

A FOURIER TRANSFORM INFRARED SPECTROSCOPIC STUDY OF THE REACTION BETWEEN POLY (VINYL PYRIDINE)S AND EPOXY COMPOUNDS*

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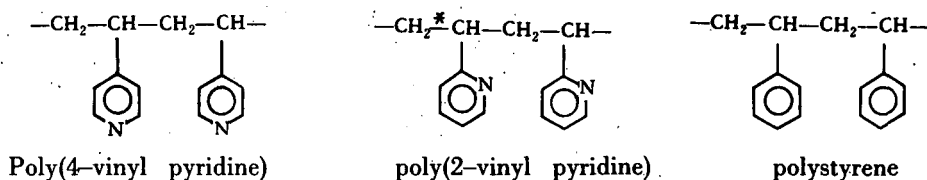
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ABSTRACT

Chemical reactions between poly (vinyl pyridine)s and 1,4-butanediol diglycidyl ether and other epoxy compounds were studied by Fourier transform infrared spectroscopy and other techniques. The epoxy group was found to react with the pyridine side group of poly (4-vinyl pyridine), forming crosslinked networks which contain cyclic amide structures. The reaction was also observed in the interfacial region of poly(vinyl pyridine) and γ -glycidoxy propyl trimethoxysilane hydrolyzate (γ -GPS) coatings on PET fiber substrates. Poly(2-vinyl pyridine) does not show the same reaction.

INTRODUCTION

Poly (vinyl pyridine)s resemble polystyrene in their physical properties as might be expected from their structures.



The similarity of pyridine to benzene with respect to their aromatic structure, and in particular the stability of the aromatic character, is well known^[1]. However, the vinyl pyridine polymers have some distinct features due to the presence of the basic nitrogen atom in the side group. The tertiary nitrogen atom makes the compounds a convenient starting point for the preparation of polyelectrolytes containing chain polycations. Insoluble ion exchange resins can be made by crosslinking with dihalides, such as ethylene bromide^[2]. Vinyl-pyridines can be copolymerized with butadiene and styrene to form latices which provide adhesion of rubber to rayon, nylon, or polyester fiber^[3-6]. Acrylonitrile-vinylpyridine copolymer fibers are of great interest because they can be dyed with conventional acid dyestuffs^[2]. In all these applications of poly (vinyl pyridine)s, the conjugated structure of the side chain remains unchanged.

In our previous study^[7-9], we found that pyridine derivatives, especially 4-ethylpyridine or 4-methylpyridine, could combine with an epoxy group forming polymeric materials. This reaction did not induce the homopolymerization of the epoxy group, but disrupted the aromatic nature of pyridine. In this paper, we report an infrared spectroscopic study of the reactions of poly(vinyl

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pyridine)s and 1,4-butanediol diglycidyl ether in homogeneous solution and at the interfacial region of solid films.

EXPERIMENTAL

Poly(4-vinyl pyridine), poly(2-vinyl pyridine) and 1,4-butanediol diglycidyl ether were purchased from Aldrich Chemical Company. They were dried under vacuum at 60°C overnight. Samples of each poly(vinyl pyridine) and 1,4-butanediol diglycidyl ether were dissolved in dimethyl formamide (DMF) in a weight ratio of 0.9:1.1:3, and heated at 115°C with stirring. Samples were withdrawn from the system at different times, and coated on the surface of KBr plates in a thin layer. The solvent was evaporated at room temperature under vacuum for one week. The structure of the samples was determined using Fourier transform infrared spectrophotometer (Nicolet 170SX) with room temperature triglycerine sulfate (TGS) detector.

Poly(ethylene terephthalate) (PET) fiber was dipped into 2% by weight γ -glycidoxypopyl trimethoxy silane (γ -GPS) aqueous solution, removed from the solution, and dried under vacuum at 140°C for 5 min. The γ -GPS hydrolyzate formed a subcoat on the surface of the PET fibers. The subcoated fiber was dipped to a 0.2% poly(4-vinyl pyridine) ethyl alcohol solution, and heated under vacuum at 140°C for 30 min. The surface structure of neat PET fiber, subcoated PET fiber and double coated PET fiber were examined by diffuse reflectance spectroscopy. For this case Nicolet 170SX spectrophotometer with a liquid nitrogen cooled mercury cadmium telluride detector was used.

