

# Synthesis and Reactions of Polymeric Diazomethylenes

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## ABSTRACT

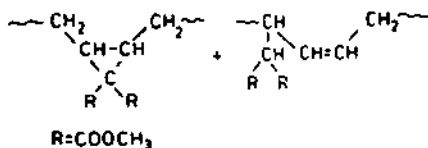
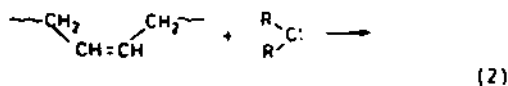
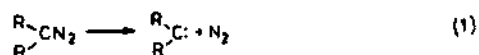
Poly (vinylbenzophenone hydrazone) (PVBPH) which was obtained from the reaction of polyvinylbenzophenone (PVBP) with hydrazine, was treated with HgO in benzene-ethanol mixture to afford PVBP with diazomethylene functions. Polymer samples prepared by this way contained only small fraction of side chains having diazomethylene groups. These groups decomposed when exposed to daylight as evidenced by the disappearance of the magenta color and the azo band in its IR spectrum. Furthermore, catalyzed reaction with a cyclic olefin was realized using Cu(II) acetylacetonate.

KEY WORDS: Diazomethylene, polyvinylbenzophenone, dimerization.

## INTRODUCTION

Catalytically, thermally and photochemically induced decompositions of diazocompounds yield carbenes as well as carbenoids<sup>1</sup>.

Photolytic or catalytic decompositions of diazocompounds in the presence of olefines give high yields of addition and insertion products together with some dimer formation at different rates. We have recently extended<sup>2</sup> these reactions to the modification of polybutadienes through the generation of highly reactive carbenes formed upon decomposition of dimethyldiazomalonate according to the following reactions.



Accordingly, it was considered that the introduction of diazomethylene groups into a supporting polymer would provide convenient route to generate carbenes on a polymer. Desired groups may then be introduced to the polymer, when decomposition of the diazo groups conducted in the presence of appropriate olefines. Alternatively, diazo groups in the new polymer react<sup>3</sup> rapidly and efficiently with carboxylic acids giving the corresponding polymer ester. Chapman *et al.*<sup>3</sup> prepared poly (styrene-2% divinylbenzene) with diazomethylene groups and immobilized penicillin GI(s)-oxide to the polymer.

In the present work, we describe the preparation of polymeric diazomethylene from polyvinylbenzophenone (PVBP) with the aim of generating reactive carbenes on a polymer.

## EXPERIMENTAL

### Materials

Polyvinylbenzophenone (PVBP) was readily available. Hydrazine hydrate (Merck) was dehydrated by distilling on KOH pellets. Solvents, copper (II) acetylacetonate and cyclopentene (Fluka) were used without further purification.

**Preparation of Poly(vinylbenzophenonehydrazone)  
(PVBPH)**

Anhydrous hydrazine (10 ml) was added to the solution of 1.07 g PVBP in a mixture of 35 ml benzene and 12.5 ml ethanol and heated at reflux for 6 h. The mixture was poured into 150 ml methanol after standing overnight at room temperature. The waxy precipitate was then obtained upon cooling in a refrigerator. The product was washed successively with methanol and ether, and dried. Analysis: Found C, 85.0%; H, 5.98%; N, 0.92%; Calcd: C ... %, H, ... %, N ... %.

**Preparation of Polyvinylbenzophenone-diazomethylene  
(PVBPD)**

PVBPH (0.89) prepared above was dissolved in the mixture of 35 ml benzene and 10 ml ethanol. 1 g  $\text{Na}_2\text{SO}_4$ , 5 g HgO and 1 ml ethanolic KOH were added to this solution and stirred for 24 h at 15–20°C in the dark. HGO and Hg was precipitated by cooling the mixture in a refrigerator and filtered off. The red filtrate was precipitated in cold methanol, washed with methanol and ether, and dried.

**Catalyzed Reaction of PVBPD**

Solution of 0.200 g PVBPD and 6 ml cyclopentene and catalytic amount of copper (II) acetylacetonate in 20 ml benzene was heated at reflux. The course of the reaction was followed by IR analysis of a small aliquot of this solution.

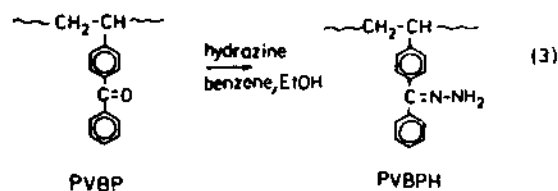
**Analysis**

Infrared spectra were measured on a Simadzu IR-400 model spectrophotometer.  $^1\text{H-NMR}$  spectra were run on a Bruker-200 spectrometer in  $\text{CDCl}_3$  solution with tetramethylsilane as internal standard. Gas chromatographic analysis was performed on a Simadzu instrument, Model 5A with FID using the column 3m, 3%OV-17 Chromosorb W 60/80 mesh.

**RESULTS AND DISCUSSION**

Preparation of polymeric diazomethylene was realized using PVBP having molecular weight of  $10^6$  as determined by light scattering measurements. Reaction of this keto polymer with anhydrous hydrazine was effected by refluxing in benzene-EtOH mixture according to the following reaction.

