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Studies on diacetylenic vinyl compounds
I. Phenyl-4'-vinylphenyl butadiyne

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ABSTRACT

Phenyl-4'-vinylphenyl butadiyne was synthesized, and its polymerization under various conditions was quantitatively studied. The polmerization in solution using azobisisobutyronitrile as an initiator was very slow and the yield was low. The polymerization in molten state at 80°C gave mostly an insoluble polymer, but a small part was soluble in chloroform, which was the vinyl polymer. Irradiation with UV light in the crystalline state also gave soluble and insoluble polymers, and the soluble polymer was the vinyl type. The monomer readily polymerized at -78°C in tetrahydrofuran with n-butyl lithium to give poly(p-phenylbutadiynyl styrene).

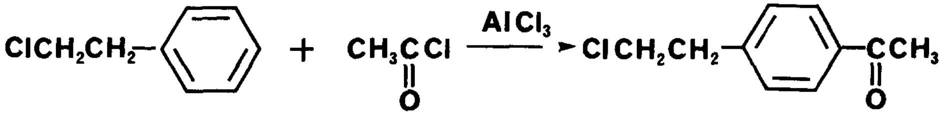
INTRODUCTION

The polymerizations of diacetylenes have been widely studied, especially those in the solid state(1). However, little has been reported on their polymerizations in solution or in the molten state, probably because some of them just do not polymerize under such conditions, and also, if they polymerize, the majority give insoluble or infusible polymers. These polymerizations are of little interest academically, as they cannot be controlled. The present authors are interested in preparation of processable highly conjugated polymers having good mechanical strengths, and as a part of the studies, some monomers which have both vinyl and acetylenic groups are being synthesized and their polymerizations by the vinyl groups and acetylenic groups are being studied. In this paper the synthesis of phenyl-4'-vinylphenyl butadiyne and its polimerizability are reported.

EXPERIMENTAL

Monomer preparation

Phenyl-4'-vinylphenyl butadiyne(PVPB) was synthesized by the Chodkiewicz-Cadiot coupling reaction of 4'-ethynyl styrene and phenylbromoacetylene(2). 4'-Ethynyl styrene was prepared by the method reported by Greber and Egle(3) as shown below:



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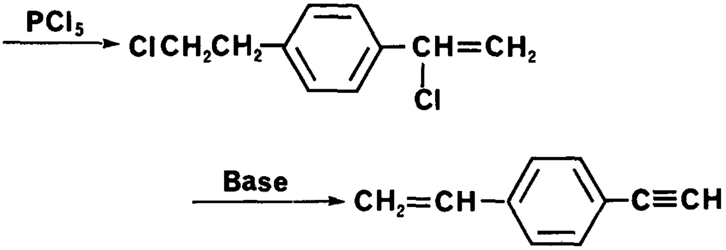
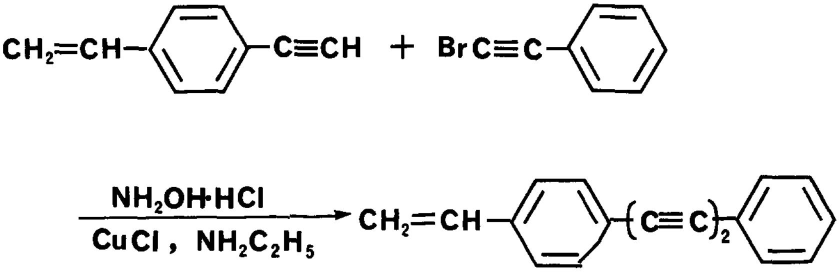


Phenylbromoacetylene was prepared by the reaction of bromine with phenylacetylene(4). The coupling reaction was carried out in methanol at room temperature under nitrogen.