The FTIR spectra were taken at a resolution of 2 cm^{-1} with coaddition of 200 scans. The spectra are shown in an absorbance mode. The difference between the maximum and minimum absorbance is designated as ΔA and is shown in absorbance units. The diffuse reflectance spectra are displayed in Kubelka-Munk units. UV-visible absorption spectroscopy was also used to confirm the structure of the reaction products. Viscometry was used to measure the change in the intrinsic viscosity of the reaction mixture.

RESULTS AND DISCUSSION

The initial solution of poly(4-vinyl pyridine) and 1,4-butanediol diglycidyl ether in DMF was a transparent, yellowish liquid. After heating at 115°C, it became a green viscous liquid. As the reaction proceeded for 40 min, a dark blue solid precipitated. The IR spectrum A in Figure 1 illustrated the mixture of poly(4-vinyl pyridine) and the epoxy compound; while spectrum B corresponds to the reaction products. In spectrum A, the stretching mode of the aromatic ring shows strong absorption at 1600 and 1420 cm^{-1} , and the epoxy group shows a weak absorption band at 915 cm^{-1} . In spectrum B which is due to the products after the reaction proceeded for 30 min, the band at 915 cm^{-1} disappeared. A new band at 1650 cm^{-1} with a shoulder at 1670 cm^{-1} appears.

Under similar conditions poly(2-vinyl pyridine) shows little reactivity with 1,4-butanediol diglycidyl ether. The spectral information about this reaction can be seen in Figure 2.

In Figure 2, spectrum A illustrates the initial mixture of poly-(2-vinyl pyridine) and 1,4-butanediol diglycidyl ether, whereas spectrum B is due to the mixture which has been heated for 30 min at 115°C. Spectrum C is the difference of spectra B and A. As can be seen from the spectral

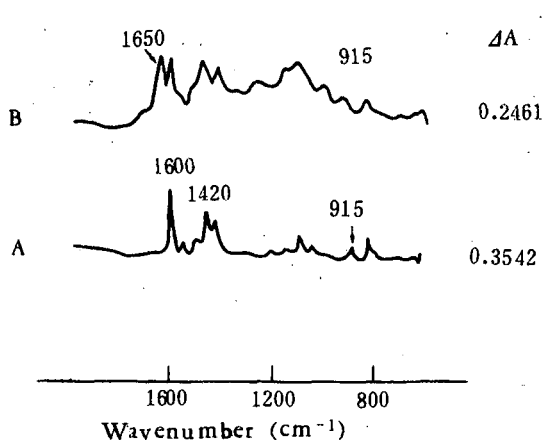


Fig. 1 IR spectra of (A) poly(4-vinyl pyridine) mixed with 1,4-butanediol diglycidyl ether; (B) reaction products

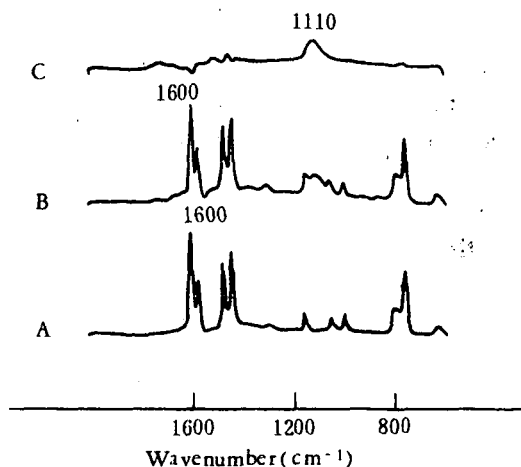
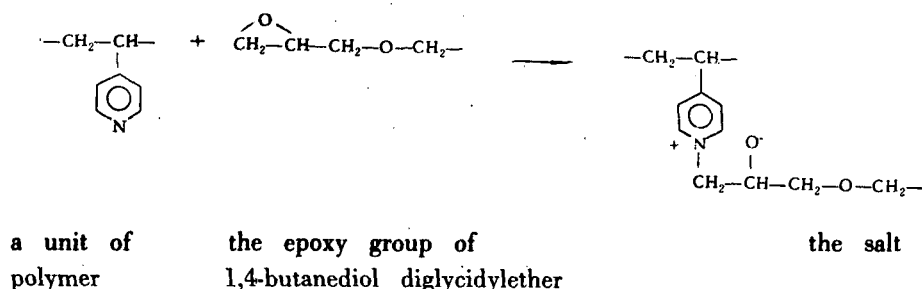


Fig. 2 IR spectra of (A) mixture of poly(2-vinyl pyridine) and 1,4-butanediol diglycidyl ether; (B) heated mixture; (C) difference spectrum (B-A).

