

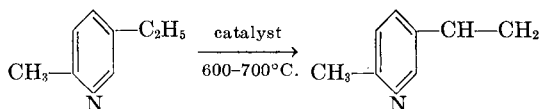
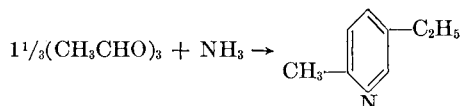
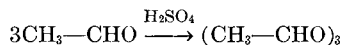
Properties of Homopolymers of 2-Methyl-5-vinylpyridine

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INTRODUCTION

2-Methyl-5-vinylpyridine (MVP) is prepared industrially by catalytic dehydrogenation of 2-methyl-5-ethylpyridine (MEP) which has been synthesized from acetaldehyde and ammonia, according to the following reactions:



Copolymers of MVP with acrylonitrile and with butadiene, are important industrially as textiler and elastomers, respectively.

Vinylpyridine monomers have been shown to polymerize readily; in the absence of inhibitors viscous and colored polymers are obtained in a short time at room temperature. The polymerization of vinylpyridine in general or MVP in particular is reported to be catalyzed in suspension by inorganic agents,¹⁻⁴ in aqueous acidic solutions by radical catalysts,⁵⁻⁷ by copper salts,⁸ etc.

The most interesting feature of polyvinylpyridines is the reactivity of the nitrogen atom; polyvinylpyridines can in fact be quaternized with halides, sulfates, etc., giving strongly polar derivatives that are in general water-soluble; aqueous solutions of very high viscosity can be obtained by dissolving high molecular weight polyvinylpyridines in acids.

A number of studies have been completed on the derivatives of polyvinylpyridines as polyelectrolytes (especially poly-2- and poly-4-vinylpyridines) by Fuoss and co-workers⁹ and by Strauss and co-workers.¹⁰

The formation of addition compounds between alkyl halides and polyvinylpyridine that have surfactant cationic properties has been reported.¹¹⁻¹²

The MVP homopolymers, either unchanged or quaternized at the nitrogen, can be used as emulsifiers for synthetic polymers,^{7,13} as textile auxiliaries,¹⁴ in the photographic field,¹⁵ etc.

In the present paper the properties and processing characteristics of the homopolymers of MVP are reported.

EXPERIMENTAL

Monomer

The MVP used is commercially produced by ACSA S.p.A., Porto Marghera, Italy. It contains inhibitor and a small amount of methylethylpyridine (MEP). It was first flash-distilled to remove the inhibitor and then fractionally crystallized to remove MEP. Owing to the large difference between the freezing points of MVP and MEP a high-purity monomer was obtained in this way.

The purified monomer contained on the average (as determined by chromatographic analysis, freezing point determination, and K. Fischer water titration) 98-99 mole-% MVP, 1-2 mole-% MEP, and 0.2-0.3 mole-% water. The monomer was used immediately to avoid spontaneous polymerization; the absence of polymer was determined by pouring into *n*-hexane, in which it is insoluble.

Polymerization

The monomer was reacted via suspension polymerization to produce homopolymers at three levels of molecular weight. The resulting polymers, after a thorough washing with water, were dried under vacuum at 60°C. for 24 hr. and at 150°C. for 20 min. MVP homopolymers (PMVP) of three molecular weights, designated as types A, B, and C, were obtained.

Polymer

The molecular weights were determined in methanol at 20°C. with the use of a Hellfritz

osmometer (membrane "Fein"). The weights obtained were as follows: type A polymer 100,000, type B 250,000, and type C 380,000.

The dried samples contained less than 0.5% residual monomer and less than 0.5% water. The residual monomer was determined by infrared analysis in a solution of highly purified *n*-hexane, after precipitation of the polymer dissolved in chloroform. The water was determined by the K. Fischer method with the polymer dissolved in methanol.

RESULTS AND DISCUSSION

Owing to the marked hygroscopicity of this material, it was necessary, immediately before working, to dry it for about 2 hr. in a vacuum oven at a temperature of 100°C. Following this, the material was dry-compounded with 1% stearic acid.

