Polymer Bulletin 21, 453-458 (1989)

Polymer Bulletin

Studies on diacetylenic vinyl compounds

III. The solid state polymerization of phenyl-4'-vinylphenylbutadiyne

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ABSTRACT

The thermal and radiation polymerization of phenyl-4'-vinylphenylbutadiyne(PVPB) in the solid state was investigated. Both soluble and insoluble products were formed. The amount of insoluble fractions increased with increase in the conversion. The soluble polymers were partially crystalline but the insoluble polymers were amorphous. The molecular weights of soluble polymers were mostly less than 2000. The weight retention of the insoluble polymers obtained by the UV irradiation was very high being more than 80% at 1000°C, while the polymers obtained thermally or by gamma irradiation lost considerable amounts at 600°C.

INTRODUCTION

The solid state polymerizations of diacetylenes have been studied by many researchers(1) since Wegner(2) reported the unique topochemical polymerization in the crystalline state. In order to obtain processable functional polymers having a high degree of unsaturation, the present authors are studying the synthesis and polymerization of vinyl monomers which contain diacetylene groups. Previously we reported the synthesis and polymerization of phenyl-4'-vinylphenylbutadiyne(PVPB)(3) and its copolymerization with styrene and methylmethacrylate was also reported(4). Some diacetylene containing methacrylates such as 6-phenylhexa-3,5-diynyl methacrylate, 13-phenyltrideca-10,12-diynyl methacrylate, etc were also prepared and their polymerizability was investigated(5). PVPB can be polymerized by anionic initiators such as n-butyl lithium(3) but it does not polymerize with a free radical initiator in solution due to the interaction of the propagating radical with the diacetylene group(4,6). In this work PVPB was polymerized in the solid state by means of gamma-ray and ultraviolet irradiation, and also thermally at temperatures below its melting point. The results are presented in this paper.

EXPERIMENTAL

PVPB

PVPB was prepared from 2-chloroethylbenzene by the method reported in the previous work(3). It was purified by repeated recrystallization from methanol.

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Polymerization

Thermal polymerization was carried out by heating PVPB crystals in a glass tube placed in a constant temperature bath. The photopolymerization was carried out at room temperature under nitrogen using a high pressure mercury lamp. The crystals suspended in a aqueous solution of isopropanol, and the suspension was stirred by a magnetic stirrer during the irradiation. The light intensity was measured by dosimetry using pottasium ferrioxalate(7). The gamma-ray irradiation was carried out using a Gamma Beam 651 PT of 50,000 Curies of Co-60. Irradiation under pressure was also carried out in order to see the effect of external pressure on the polymerization. The crystals were ground to powder and compressed to a disk. The radiation dose was determined by the method of Fricke(8).

Characterization of polymerization products.

After polymerization the contents of polymerization tube were poured into methanol in order to remove unreacted PVPB. The methanol insoluble fraction was filtered, washed well with hot methanol, dried in vacuum, and taken as the yield.

A DuPont Thermogravimetric Analyzer Model 990 was used for the thermogravimetric analysis of the polymerization products. The samples were heated under nitrogen at a heating rate of 10°C/min.

The molecular weights were determined in tetrahydrofuran by GPC using a Varian Model 5000 apparatus with a TSK G4000H8 column.

The X-ray diffraction patterns were taken using a Philips PW 1410 X-Ray Spectrometer with Philips pulse shaper PW1365.

RESULTS AND DISCUSSION

The results of thermal polymerization are shown in Table 1. Almost no polymerization took place at 60°C over a period of 120 hrs. At 70°C a higher conversion rate was attained and a dark brown solid, insoluble in methanol, was obtained. of which more than 50% was found to be insoluble in any solvent. The soluble fraction had an average molecular weight of 1870. At 80°C at which PVPB melts, a black insoluble solid was obtained.

TABLE 1. THERMAL POLYMERIZATION

Run	Temp(°C)	Time(hr)	Yield*(%)	SF**(%)	MWt.
T-1[a]	60	120	0.16	100	-
T-2	60	120	0.28	100	-
T-3[a]	70	120	5.6	100	750
T-4	70	192	60.7	42	1870
T-5	80◊	120	100	0	-

*:Methanol insoluble solid.
**:Chloroform soluble fraction.
[a]:Under nitrogen; others in air.
◊:above the mp of PVPB.(molten state)

Table 2 shows the results of UV irradiation. In this case also both soluble and insoluble products were obtained. The molecular weights of soluble products were those of oligomers, the degree of polymerization being in the range of 2 to 8. The polymers become insoluble when the molecular weights exceed about 2000. The yields were low indicating that PVPB is not readily polymerized by UV irradiation.

TABLE 2. UV IRRADIATION.