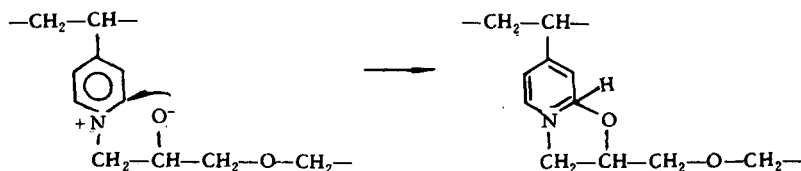
changes, the reaction proceeded much slower than that with poly(4-vinyl pyridine). The increase of the band at 1110 cm^{-1} indicates some homopolymerization of the epoxy group. There is almost no new band appeared in the region of $1620\text{--}1670\text{ cm}^{-1}$.

From our previous study, we proposed a reaction scheme between 4-ethyl pyridine and epoxy compounds [7-9]. A similar reaction scheme may be applied to the reaction of 1,4-butanediol diglycidyl ether and poly(4-vinyl pyridine).

The first step of the reaction involves a nucleophilic attack of the basic nitrogen on the 3-membered epoxy ring of 1,4-butanediol diglycidyl ether, forming a salt:

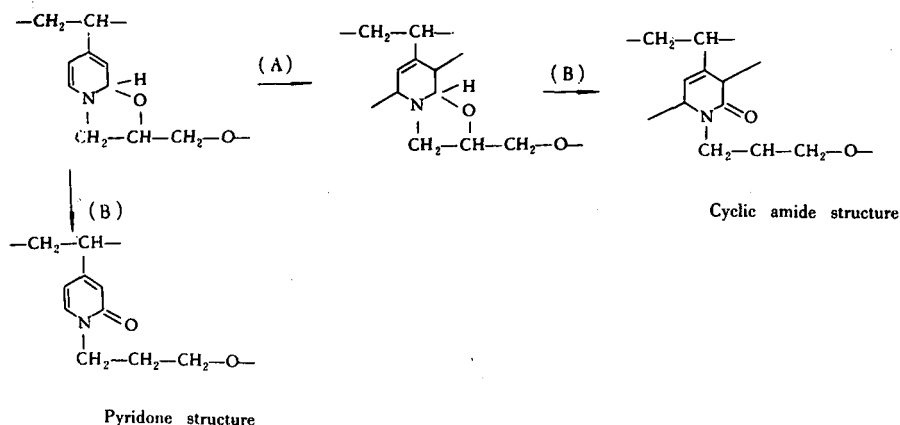


The salt was unstable and a second nucleophilic attack of the oxygen ion on the α -position of the ring occurred immediately:



If the H atom in the α -position was substituted by an alkyl group both steps 1 and 2 would proceed much slower due to the steric effect, as in the case of poly(2-vinyl pyridine).

In the second step, the aromatic structure of pyridine is destroyed, forming a conjugated 3,5-diene in the 6-membered ring which is connected with the main chain of the polymer. The conjugated 3,5-diene may undergo addition or Diels-Alder reaction (A) upon heating^[10,11]. This reaction may lead to crosslinking in the system. Also rearrangement (B) may take place upon heating to form a cyclic amide^[9] or pyridone structure^[12-18].



The final product was a dark blue solid, which was difficult to dissolve in solvents. The carbonyl group of the cyclic amide structure shows strong absorption at 1650 cm^{-1} in spectrum B of Figure 1. The carbon carbon double bonds and the pyridone structure cause the band broadening in the region between 1680 and 1620 cm^{-1} . In spectrum B, there are some bands which are due to the vibrational absorptions of the residual part of 1,4-butanediol diglycidyl ether, such as the C-O-C stretching absorption at 1110 cm^{-1} and the CH_2 deformation at 1460 cm^{-1} .