13.1 g (0.102 mole) of ethynyl styrene were dissolved in a mixture of 25 ml of methanol and 20 ml of 70 % aqueous solution of ethylamine. Then 0.25 g of cuprous chloride and 0.5 g of hydroxylamine hydrochloride were added. To this solution, 18.5 g (0.105 mole) of phenylbromoacetylene were added dropwise with efficient stirring at room temperature. After 2 hours 1 g of potassium cyanide was added, and the volatile components were evaporated at room temperature in vacuum. The remaining solid was thoroughly washed with water and with heptane, and the yellowish solid was recrystallized from methanol. 14 g (58% yield) of colorless flake crystals were obtained. mp. 78°C. Elemental analysis: C; 94.05%, H; 5.18%. Calcd. for $C_{18}H_{12}$: C; 94.74%, H; 5.26%.

Polymerizations

(1) Free radical polymerization in solution: 2 g of PVPB were dissolved in 4 ml of benzene containing 2,2'-azobisisobutyronitrile(conc.= 3 x 10^{-2}M), and the solution was heated at 70°C for 15 hrs under an argon atmosphere. The solution became yellow but no appreciable amount of polymer precipitated when poured into methanol, and unreacted monomer was recovered. 1 g of PVPB was dissolved in 2 ml of toluene containing the same initiator (conc.= 2 x 10^{-2}M) and the solution was sealed off in vacuum after repeated freeze and degas process. The polymerization was carried out at 55°C for 16 hrs. The system became deep yellow but viscosity did not increase apparently. 0.0048 g of methanol insoluble yellow polymer was obtained.

(2) Molten state thermal polymerization: 1 g of PVPB was heated at 80°C for 7 hrs under argon and a pale brown solid was washed with methanol. The methanol insoluble polymer(almost 100% yield) was mostly insoluble in solvents such as chloroform and dimethyl formamide, and less than 10% was soluble in chloroform, which was subjected to GPC for molecular weight determination(Fig.1).

(3) Photopolymerization: 1 g of finely ground PVPB crystals were suspended in 10 ml of water in a Pyrex tube with 2 cm diameter and with an argon inlet. The suspension was stirred with a magnetic stirrer, and it was irradiated with a 100W high pressure mercury UV lamp with a distance between the lamp and tube of 8 cm, at room temperature for 10 hrs. The PVPB crystals floated in water at the beginning stage but as the polymerization proceeded they became yellow and sank in water indicating increased density. The crystals were washed with methanol to remove unreacted PVPB. The remaining pale yellow solid(45% yield) also contained a fraction(about 10%) insoluble in chloroform and DMF

(4) Anionic polymerization: 2 g of PVPB were dissolved in 10 ml of dry tetrahydrofuran and a small amount of n-hexane solution (1.3 M) of n-butyl lithium was added at -78°C under argon. A deep blue color appeared immediately. After stirring for 30 minutes at this temperature, the deep blue slightly viscous solution was poured into methanol. The pale yellow polymer precipitated was filtered, washed with methanol and dried in vacuum. The yield was almost quantitative. The molecular weight was determined by GPC (Fig.1). Elemental analysis: Found: C; 94.35%, H; 5.10%. Calcd. for $C_{18}H_{12}$: C;94.74%, H;5.26%.

General

All chemicals used for synthesis of PVPB were supplied by Aldrich Chemical Company, and they were used without further purification. The solution of n-butyl lithium was supplied by Alfa Products. The solvents for the polymerization were purified by the usual methods before use.

Elemental analysis were performed by Micanal Laboratories of Tucson, Arizona.

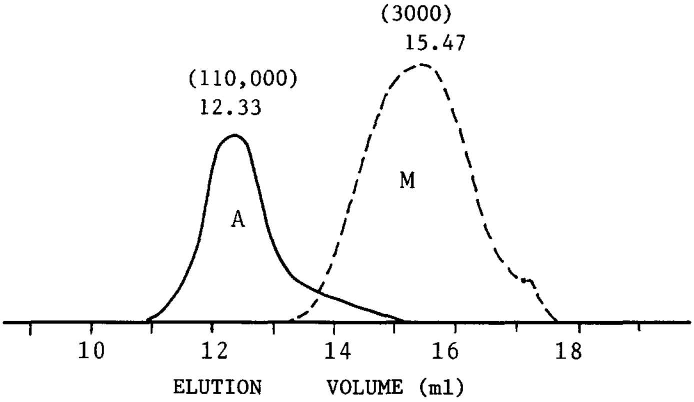


Fig.1. GPC Distribution for the polymer obtained by anionic polymerization(A) and by the molten state polymerization(M).