Run	Intensity (Einstein/hr)	Dose (Einstein)	Yield (%)	SF** (%)	MWt
UV-1	2.3×10^{-8}	1.15×10^{-6}	2.7	49	1200(49%) 740(28%) 500(18%)
UV-2	4.13×10^{-8}	2.19×10^{-6}	4.6	72	1400
UV-3	"	2.43×10^{-6}	8.5	59	1800

**:Chloroform soluble fraction.

The results of gamma-ray irradiation are shown in Table 3. The polymerization at room temperature was very slow and the yields were very low. Almost no reaction took place in vacuum, while the presence of oxygen accelerated the polymerization to some extent. The combination of heat and radiation yielded more polymeric products than the heat or irradiation alone.

TABLE 3. GAMMA IRRADIATION

Run	Intensity (Mrad/hr)	Dose (Mrad)	Atm.	Yield(%)	SF(%)	MWt
G-1*	0.86	31.2	in vac.	0.36	100	-
G-2	0.86	31.2	in vac.	0.42	100	500
G-3	0.86	26.3	in air	0.65	100	-
G-4	1.20	53.9	in air	2.13	100	500
GT-1**	0.86	50.0	in air	51.6	31	1700
GT-2***	0.70	50.0	in air	2.3	89	2300

*:Without compression; others were compressed to disks with 9 ton/cm².

***:at 48°C, **:at 68°C, others at room temperature.

IR spectra of poly(PVPB) have peaks due to alkyl groups at 2860-1980 cm^{-1}. It is clear that vinyl polymerization took place. However the peak of the vinyl double bond at 1645 cm^{-1} was still observed for the polymers obtained by thermal or gamma-ray irradiation polymerization. The 1-H NMR spectra also indicated the existence of vinyl protons in the soluble oligomers; $H_2C=$:4.97-5.58 ppm; =CH:6.23-6.58 ppm. These results indicate that the polymerization proceeded not only by the vinyl group but also by the diacetylenic group. The polyfunctionality of PVPB can be also noted from the X-ray diffraction patterns of PVPB and its polymerization products, as shown in Fig. 1. The soluble oligomer remained crystalline to some extent, but the insoluble polymer was totally amorphous.

The linear poly(PVPB) obtained by anionic polymerization initiated by n-butyl lithium is soluble in organic solvents such as THF and chloroform, but gradually becomes insoluble on standing at room temerature for several weeks. It also becomes insoluble and dark brown when irradiated with gamma-rays. The simple diphenylbutadiyne does not undergo any reaction under the conditions of the aforementioned reactions. It seems that vinyl poly-

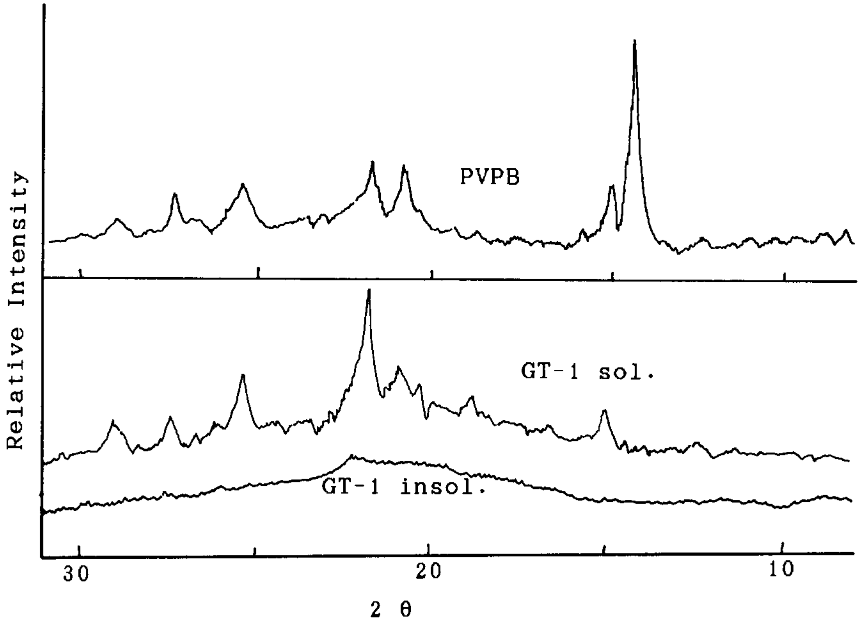

Fig. 1. X-Ray diffraction patterns of PVPB and its polymerization products.