Pyridone shows a strong absorption at 300 nm in the UV region^[19-21]. In order to verify the appearance of pyridone structure, ethanol was used to attract a portion of the reaction product, and

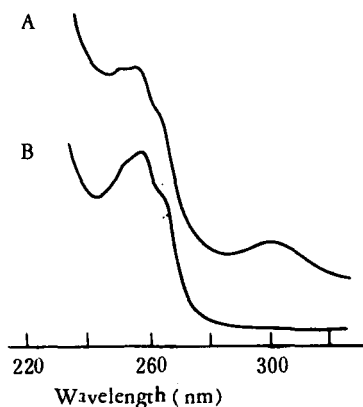


Fig. 3 UV spectra of (A) poly(4-vinyl pyridine) and an epoxy compound mixed together, and heated at 115°C for 30 min.; (B) pure poly(4-vinyl pyridine).

UV spectra were obtained. Spectrum A in Figure 3 is due to poly(4-vinyl pyridine), spectrum B is due to the extracted portion of the reaction products. The new band at 300 nm is due to the pyridone structure.

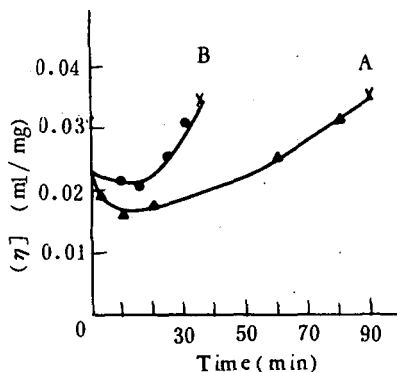


Fig. 4 Intrinsic viscosity of the reaction products of (A) poly(4-vinyl pyridine) with glycidyl ether; (B) poly(4-vinyl pyridine) with 1,4-butanediol diglycidyl ether.

The change of molecular weight of the polymer can be observed by the measurement of the viscosity. Figure 4 shows the change of intrinsic viscosities of poly(4-vinyl pyridine) reacted with 1,4-butanediol diglycidyl ether and allyl glycidyl ether in DMF solution. The intrinsic viscosity depends on the nature of polymer and solvent, and the molecular weight for a given polymer/solvent combination. Figure 4 shows the viscosity of polymer samples in DMF solution. In the first period, the viscosity reduced slightly. We explain this phenomenon by the change of the structure of the polymer. In the second period, the viscosity increased due to the increasing of molecular weight by cross-linking. After the reaction proceeded for certain time, the highly crosslinked polymer could not be dissolved in DMF, the viscosity measurement was ceased at this point. It can also be seen that the molecular weight of the polymer increased faster by reaction with 1,4-butanediol diglycidyl ether than allyl glycidyl ether. This is due to the fact that each molecule of 1,4-butanediol diglycidyl ether contains two epoxy groups, while allyl glycidyl ether contains only one.

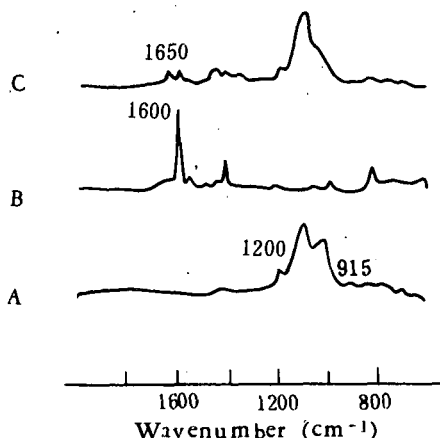
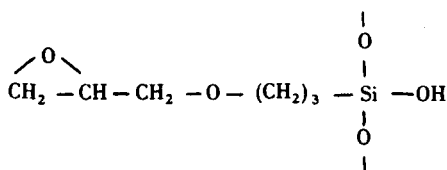


Fig. 5 IR spectra of (A) γ -GPS hydrolyzate; (B) poly(4-vinyl pyridine); (C) reaction product of γ -GPS hydrolyzate and poly(4-vinyl pyridine).