The polymer molecular weights were determined for chloroform solutions by GPC using an IBN 10 µm(100 - 900 MW), Zorbax 60S (DuPont 10^2- 10^4 MW), Zorbax 300S (DuPont $3x10^3$- $3x10^5$ MW) columns, a Spectrophysics 8200 UV detector and a polystyrene calibration curve. Results are shown in Fig. 1.

The infrared spectra of PVPB (KBr disk) and the polymers (films cast on NaCl plate) were taken using a Perkin Elmer Infrared spectrophotometer Model 1420. The NMR spectra were taken in deuterated chloroform using a Varian EM 360 60 MHz NMR Spectrometer, and UV spectra were taken in tetrahydrofuran using a Perkin Elmer Lambda 9 UV/VIS/NIR spectrophotometer.

RESULTS AND DISCUSSION

Although the monomer PVPB was purified repeatedly by recrystallization from methanol before polymerization to make certain that no copper ion remained in the crystals, it did not give high polymers by the free radical polymerization in solution, and the yield was very low. This poor polymerizability may be attributed to the interaction of propagating PVPB radicals with the diacetylene groups. The free radical copolymerization of PVPB with styrene and with methylmathacrylate take place although the rates are slow(5). The yield increases with increase in the comonomer concentration, and the copolymers are all soluble in chloroform. Therefore, the interaction between the prapagating PVPB radicals with the diacetylene groups, is considered to be a weak one, unable to stop the propagation totally or to form crosslinked polymers by the chain transfer. The color of the propagating anion of PVPB in THF is deep blue while that of styrene is red. Therefore in the free radical polymerization also, the propagating PVPB radicals are more stable than the styryl radicals, but this alone cannot explain the slow polymerization of PVPB.

The observation that PVPB crystals floating in water before the irradiation of UV light, sank as the polymerization proceeded, indicates the increase in density with the polymerization. The monomer PVPB is stable on standing in an open space at room temperature for weeks without any sign of polymerization or coloring. The soluble polymer obtained by the UV irradiation in the crystalline state had an NMR spectra of the vinyl type, similar to that shown in Fig.2 (B), and it is unlikely that the polymerization of diacetylene groups took place. The change of color; from colorless to yellow, during the polymerization, however, shows formation of a certain conjugated system, probably between the diacetylene groups which are brought close together by the polymerization of vinyl linkages.

The polyPVPB and copolymers are all yellow although the color intensity depends on the polymerization conditions. The polymer obtained by the anionic polymerization is less colored than those obtained by the radical polymerizations. The yellow color cannot be removed by the reprecipitation, and the color intensity increases on standing in an open space at room temperature, and chloroform insoluble fractions are formed. The yellow polyPVPB has an absorption starting at about 500 nm with a λ max of 380 nm in THF. The absorption intensity increased with time left to stand in the open space. This also indicates a reaction between the diacetylene units is taking place in the

