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Synthesis of Poly[1,3-diphenyl-5-(p-vinylphenyl)-2-pyrazoline]

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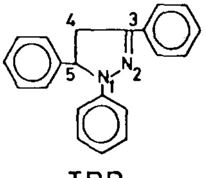
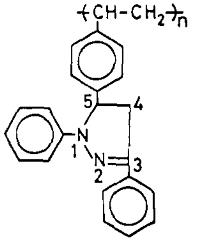
Introduction

Interest has been expanding in 1,3,5-triphenyl-2-pyrazoline (TPP) and its derivatives. Recent studies have shown that these compounds possess some interesting physical and chemical properties. They are strongly fluorescent (LEAVER, RIVETT 1974; STRAHLE et al. 1976), for which the nearly planar conjugated π-system Ar-N-N=C-Ar in the pyrazoline ring is responsible. They are photoconductive, and readily form a glassy state at near or above room temperature which is kept for quite a long period of time (SANO et al. 1976). They have been used as fluorescent whitening agents for wool and certain synthetic fibers (WAGNER et al. 1966). Some derivatives of TPP have found a successful application for use in electrophotography (MELZ et al. 1977).



TPP



It is of interest to synthesize polymers having a TPP or 1,3-diphenyl-2-pyrazoline (DPP) ring as pendant groups in view of exploring new materials of modified TPP and studying the polymer effect on the spectral and electrical properties. Such a polymer has previously been prepared and its photoconductive behavior has been examined (MORIMOTO et al. 1963; TSUKAHARA et al. 1966); however, the method of the preparation employs the reaction of a polymer, that is, a DPP moiety is introduced into polyvinylacetophenone which was prepared by the acetylation of polystyrene. We wish to report here the first successful synthesis of a vinyl polymer having a TPP ring as pendant groups, poly[1,3-diphenyl-5-(p-vinylphenyl)-2-pyrazoline]. A full account will be reported later.

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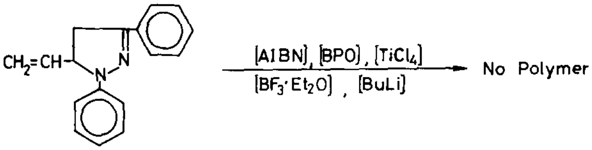
Experimental

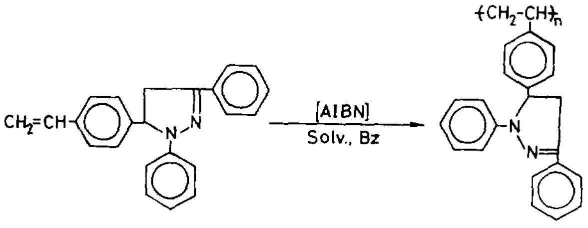
Materials. Two vinyl monomers, 1,3-diphenyl-5-vinyl-2-pyrazoline (mp 76-77.5°C) and 1,3-diphenyl-5-(p-vinylphenyl)-2-pyrazoline (mp 74-75°C), were prepared as described in the later section, purified by neutral alumina column chromatography followed by repeated recrystallizations from methanol, and dried in vacuo. The structures were identified by the IR, UV, NMR, and mass spectra and the elemental analysis.

Polymerization. Polymerizations were carried out in a glass tube of 2 cm in diameter connected to a vacuum line. The polymerization solution involving the monomer and the initiator was evacuated by repeated freeze-pump-thaw cycles at 2 x 10^{-2} Torr, sealed off, and then allowed to stand for an appropriate time in a thermostat. The polymerization solution was poured into a large volume of methanol to precipitate polymers. Polymers were reprecipitated from benzene-methanol and further purified by the Sohxlet extraction with methanol to remove the monomer.

Results and Discussion

Synthesis and Polymerization of Vinyl Monomers Having DPP and TPP Rings as Pendant Groups. 1,3-Diphenyl-5-vinyl-2-pyrazoline was prepared according to the known method of employing the 1,3-dipolar cycloaddition reaction between butadiene and benzoyl chloride phenylhydrazone in the presence of triethylamine in benzene (HUISGEN et al. 1962). A new monomer, 1,3-diphenyl-5-(p-vinylphenyl)-2-pyrazoline, was synthesized in a similar manner by using p-divinylbenzene in place of butadiene in 47% yield.





