

## Preparation, Glass Transition Temperature, and $\delta$ Relaxation Effect of Poly(vinyl Isonicotinate)

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### Synopsis

Poly(vinyl isonicotinate) was prepared by esterification of poly(vinyl alcohol) with isonicotinoyl chloride in pyridine solution. Poly(vinyl nicotinate) was also prepared. Density, refractive index, and glass transition of the polymers were determined. The low temperature dynamic mechanical properties of poly(vinyl isonicotinate) are characterized by a relaxation effect which is associated with thermally excited motions of the pyridine rings ( $\delta$  relaxation). The strong displacement of such a phenomenon toward higher temperatures, with respect to poly(vinyl benzoate), is interpreted as due to the elevated polarity of the pyridine ring.

### Introduction

It is well known that the low temperature mechanical behavior of polymers containing phenyl side groups [polystyrenes and poly(vinyl benzoates)], is characterized by a  $\delta$  relaxation effect, which has been related to some thermally excited motions of the aromatic nucleus.<sup>1-5</sup>

This phenomenon is strongly influenced by the presence of substituent atoms or groups and, in particular, by their position in the benzene ring and by their nature. It has been shown in fact that the substitution of different groups in the *ortho* and *meta* positions makes, in most cases, the  $\delta$  relaxation effect no longer detectable, at least with the dynamic mechanical methods at medium frequencies used by us. Instead, in the *para*-substituted polymers examined up to now, the  $\delta$  relaxation effect is shown by damping peaks at temperatures and with intensities which vary with the type of the substituent.

The experimental results previously obtained<sup>3-5</sup> suggested that the activation energy of the  $\delta$  relaxation, and therefore its position on the temperature scale, depends essentially on the polarity which the phenyl ring assumes as result of the substitution in the *para* position with different groups, more than on the steric hindrance of the latter.

A valid confirmation of the above hypotheses is provided by the study of the dynamic mechanical properties of poly(vinyl isonicotinate), in which the heterocyclic ring, while not containing hindering substituents, has an elevated polarity.

### Experimental

Owing to the well-known difficulties in the preparation of vinyl esters of acids containing heterocyclic nitrogen atoms,<sup>6</sup> the polymer was prepared by esterification of commercial poly(vinyl alcohol) by a technique already used.<sup>5, 7</sup>

Isonicotinoyl chloride was obtained by reaction of the corresponding acid with an excess of thionyl chloride, as described in the literature.<sup>8</sup>

To a suspension of 4 g. of dry poly(vinyl alcohol) (Elvanol 71-30) in 150 cc. of anhydrous pyridine at 60°C. was added 14 g. of the acid chloride; the addition being at such a rate as not to cause the temperature to rise above 65°C.

The reaction mixture, maintained at 60°C. for 20 min. after the addition, was then diluted with pyridine and filtered in an excess of water with vigorous agitation to precipitate the polymer. This precipitation was repeated until no chlorine ions were detected. The poly(vinyl isonicotinate) so obtained was dried under vacuum at 80°C. to constant weight.

The degree of esterification was estimated by determination of the nitrogen content. It is practically complete if an excess of about 15% of acid chloride is used.

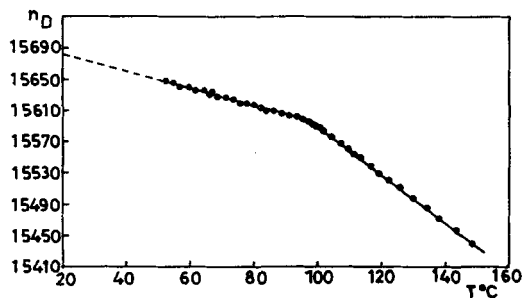


Fig. 1. Refractive index vs. temperature for poly(vinyl isonicotinate).

Dry poly(vinyl isonicotinate) is a hard, pale yellow solid, which can be easily reduced to fine powder. It is readily soluble in pyridine, dimethylformamide, and chloroform and insoluble in ether, aliphatic hydrocarbons, acetone, benzene, and alcohols. The differences between these solubility data and those given in the literature for poly(vinyl nicotinate) obtained by direct polymerization of the monomer<sup>6</sup> may presumably be attributed to the differences in molecular weight of the two samples, rather than to differences in their chemical structure. In fact, a sample of poly(vinyl nicotinate) prepared by us through the esterification of poly(vinyl alcohol) (Elvanol 71-30), showed the same solubility characteristics as the poly(vinyl isonicotinate) now described.

The compression-molded polymer is a clear, yellowish solid. Its density, determined by flotation in aqueous solutions of sodium bromide at 20°C. is 1.288 g./cc.

TABLE I

	N, %	Degree of esterification, %	$d^{20}$ , g./cc.	$n_D^{20}$	$[dn/dT]_0 \times 10^4$	$[dn/dT]_i \times 10^4$	$T_g$ , °C.
Poly(vinyl isonicotinate)	9.21	95	1.288	1.5682	-1.049	-3.166	98.5
Poly(vinyl nicotinate)	9.28	98	1.296	1.5754	-1.070	-2.923	86.5

The glass transition temperature was determined refractometrically on a polymer film prepared by evaporation of a dilute solution in chloroform (Fig. 1).