The product was characterized by infrared spectra on KBr disc. As shown in Fig. 1, intensity of the aromatic band at  $1600\text{ cm}^{-1}$ , which also possesses



$>\text{C}=\text{N}$  vibrations, increased as compared to the carbonyl band at  $1660\text{ cm}^{-1}$  indicating conversion of carbonyls to hydrazone groups to a certain extent. The

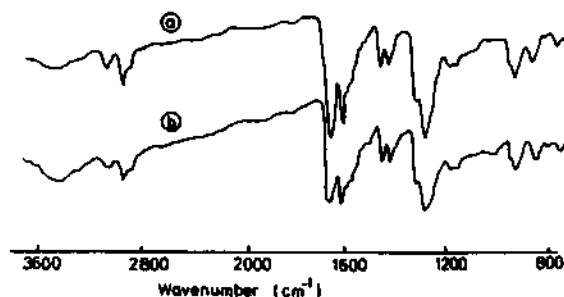


Fig. 1. IR spectra of (a) the initial PVBP (b) PVBPH.

$^1\text{H-NMR}$  data are in agreement with the expected structures. The spectrum of PVBPH (Fig. 2) displays

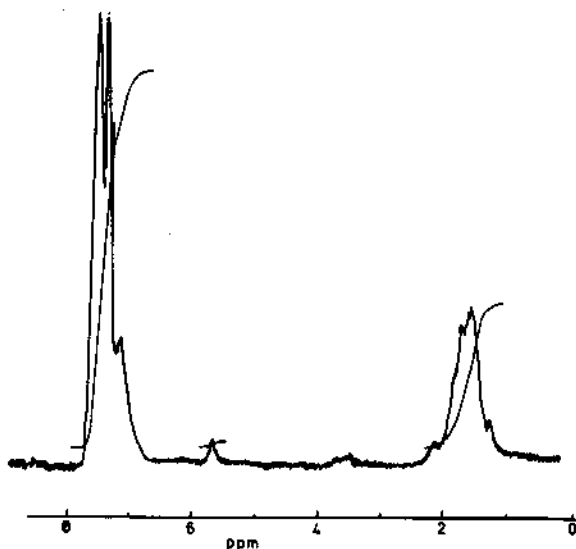
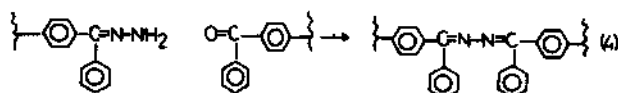
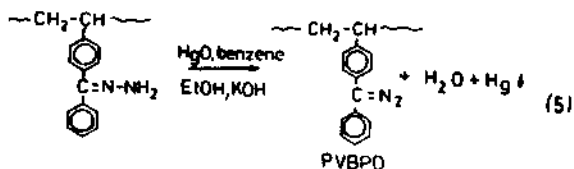


Fig. 2. NMR spectrum of PVBPH.

three resonances at 1.44–1.79, 5.66 and 7.11–7.47 ppm attributable to aliphatic, hydrazone and aromatic protons, respectively. The ratio of the integrated intensity of  $\text{NH}_2$  protons to aromatic protons indicates that the molar conversion of the keto group to hydrazone was 7%. The agreement between this value and that obtained from elemental analysis (6.85%) clearly indicates the low conversion which may result from the steric hindrance. Partial crosslinking observed during the reaction may be the result of intermolecular azine formation as indicated below. Further investigations were carried out in the soluble portion of the product.

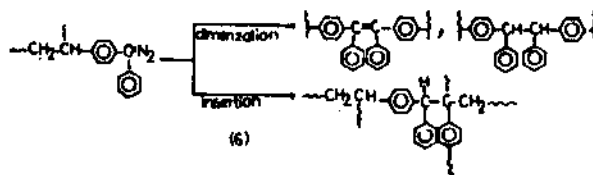


The hydrazone groups were oxidized into diazo groups by using  $\text{HgO}$  with the catalytic effect of  $\text{KOH}$ . The conversions were almost quantitative as evidenced by the disappearance of  $\text{NH}_2$  protons in NMR spectrum of the product.



The deep magenta colored PVBPD exhibited expected bands in its IR spectrum (Fig. 3a). On storage of a thin film in the daylight for 4 h, polymer containing diazomethylene groups lost its activity as determined by the disappearance of the azo band at  $2050\text{ cm}^{-1}$  (Fig. 3b). It should be pointed out that this treatment led to a completely insoluble product resulting from dimer formation and insertion reaction to tertiary C-H bond of the polymeric carbene according to the following scheme.

The occurrence of addition product is not probable due to the absence of an olefinic structure in the



system. On the other hand, cyclopentene was allowed to react with the polymeric carbene which is formed by catalytic decomposition of PVBPD. Gas

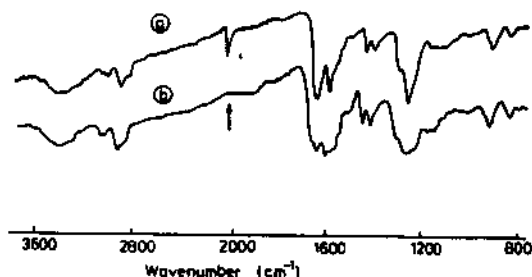


Fig. 3. IR spectra of PVBPD: (a) before, and (b) after exposure to the daylight for 4 h.

chromatographic analysis of remaining cyclopentene revealed that significant amount of the diazo groups was reacted with the cyclic olefin. In this case, addition reaction via cyclopropane formation is probable.

Further studies are now in progress to prepare diazo methylene from monomeric vinylbenzophenone in order to avoid steric limitations and crosslinking due to intermolecular azine formation.

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