Injection Molding

In general, the molding was rather easily performed. The products obtained had smooth and transparent surfaces, and a yellowish color. The

TABLE I
Conditions of Injection Molding

	Product A	Product B	Product C
Temperature, °C.	190-200	220-240	240-280
Pressure, kg./cm. ²	1000	1000	1500-2000

molded samples were easily removed from the metallic mold cavity. The temperature and pressure of molding were varied as shown in Table I.

Compression Molding

The working temperatures were found to be near the lower limits of the injection molding temperatures, with pressures that varied from 100 to 400 kg./cm.² The material (though compounded with about 1% stearic acid) showed slight tendency to stick to the mold.

The mold shrinkages (in./in.; ASTM D 955, samples 1/4 in. instead of 1/8 in. thick) were found to be: 0.006 for type A, 0.007 for type B, and 0.006-0.007 for type C.

During cooling, the material showed some tendency to retain internal stresses that sometimes developed in a relatively short time. For this

TABLE II
Physical Properties of PMVP

ASTM test no.	Property	Polymer		
		A	B	C
D 792	Specific gravity, g./cm. ³	—	—	1.103 ± 0.03
D 696	Thermal expansion, ^a cm. × 10 ⁵ /°C.	9.7	—	7.7
D 864	Thermal dilatation, ^b cm ³ × 10 ⁴ /°C.	3.9-7.1 ^c	—	2.9-5.2 ^d
D 635	Flammability, in./min. ^e	—	0.9-1.0	0.86-0.97
D 570	24-hr. water absorption, ^f %	—	—	14.03
—	Luminous transmittance, ^g %	—	—	80

^a Test range, 14-80°C.

^b Impact test bars (1/2 × 1/4 in.) worked at lathe; range of test 25-98°C.

^c *T_g* 72-73°C.

^d *T_g* 84-85°C.

^e The rate of flame propagation is near to that for polystyrene. However, it can be noted that combustion occurs differently in the two materials. With polystyrene, complete combustion of one part of the material is obtained while the other part melts and flows down. After combustion of PMVP, only a carbon residue remains.

^f None of the materials was water-soluble; the samples after immersion in water did not appear significantly different. The material was a little tacky and after drying showed a profusion of microcracks.

^g The value for the type C PMVP sample refers to a 1 mm. thickness. Green light was used with the Brice-Phoenix photometer.

reason, we generally adopted the practice of annealing the sample. The molded samples were readily machined.

Properties of the MVP homopolymers are shown in Tables II, III, IV, and V and in Figure 1. Samples of polystyrene (PS) were tested for the same properties for comparison. Before testing, all specimens were submitted to ordinary conditioning appropriate to the particular test method; in the majority of cases, however, this was ASTM D 618 B. The specimens, being very hygroscopic, were tested immediately after conditioning; under these conditions the moisture content (as determined by weight loss) was negligible.

TABLE III
 Mechanical Properties of PMVP

ASTM test no.	Property	Polymer		
		A	B	C
D 256	Impact strength, ^a kg.-cm./cm.	0.86	1.04	1.07
D 785	Rockwell M hardness	105-108	105-108	105-110
D 638	Tensile strength ^b kg./cm. ²	180-200	350-400	400-450
—	Elongation at break, %	0.64-0.67	1.3-1.4	1.3-1.5
D 695	Compression strength, ^{b,c} kg./cm. ²	—	—	1300-1400
—	Deformation at break, %	—	—	6.5-7.5
—	Modulus of elas- ticity, kg./ cm. ²	—	—	6.5-7.5
D 638	Tension	ca. 32,000	ca. 35,000	ca. 35,000
D 695	Compression	—	—	30,000
D 621	Load deforma- tion, ^d %	—	—	0.33

^a Izod notch tests performed on samples $\frac{1}{2} \times \frac{1}{4}$ in. in machine with 1 lb./ft. maximum scale reading, and on samples $\frac{1}{2} \times \frac{1}{2}$ in. in machine with 60 kg./cm. maximum scale reading, yielded identical results.