Table I lists the main physical characteristics of poly(vinyl isonicotinate), compared with those of the analogously prepared poly(vinyl nicotinate). The 20°C. values of the refractive index were obtained by extrapolation of the experimental data.

The dynamic mechanical properties of poly(vinyl isonicotinate) were determined on a polymer disk (36 mm. diameter and 3 mm. thickness). The experimental measurements of the internal damping  $Q^{-1}$  ( $Q$  = resonance coefficient) and of the sound velocity  $v$  were carried out by means of an electrostatic method for flexural vibrations<sup>9,10</sup> at frequencies of 5–10 kHz. In Figure 2 the results of these measurements are plotted.

The curve of the damping factor  $Q^{-1}$  shows a strongly accentuated peak ( $Q_m^{-1} = 21 \times 10^{-3}$ ) at 227°K. for a frequency of 8.20 kHz. The relaxa-

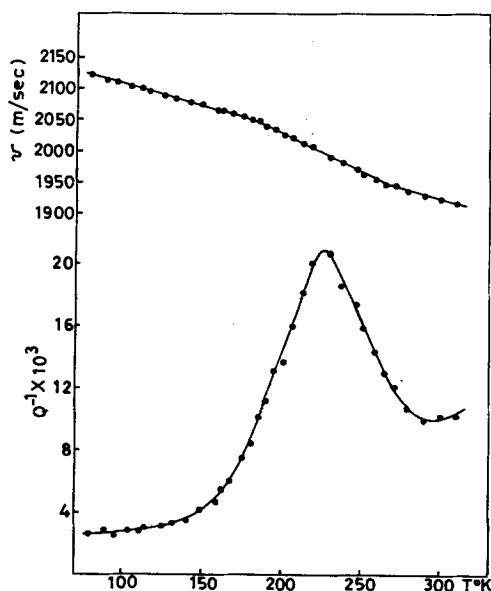


Fig. 2. Damping factor  $Q^{-1}$  and sound velocity  $v$  vs. absolute temperature for poly(vinyl isonicotinate).

tion phenomenon responsible for such a damping effect also causes a change in the temperature coefficient of sound velocity at about 180°K.

### Conclusions

Some unpublished results obtained in our laboratories<sup>11</sup> demonstrated that the poly-4-vinylpyridine shows a mechanical behavior which is very similar to that of the corresponding poly(vinyl ester) now examined. This fact should rule out the association of the relaxation effect of poly(vinyl isonicotinate) with the mobility of the carboxyl groups which bind the pyridine rings to the main chain ( $\beta$  relaxation). Instead, this relaxation effect could be attributed to thermally excited motions of the pyridine rings, analogous to those of the phenyl rings already shown for polystyrene, poly(vinyl benzoate), and all their *para*-substituted derivatives ( $\delta$  relaxation).

Furthermore, since the steric hindrance of the pyridine ring is practically identical to that of the unsubstituted phenyl group, the strong displacement of the damping maximum toward higher temperatures observed passing from poly(vinyl benzoate) to poly(vinyl isonicotinate) must be attributed to the differences in polarity of the two rings.

These results clearly prove that the polarity of the side aromatic or heterocyclic rings has a very marked influence in determining the temperature at which, for a given frequency, the  $\delta$  relaxation effect appears.

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### Résumé

L'isonicotinate de polyvinyle de même que le polynicotinate de vinyle a été préparé par estérification de l'alcool polyvinylique avec le chlorure d'isonicotinoyl en solution pyridinique. On a déterminé la densité, l'indice de réfraction et la transition vitreuse du polymère. Les propriétés mécaniques dynamiques à basse température de l'isonicotinate de polyvinyle sont caractérisées par un effet de relaxation qui est associé avec mouvements thermiquement excités des anneaux pyridiniques (relaxation  $\delta$ ). Le déplacement appréciable d'un tel phénomène vers les plus hautes températures, comparé au benzoate de polyvinyle, est interprété comme étant dû à la polarité élevée de l'anneau pyridinique.

### Zusammenfassung

Polyvinylisonicotinat und Polyvinylnicotinat wurden durch Veresterung von Polyvinylalkohol mit Isonicotinoylchlorid in Pyridinlösung dargestellt. Dichte, Brechungsindex und Glasumwandlung der Polymeren wurden bestimmt. Die dynamisch mechanischen Eigenschaften von Polyvinylisonicotinat bei tiefen Temperaturen werden durch einen Relaxationseffekt charakterisiert, der auf thermisch angeregte Bewegungen des Pyridinringes ( $\delta$ -Relaxation) zurückzuführen ist. Die starke Verschiebung einer solchen Erscheinung zu höheren Temperaturen, wenn man mit Polyvinylbenzoat vergleicht, wird der höheren Polarität des Pyridinringes zugeschrieben.

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