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Electron-Beam Chemistry

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Electron Beam Chemistry of Poly(4-Vinyl Pyridine) and its Quaternized Salts

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SUMMARY

Poly(4-vinyl pyridine) and its quaternized salts have been studied under electron beam. The electron beam sensitivity of poly(4-vinyl pyridine) was found to be increased upon both increasing molecular weight and decreasing molecular weight distribution. This was attributed to the crosslinking behavior of poly(4-vinyl pyridine) under electron beam. The electron beam sensitivity of poly(4-vinyl pyridine) was improved by several orders of magnitude by quaternizing. The relationship between the electron beam sensitivity and the degree of quaternization has been studied and several mechanisms have been postulated.

INTRODUCTION

Since poly(4-vinyl pyridine) plays a central role in the field of polyelectrolyte research, solution properties of such polymers have been extensively studied (MORAWETZ 1965). Electron beam chemistry of poly(4-vinyl pyridine) in the solid state, however, has been neglected. The presence of pyridine pendant groups provides the potential for many interesting chemical and physical changes upon electron beam irradiation; however, the nonspecific interaction between the electron beam and the chemical bond renders such studies difficult. With the possible use of this polymer as a microlithographic resist material (LEE 1982), we have studied poly(4-vinyl pyridine) and its derivatives under electron beam. This paper will discuss the relationship between electron beam sensitivities and the degree of N-quaternization in the polyvinylpyridine system. This will provide a basis for understanding the mechanism of electron beam interaction with the polymer.

EXPERIMENTAL

Solvents were purified according to the literature methods. 4-Vinyl pyridine (Aldrich Chemical Co.) was polymerized with a variety of catalysts, such as benzoyl peroxide, n-butyl lithium and $TiCl_4/AlEt_3$ (see Table I). Poly(4-vinyl pyridines) were characterized by IR and NMR. NMR spectra were measured on a Varian EM390 spectrometer. IR spectra were obtained using a Perkin-Elmer Model 299B spectrophotometer. A typical polyvinylpyridinium salt preparation follows: five grams poly(4-vinyl pyridine) were dissolved in 50 ml nitromethane. To this solution was added dropwise with stirring, a solution of 11.39g (0.08 mole) methyl iodide dissolved in 10 ml nitromethane. The resulting mixture was stirred overnight at ambient temperature. The supernatant was decanted from the rubbery poly(4-vinyl-N-methylpyridinium iodide) which was precipitated from solution. The resulting colloidal suspension was concentrated by removal of the solvent and methyl iodide under reduced pressure. Extensive washing of the residue with nitromethane and acetonitrile yielded, after drying, a water-soluble solid. The NMR spectrum D_2O) showed a peak at 6.2ppm N-CH_3). The degree of quaternization was determined by NMR integration or elemental analyses.

An approximately 8000 Å film of poly(4-vinyl-N-pyridinium iodide) was cast from distilled water solvent, by conventional spinning (MAISSEL and GLANG 1970) on a silicon wafer. The coated wafer was baked for one hour at 120°C before electron beam exposure. Each coated silicon wafer mounted on the aluminum substrate was exposed to a 20 kv electron beam using a JEOL U3 scanning electron microscope. Exposure produced rectangles, each having a different dose by varying scan time, beam current, and magnification. The beam current was measured by means of a Faraday cup located in the instrument, and a Keithley electrometer. The film was developed in distilled water (1-5 minutes) and the thickness was measured by a NANOSPEC/AFT film thickness monitor. Electron beam sensitivities of the films were calculated at the dose level at which 70% of the film remained after development.

RESULTS AND DISCUSSION

In order to obtain materials having a variety of molecular weights and molecular weight distributions, 4-vinyl pyridine was polymerized by free radical, anionic and Ziegler-Natta processes. Electron beam sensitivities of the resulting polymers were evaluated using conventional scanning electron microscopy at varying dose levels.