^b Breaking occurred without prior yielding.

^c Cylindrical samples $\frac{1}{2}$ in. high and $\frac{1}{4}$ in. in diameter.

^d Temperature of test $23 \pm 1^\circ\text{C}$., r.h. 50%.

 TABLE IV
 Electrical Properties of Type PMVP^a

Frequency, cycles/sec.	Dielectric constant ^b	Dissipation factor ^b	Loss factor ^b
100	4.32-4.70	0.068-0.074	0.29-0.35
1000	3.95-4.29	0.062-0.070	0.24-0.29
100,000	3.38-3.69	0.047-0.051	0.17-0.18

^a Volume resistivity at 50°C . $>10^{14}$ ohms/cm. (ASTM D 257). Disk-shaped specimens; 4 in. diameter; 0.08 in thickness; electrode (internal to the guard ring), diameter 3.2 in.; galvanometer readings; conditional ASTM D 618 A.

^b ASTM D 150.

 TABLE V
 Heat Resistance Properties of PMVP

Property	Polymer		
	A	B	C
Flow temperature, ^a $^\circ\text{C}$.	118.2	135.3	154.5
Temperature of distortion under 264 psi, ^b $^\circ\text{C}$.	82	88	90

^a ASTM D 569.

^b ASTM D 648.

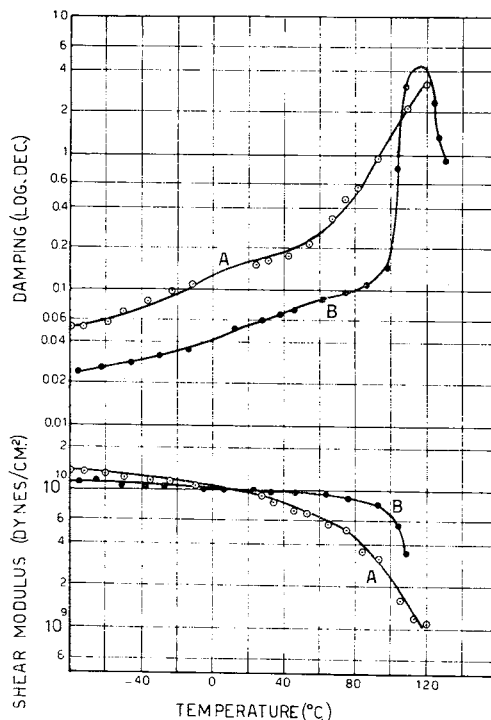


Fig. 1. Dynamic-mechanical properties of (A) type B PMVP (M.W. 250,000) and (B) polystyrene (M.W. 150,000).

Dynamic-Mechanical Tests

The data shown in Figure 1 were obtained in dynamic mechanical tests of PMVP and PS. Type B PMVP was used. The apparatus was a torsion pendulum, and the specimens were injection-molded with dimensions of $0.0423 \times 0.3480 \times 3.563$ in.

Measurements were performed up to temperatures of about 120°C .; at more elevated temperatures, owing to the high shrinkage of PMVP, correct calculations could not be made. However, it can be seen from Figure 1 that for PMVP the damping should be maximum near 130°C .; this indicates the location of the second-order transition temperature T_g . Under the same conditions PS (of M.W. 150,000) shows a T_g near 120°C . The amorphous structure of PMVP, as well as that of the PS, is indicated by the lack of peaks in the damping.

Of interest is the very different behavior shown by the plots of G_a versus temperature for the two materials. PMVP shows a pronounced and continuous decrease in G_a with the temperature; on the other hand PS in the same temperature interval shows only a very small and gradual decrease in rigidity, and then a rapid decrease in the vicinity

of T_g . This behavior is rather curious, since the preceding tables show that the heat distortion temperature, while of the same order of magnitude for both materials, is somewhat higher for PMVP.