1,3-Diphenyl-5-vinyl-2-pyrazoline underwent no polymerization with any free radical, cationic, and anionic initiators used in the present study; however, 1,3-diphenyl-5-(p-vinylphenyl)-2-pyrazoline was successfully polymerized under free radical initiation with 2,2'-azobisisobutylonitrile (AIBN). As an example, the vinyl polymer was obtained in 63% yield under the conditions; monomer concentration, 0.5 mol/l; AIBN concentration, 2 x 10^{-3} mol/l; solvent, benzene; reaction temperature, 80 ± 0.1°C; reaction time, 5 hr. Typical time-conversion curves are shown in Fig. 1. The analysis of the initial polymerization rate for the AIBN initiated polymerization of 1,3-diphenyl-5-(p-vinylphenyl)-2-pyrazoline in benzene revealed the features characteristic of an ordinary free radical polymerization, following the relationship R_p $[M][I]^{1/2}$, where R_p, [M], and [I] stand for the initial polymerization rate, the monomer and initiator concentrations, respectively. The apparent activation energy E_a obtained for the polymerization was 22 kcal/mol, hence the value of $(E_p - E_t/2)$ is calculated to be 7 kcal/mol by using the known value of the activation energy for the AIBN decomposition.

Characterization of the New Vinyl Polymer, Poly[1,3-diphenyl-5-(p-vinylphenyl)-2-pyrazoline]. The structure of the polymer obtained by the free radical polymerization of 1,3-diphenyl-5-(p-vinylphenyl)-2-pyrazoline was identified as the pure vinyl polymer based on the data of the IR, UV, and NMR spectra and the elemental analysis. The polymer was easily soluble in benzene, tetrahydrofuran, dichloromethane, dimethylformamide, and dimethylsulfoxide, partly soluble in acetone and acetonitrile, but insoluble in n-hexane, diethyl ether, and alcohol. The number-average molecular weight of the polymer determined by means of a vapor pressure osmometer was ca. 9,000. The polymer was thermally stable below 200°C, softened at ca. 205°C, and became subject to weight loss above 350°C as determined from the TGA measurement.

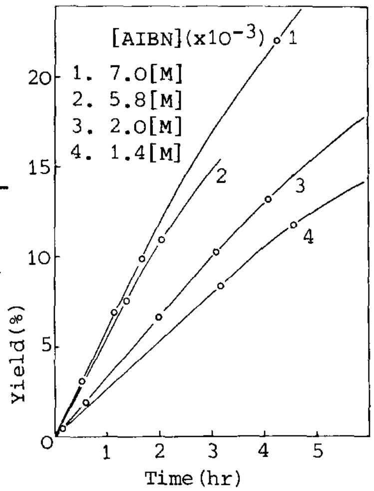


Fig. 1. Time-conversion curves for the AIBN initiated polymerization of 1,3-diphenyl-5-(p-vinylphenyl)-2-pyrazoline in benzene at 60°C. [Monomer]= 0.2 mol/l.

Examination of the spectral properties of the presently synthesized poly[1,3-diphenyl-5-(p-vinylphenyl)-2-

pyrazoline] with reference to the model compound TPP showed the following features characteristic of the polymer. That is, the fluorescence band for the polymer is red-shifted relative to TPP in the same solvent, whereas the absorption band is almost the same between the polymer and TPP; the fluorescence band position for the polymer is less sensitive to the solvent polarity than for TPP the fluorescence band of which undergoes a significant red shift on going from nonpolar to polar solvents; and the fluorescence quantum yield for the polymer is reduced as compared with that for TPP in the same solvent (fluorescence quantum yield in benzene: 0.89 for TPP, which decreases in polar solvents; 0.69 for the polymer). These spectral features characteristic of the polymer are understood in terms of the nearby pendant TPP chromophore playing a role of a sort of solvation toward the electronically excited TPP chromophore. Further studies on the properties and application of the polymer including the synthesis of new polymers containing TPP rings are in progress.

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