TABLE I

EFFECT OF MOLECULAR WEIGHTS AND MOLECULAR WEIGHT DISTRIBUTIONS ON THE ELECTRON BEAM SENSITIVITES IN POLY(4-VINYL PYRIDINES)

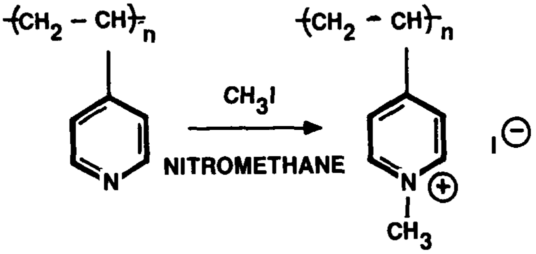
CATALYST	SOLVENT	$\bar{M}_v$	$\bar{M}_w/\bar{M}_n$ a)	E Beam Sensitivites b) (coul/cm^2)
$TiCl_4/AlEt_3$	toluene	8,000	4.5	7.0×10^{-2}
Benzoyl Peroxide	bulk	20,000	2.8	1.0×10^{-2}
Benzoyl Peroxide	THF	70,000	1.9	3.5×10^{-3}
BuLi	THF	120,000	1.4	1.1×10^{-4}

a) Determined by GPC.

b) Calculated at the dose level at which 70% of the film remained after development.

As shown in Table I, electron beam sensitivites increased with increasing molecular weights. This indicates typical crosslinking upon electron beam irradiation. As the polymer chains become longer, fewer crosslinking sites need to be generated. The relationship between molecular weight distribution and electron beam sensitivity of poly(4-vinyl pyridine) has also been studied. Table I shows that a polymer having a narrow molecular weight distribution is more sensitive to electron beam than a polymer having a broad molecular weight distribution. High dose levels are required to crosslink the large number of broadly distributed chains while narrowly distributed chains demand only a few crosslinking sites.

It was gratifying to note that the electron beam sensitivity of poly(4-vinyl pyridine) was improved by orders of mangnitude by quaternizing. To study systematically the effect of N-quaternization on the electron beam sensitivity of poly(4-vinyl pyridine), we have prepared a number of poly(4-vinyl-N-methylpyridinium iodides) having various degress of N-quaternization while keeping molecular weight and molecular weight distribution constant. The scheme of N-quaternization of poly(4-vinyl pyridine) is as follows:



The relationship between the degree of N-quaternization and electron beam sensitivities of the resulting polymers is shown in Figure 1.

Sensitivites were increased with increased degree of N-quaternization. Since all polymers thus tested had identical molecular weights and molecular weight distributions, the degree of N-quaternization, i.e., the relative abundance of positively charged nitrogen atoms, appears to be the influential factor in governing electron beam sensitivity.