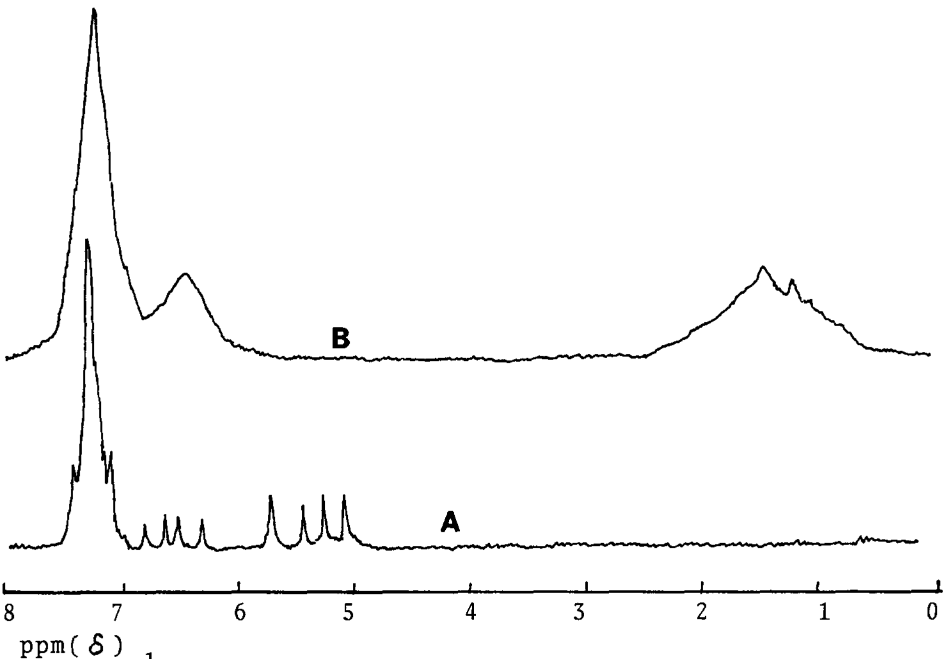


Fig. 2. ^{1}H NMR spectra of PVPB(A) and polyPVPB obtained by anionic polymerization(B).

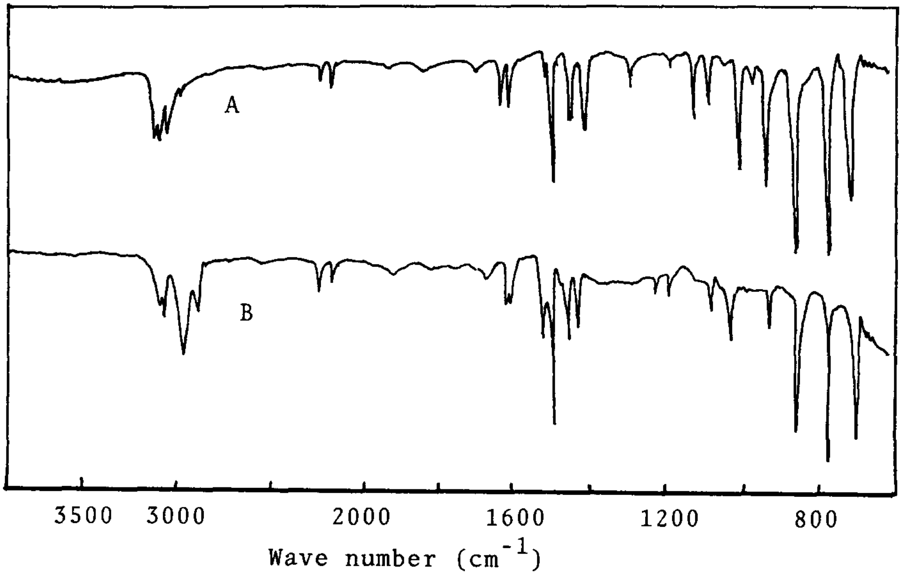


Fig. 2. IR spectra of PVPB(A) and polymer obtained by anionic polymerization(B).

solid polymer. Therefore polyPVPB can be crosslinked with radiation or heat, and it may be used as a photoresist.

The higher polymerizability in the crystalline state than in solution, is thought to be due to the restricted mobility of propagating radicals in the crystalline state, thus their interaction with the diacetylene groups being reduced. More detailed studies are being made on this photopolymerization in the solid state, and the results will be reported in future.

The polymerization in the molten state is considered to be not interesting because the product is mostly insoluble and infusible. The molecular weight of a soluble polymer obtained by the molten state polymerization was very small as shown in Fig. 1.

Fig. 2 shows NMR spectra for both monomer and polymer. The spectra of polymer resemble to those of polystyrene and poly(phenyl vinyl ketone) and there is no doubt that the polymer is the vinyl polymer. Infrared spectra of the monomer and the polyPVPB are shown in Fig. 3.

From the above studies it seems that polyPVPB having high molecular weights cannot be obtained by the ordinary free radical polymerization in solution, but high molecular weight homopolymer would be obtained by the anionic polymerization if more strict polymerization conditions are employed. The polymerization in the crystalline state is interesting because, apart from obtaining a crystalline polymer, there may be a possibility of polymerizing the diacetylene groups in the crystalline vinyl polymer.

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