The IR spectra in Figure 5 show the reaction between γ -GPS hydrolyzate and poly(4-vinyl pyridine). γ -GPS was dissolved in water, and the solution was evaporated under air, to a viscous residue. Then, the residual was dried under vacuum at room temperature for one day. Spectrum A in Figure 5 is due to the dried γ -GPS hydrolyzate which has the formula:



The band at 915 cm^{-1} is due to the overlapping bands of the epoxy group and the silanol group. The band at 1200 cm^{-1} is due to the Si—C stretching mode which can be used as the internal standard. Spectrum B in Figure 5 is due to poly(4-vinyl pyridine) whereas spectrum C is due to the reaction product. As compared to the band at 1200 cm^{-1} , the intensity of the 915 cm^{-1} band is reduced after reaction. Some changes appear in the region between 1100 and 1000 cm^{-1} , because of the self-condensation of the silanol group of the hydrolyzate upon heating^[22,23]. A new band appears in spectrum C at 1650 cm^{-1} . This spectral change is similar to Figure 1. It indicated that poly(4-vinyl pyridine) reacted with the epoxy group of γ -GPS hydrolyzate forming amide groups.

The reaction could be observed not only in solution system, but also in the interfacial region of solid polymers. The γ -GPS was coated on the surface of PET fiber, and heated under vacuum at 140°C for 10 min. Poly(4-vinyl pyridine) was topcoated. The thickness of both layers was controlled to about 50 nm on average. The coated samples were heated at 140°C for 30 min. The structure of PET fiber and coatings were studied by the diffuse reflectance technique^[24]. The fibric samples were chopped into 1–2 mm lengths and mixed with KBr powder, the diffuse reflectance spectra were taken. Figure 6 shows the difference spectra of the coated PET fiber minus the untreated PET fiber.

Spectrum A in Figure 6 is due to the sample before heating, the band at 1600 cm^{-1} is due to the pyridine ring. A new band at 1650 cm^{-1} appears in spectrum B. Because the reaction occurred

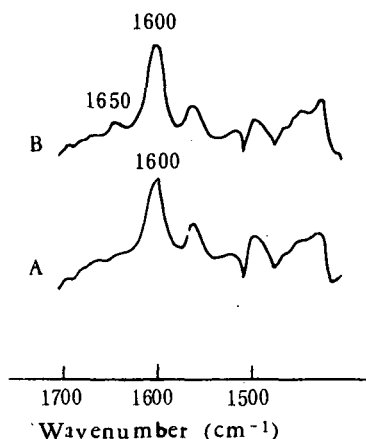
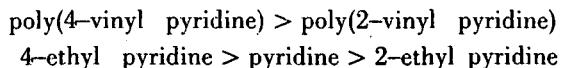


Fig. 6 IR diffuse reflectance spectra of coated PET fiber minus the untreated PET fiber (A) before heating; (B) after heating.

within the limited interfacial region, the new band at 1650 cm^{-1} is weak. Since a similar reaction has been observed in solution, as the systems shown in Figures 1, 2, and 5 we can conclude that the new band at 1650 cm^{-1} is due to the carbonyl group of the reaction products. The diffuse reflectance IR technique clearly shows the reaction in the interfacial region.

The reactivity of the poly(vinyl pyridine)s follows an order similar to that of the alkyl-pyridines which we have reported^[7-9]. The following reactivity order was observed.



The entire reaction rate of poly(4-vinyl pyridine) is lower than that of 4-ethyl pyridine. This is due to the fact that the mobility of the polymer segments is smaller than that of small molecules.

CONCLUSION

The chemical reactions of poly(vinyl pyridine)s and some epoxy compounds were studied both in homogeneous solution and in solid states. The pyridine group reacted with the epoxy group upon heating, forming crosslinked networks, which contains pyridone and cyclic amide structure. This reaction was also observed in the interfacial region of poly(4-vinyl pyridine) and γ -GPS hydrolyzate coatings on PET fiber substrate.

Since pyridine has been considered to have great chemical stability in most conditions^[25], the phenomenon reported in this paper opens a new possibility in polymer chemistry and in elucidation of the reaction mechanism of the coatings used in the adhesion promotion of rubber to tire cord.

Keywords:

poly(4-vinyl pyridine); poly(2-vinyl pyridine); epoxy compound; cyclic amide; FTIR; PET fiber; interfacial reaction

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