Thermal Stability

The thermal stability of PVP was characterized by comparing it with the behavior of polystyrene in an oven at a temperature slightly lower than the softening point of the latter. In general, no significant discoloration was noted except in the type A product which become slightly brown. The test was performed at 120°C. for a total time of 920 min. Specimens of both PMVP and polystyrene were withdrawn and examined every 40 min.

Weather-o-Meter

Tensile test samples $\frac{1}{2}$ in. thick were introduced into a Weather-o-Meter apparatus (model D MC-HR, Atlas Development Co., Chicago) according to ASTM E 42; distilled water was used at a temperature of 30°C. The samples were examined at intervals of 100 hr. over a period of 1000 hr. In general, a significant deterioration of the PMVP samples was noted due to swelling (mainly along the flow line of molding), and also development of surface opacity. No significant discoloration was noted. In polystyrene, under the same conditions, only surface opacity appeared.

Behavior Toward Chemical Agents

PMVP is swelled by water but is relatively unaffected by alkalies. It is soluble in either con-

centrated or dilute acid, and in alcohol, halogenated hydrocarbons, benzene, and toluene; it is insoluble in gasoline and ether.

Results of Moisture Conditioning

In view of the marked hygroscopicity of the PMVP, the samples were exposed initially to the standard conditioning and then immersed for 24 hr. in water according to ASTM D 618 D, immediately prior to testing. The results are shown in Table VI.

CONCLUSIONS

From the foregoing, it can be seen that poly-2-methyl-5-vinylpyridine has many properties essentially similar to those of polystyrene. The conditions for molding are nearly the same, PMVP requiring only slightly more elevated temperatures and pressures. The material is essentially amorphous, as indicated in particular by the dynamic-mechanical curves. The heat distortion temperature is higher for PMVP than for PS. PMVP has a slightly lower impact strength than PS, a tensile strength of the same order of magnitude as that of PS, but a slightly greater modulus. On the other hand, the Rockwell hardness of PMVP is considerably higher, as is the compression strength.

The greater fragility of PMVP is shown by the compression test: for PMVP breaking occurs instantaneously, while under the same load PS yields only slightly.

The fact that PMVP has lower tensile strength but greater hardness than PS seems to be abnormal, considering the behavior of the majority of plastics. The relatively high value of load deformation for PMVP (compared to that for PS, 0.14%) is at first sight abnormal, considering that PS is less stiff than PMVP. However, this can probably be explained by assuming that the PMVP absorbed moisture from atmosphere during the prolonged (24-hr.) test.

The volume resistivity of dry PMVP is of the order of magnitude of that of PS, i.e., notably high (see Table IV). On the other hand, the dielectric constant is higher in PMVP, indicating the strongly polar character of the pyridine nucleus. The higher loss factor for PMVP is confirming evidence of the poor dielectric properties of PMVP and suggests that this material can be heated dielectrically.

The strongly polar character of the pyridine nu-

TABLE VI
Physical Properties of Type C PMVP After Immersion in Water^a

ASTM test no.	Property	
D 256	Impact strength, ^b kg.-cm./cm.	0.95
D 785	Rockwell M hardness	36-45
D 621	Load deformation, %	1.93
	Tensile properties	
	strength, kg./cm. ²	214-238
D 638	Elongation at break, %	1.17-1.22
	Modulus of elasticity, kg./cm. ²	21,000
D 648	Temperature of heat distortion under 246 psi, °C.	58
D 257	Volume resistivity at 50°C., ohms/cm.	1.5×10^{13}

^a ASTM D 618 D.

^b Izod notch test on $\frac{1}{2} \times \frac{1}{4} \times 5$ -in. samples.

cleus is, however, of interest, in that it imparts high water absorption, solubility in acids, etc., to the molecule. It also imparts good resistance to solvents such as paraffins, etc., and suggests interesting applications of the polymer as a polyelectrolyte, a viscosity-improving agent in aqueous acidic solutions, etc. However, the high water absorption results in poor durability in outdoor use due to degradation of hardness, tensile strength, resistance to heat distortion, electrical properties, etc., resulting from water pick-up.