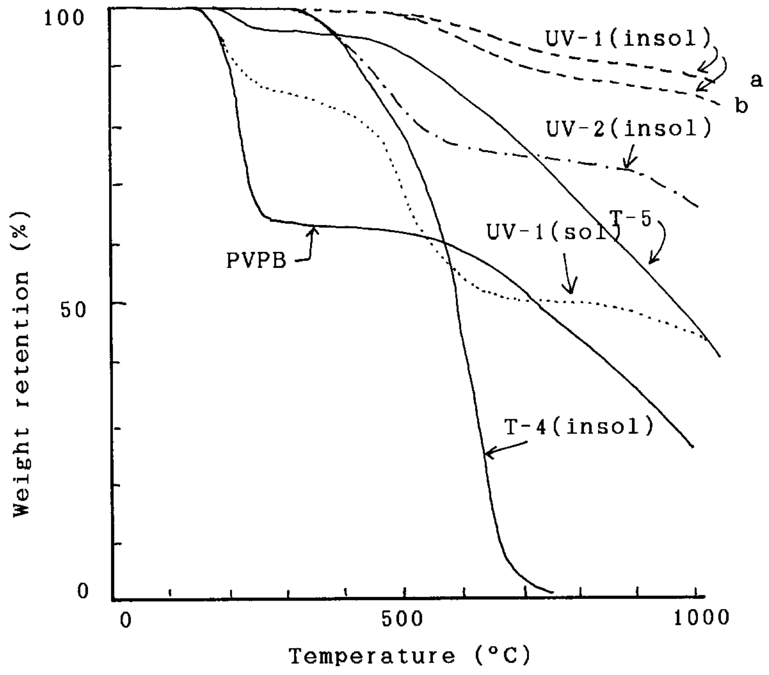

Fig. 2. Thermogravimetric analysis of PVPB and its polymerization products.(1) a, b: UV-1 repeated twice(both irradiation and TGA)

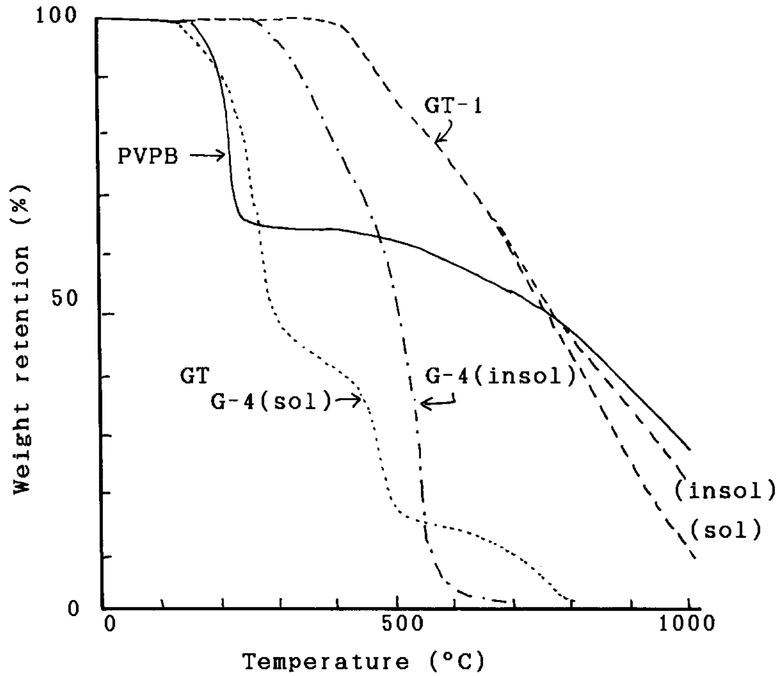

Fig. 3. Thermogravimetric analysis of PVPB and its polymerization products. (2)

merization decreases the distance between the diacetylene groups and reactions between the diacetylene groups take place forming crosslinked polymers and oligomers which contain unreacted vinyl groups.

The gravimetric analysis of polymerization products was carried out and the results are shown in Figs. 2 and 3. The weight retention characteristics vary very much depending on the methods of polymerization. It can be seen that the polymers obtained by UV irradiation are much more heat resistant than those obtained thermally and by gamma-ray irradiation. These results indicate that the structures of the polymers are different in each case. The insoluble polymers were found to be more heat resistant than the corresponding soluble oligomers, as expected. The insoluble polymer obtained by UV irradiation(UV-1 insol) exhibited amazingly high wight retentions; only about 15% weight loss at 1000°C. This high weight retention of polymers obtained by UV irradiation suggests that UV irradiation leads to a structure favorable to form a graphite-like structure at high temperatures. Its X-ray diffraction pattern could not be studied due to insufficient sample. The weight loss of 11.8% (calcd.) corresponds to the loss of the main chain. The IR spectra of UV irradiated products did not have any trace of peak due to the vinyl double bond, while the thermal and gamma-irradiated products contained unreacted vinyl groups.

The soluble oligomers undergo further reactions to form insoluble polymers on heating or radiation. It seems that the maximum molecular weight of these soluble oligomers is about 2000.

Since PVPB behaves as a polyfunctional monomer, beyond this value the polymers become insoluble. The soluble oligomers can be regarded as prepolymers, but it was impossible to produce the soluble oligomers with high yields as the insoluble fractions increase with the conversion.

AKNOWLEDGEMENT

This work was partially supported by a Grant(to T.O.) of Ministry of Education of Mexican Government(SEP) under the contract No. C88-08-0213.

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Accepted February 28, 1989 C