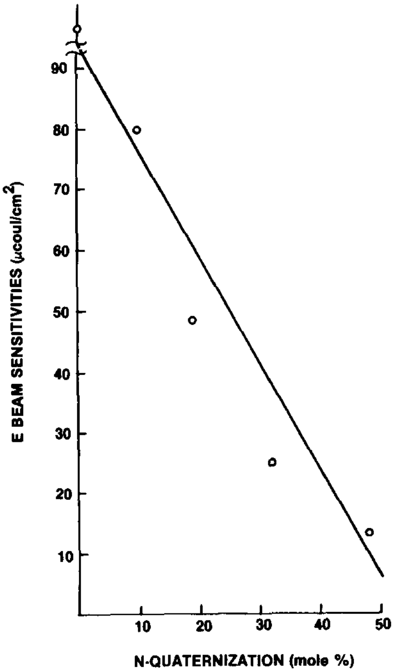
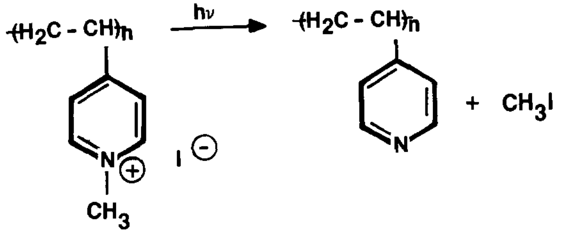
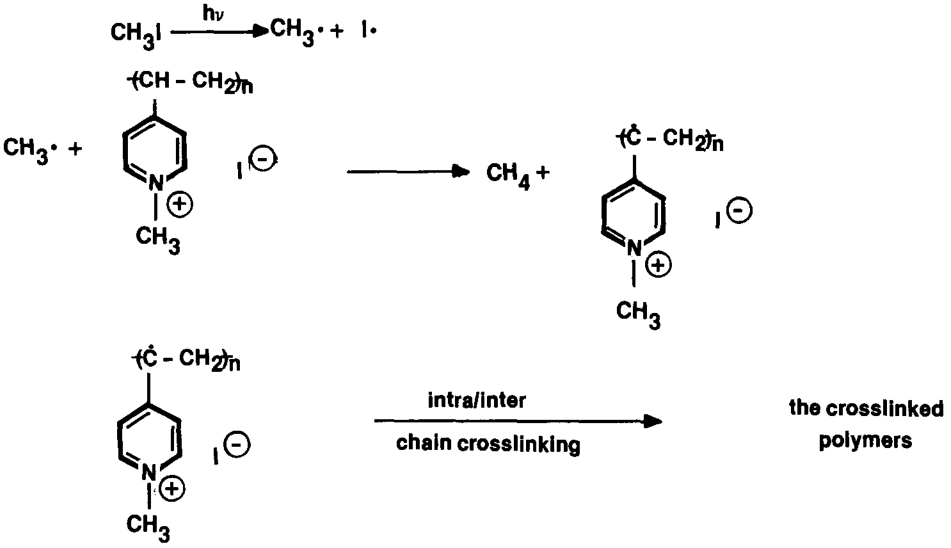


Figure 1. Effect of N-quaternization of the Electron Beam Sensitivity of Poly(4-vinyl-N-methylpyridinium Iodide)

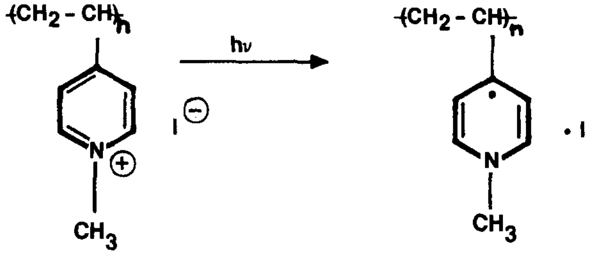
Based on these results, several possible mechanisms can be postulated. First, dealkylation of the pyridinium moiety may occur to generate alkyl iodides.



The newly generated alkyl iodide can be easily cleaved under electron beam to assist in the formation of various cross-linked polymers.



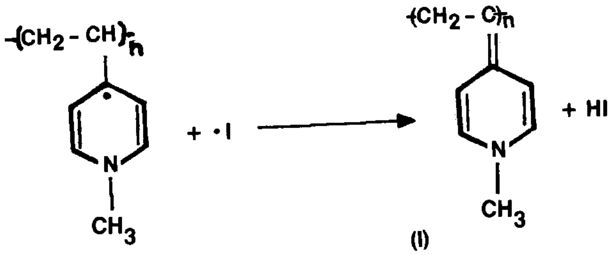
Recently, DECOUT et al. (1980) reported that the cleavage of the N-oxide bond was responsible for UV photocrosslinking of the copolymer of styrene and 4-vinylpyridine-N-oxide. Alternatively, iodide counterion may donate electrons to the electron poor pyridinium ring to form a charge transfer complex.



KOSOWER (1960) and others (VAN BERGEN and KELLOGG 1972, LARSEN et al. 1980), have reported the existence of such charge transfer radicals in monomeric pyridinium iodide chemistry.

Although the fate of such a neutral biradical is unknown, a hydrogen radical may be abstracted by the iodine radical.

Experimentally, we have observed gas formation during electron beam irradiation of the polyvinylpyridinium iodide salt. We are trying to identify gas by various trapping experiments.



(I)

If the aforementioned mechanism occurs during electron beam exposure, the polymer may be totally converted by electron beam from an ionic to a nonionic product. Spectroscopic studies are underway to verify the postulated mechanisms.

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