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References

1. Koppers Co., Inc., U. S. Pat. 2,715,118 (1955).
2. Koppers Co., Inc., U. S. Pat. 2,687,408 (1954).
3. Koppers Co., Inc., U. S. Pat. 2,673,194 (1954).
4. Koppers Co., Inc., U. S. Pat. 2,594,913 (1952).
5. E. I. du Pont de Nemours & Co., U. S. Pat. 2,491,472 (1949).
6. Phillips Petroleum Co., U. S. Pat. 2,862,902 (1958).
7. Pritchard, J. E., M. H. Opheim, P. M. Moyer, *Ind. Eng. Chem.*, **47**, 863 (1955).
8. Phillips Petroleum Co., U. S. Pat. 2,767,159 (1956).
9. Fuoss, R. M., and co-workers; see, e.g., *J. Polymer Sci.*, **6**, 511 (1951); *ibid.*, **6**, 767 (1951); *Science*, **110**, 552 (1949).
10. Strauss, U. P., and co-workers; see, e.g., *J. Polymer Sci.*, **6**, 649 (1951); *ibid.*, **9**, 295 (1952); *ibid.*, **9**, 509 (1952).
11. Eastman Kodak Co., U. S. Pat. 2,484,430 (1949).
12. E. I. du Pont de Nemours & Co., U. S. Pat. 2,487,829 (1949).
13. Phillips Petroleum Co., U. S. Pat. 2,746,943 (1956).
14. Phillips Petroleum Co., U. S. Pat. 2,702,763 (1955).
15. See e.g., E. I. du Pont de Nemours & Co., U. S. Pat. 2,448,507, 2,448,508, 2,448,525, 2,448,542, and 2,448,552 (1948); Eastman Kodak Co., U. S. Pat. 2,484,456 (1949).

Synopsis

The physical and technological properties of the homopolymers of 2-methyl-5-vinylpyridine (MVP) are reported. PMVP is rather similar in many mechanical and electrical properties to polystyrene. In addition, the pyridine nucleus imparts to the polymer a strong tendency to absorb water and great ease of quaternization with acids, halides, etc. This suggests applications of PMVP as a polyelectrolyte, a viscosity-improving agent in aqueous acidic media, etc. However, the water absorption characteristic leads to poor outdoor durability and rapid deterioration of many properties after prolonged exposure to humidity.

Résumé

On expose les propriétés physiques et technologiques des homopolymères de la 2-méthyl-5-vinyl pyridine (MVP). PMVP démontre beaucoup de propriétés soit mécaniques que électriques à peu près similaires à celles du polystyrène. D'autre côté, le nucléus pyridique cause une marquée absorption d'eau et une grande facilité de quaternization avec les acides, les halogénures, etc. Celà suggère des applications comme polyélectrolytes, agents pour améliorer la viscosité dans des milieux acides aqueux, etc. Par contre il en résulte aussi une faible résistance aux agents atmosphériques et une détérioration rapide de nombreuses propriétés après une exposition prolongée à l'humidité.

Zusammenfassung

Die physikalischen und technologischen Eigenschaften von dem Homopolymer des 2-Methyl-5-Vinylpyridine (MVP) werden beschrieben. PMVP weist viele mechanische und elektrische Eigenschaften auf, die eine gewisse Ähnlichkeit mit denen des Polystyrols besitzen. Andererseits in Folge des hydrophilen Charakters des Pyridins ist die Neigung zur Bildung quaternären Komplexverbindungen mit Säuren, Halogenverbindungen u.s.w. besonders ausgeprägt. Dieser Umstand ermöglicht eine Anwendung als Polyelectrolyt, als Viskositäts-erhöhendes Mittel in sauren wässrigen Medien. In der Folge ist aber die grosse Empfindlichkeit gegenüber der Feuchtigkeit erklärlich verbunden mit einer Verschlechterung der Festigkeitseigenschaften.

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