are extremely stable. However, the number of radicals very slowly decreases with time (over a period of months and year). However, because there was no increase in molecular weight, and it is thought that cyclization of the oligomeric diradicals takes place.

It was concluded that DPB is activated by the collision with t-butoxy radicals to form diradical, which undergo coupling to form stable dimeric diradicals. The oligomerization proceeds through coupling of diradicals. The diacetylenes with p,p' disubstituted groups are more difficult to be coupled due to the steric effect.

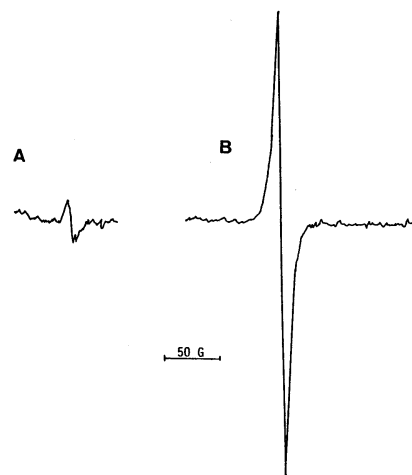


Fig. 1. ESR spectra of DPB treated in the absence (A) and presence (B) of peroxide.

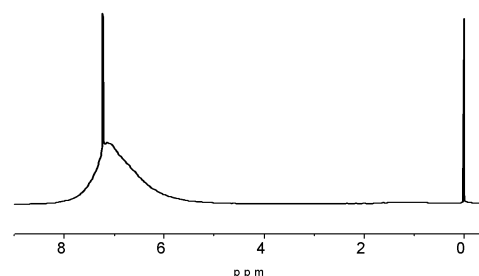


Fig. 2 ^1H NMR spectra of oligo DPB.

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