Chemistry

Academician A. V. TOPCHIEV, N. N. KAPTSOV, G. D. KALYUZHNAYA, A. I. MITYAEVA

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Abstract

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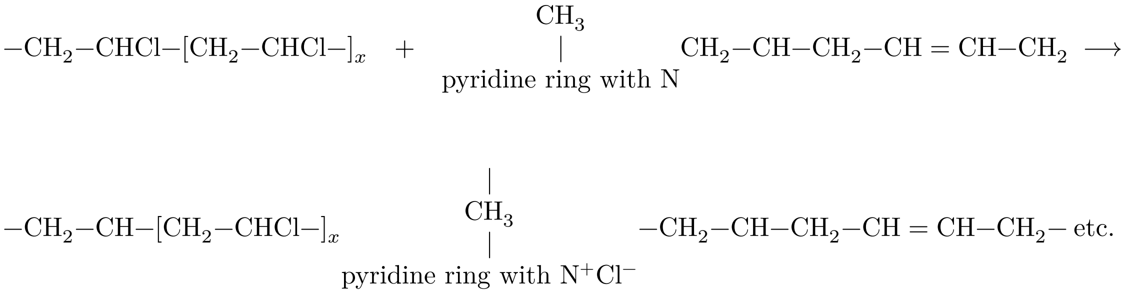
Academician A. V. TOPCHIEV, N. N. KAPTSOV, G. D. KALYUZHNAYA, A. I. MITYAEVA
and I. E. BALITSKAYA

ON THE INTERACTION OF POLYMERS AND COPOLYMERS OF 2-METHYL-5-VINYLPYRIDINE WITH AROMATIC NITRO COMPOUNDS

Polymers containing pyridine rings attract the attention of researchers because of the possibility of carrying out addition reactions at the nitrogen atom. V. A. Kargin, A. A. Berlin, and co-workers (^{1}) showed that, in the interaction of methylvinylpyridine rubber SKMVP with polyvinyl chloride, a graft copolymer with improved physicomechanical properties is formed. This phenomenon is explained by the authors as the formation of three-dimensional structures containing PVC and SKMVP macromolecules chemically bound to one another:



$$-CH_2-CHCl-[CH_2-CHCl-]_x \quad + \quad \underset{\text{pyridine ring with N}}{\overset{CH_3}{|}} \quad CH_2-CH-CH_2-CH=CH-CH_2 \longrightarrow$$

$$-CH_2-CH-[CH_2-CHCl-]_x \quad \underset{\text{pyridine ring with N}^+\text{Cl}^-}{\overset{|}{\underset{|}{CH_3}}} \quad -CH_2-CH-CH_2-CH=CH-CH_2- \text{etc.}$$

Owing to the great tendency of the nitrogen atom in the pyridine ring toward addition reactions, it seemed of interest to us to elucidate the regularities of the processes of interaction of polymers and copolymers of 2-methyl-5-vinylpyridine with various polar compounds.

Experimental Part

The polymer of 2-methyl-5-vinylpyridine, as well as its copolymers with styrene, were obtained by polymerization of the monomer mixture in the presence of benzoyl peroxide. The polymerization was carried out in ampoules. After dissolution of the resulting block in benzene and precipitation with petroleum ether, the polymer was obtained as a white powder. Some properties of the polymers used in the present work are given in Table 1.

Table 1

Polymer	Softening temperature, °C	Molecular weight	Notes
MVP polymer	186	$5.3 \cdot 10^5$	The weight-average molecular weight of the polymers and copolymers was determined by the light-scattering method
Copolymers:a) MVP–styrene (5 : 1)	175	–	Nitration of the copolymer was carried out by the action of a nitrating mixture of composition:HNO_3–73%H_2SO_4–24%at a temperature of 20°
b) MVP–styrene (3 : 1)	160–170	–	Nitration of the copolymer was carried out by the action of a nitrating mixture of composition:HNO_3–73%H_2SO_4–24%at a temperature of 20°

Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

Polymer	Softening temperature, °C	Molecular weight	Notes
c) MVP—styrene (1 : 1)		$4.3 \cdot 10^5$	Nitration of the copolymer was carried out by the action of a nitrating mixture of composition:HNO_3—73%H_2SO_4—24%at a temperature of 20°
d) nitrated copolymer (1 : 1)	decomposes above 200°	—	Nitration of the copolymer was carried out by the action of a nitrating mixture of composition:HNO_3—73%H_2SO_4—24%at a temperature of 20°

Figure 1 shows the dependence of the relative viscosity of solutions of poly-2-methyl-5-vinylpyridine on the heating time at 100°.

As solvent, a mixture of dinitrotoluene and dinitroxylene was used at a DNT : DNX ratio of 1 : 1.

Solutions of copolymers of methylvinylpyridine with styrene behave similarly (Fig. 2).

In order to determine the influence of changes in the basicity of the polymer on the reaction with dinitro compounds, a nitrated copolymer of

Fig. 1. Dependence of $\eta_{\mathrm{rel}}^{100}$ on heating time for solutions of poly-2-methyl-5-vinylpyridine.
I—1; II—2.5; III—5; IV—10 wt. %

Fig. 2. Dependence of η_{rel} on heating time for 5% solutions of copolymers of 2-methyl-5-vinylpyridine. Molar ratio MVP : styrene: I–5 : 1; II–3 : 1; III–5 : 1; IV–3 : 1; V–1 : 1; VI–1 : 1; I, II, V at 100°; III, IV, VI at 80°.

methylvinylpyridine and styrene (molar ratio of monomers–1 : 1) was also investigated. Nitration of the copolymer was carried out with a sulfuric-nitric acid mixture. The nitro product obtained was neutralized with a weak alkali solution in order to cleave acid residues from the nitrogen atoms of the pyridine nuclei.

Table 2

Change in the efflux time of solutions of the nitrocopolymer in the DNT–DNX mixture

2.5% solution, 50°						
Heating duration, min.	0	122	182	242	352	382
Efflux duration of solution, sec.	68	68.5	69.7	74.0	75.0	78.0
5% solution, 100°						
Heating duration, min.	0	30	50	65	–	–
Efflux duration of solution, sec.	101	105	115	128	–	–

From the data presented in Table 2 it is evident that solutions of the nitrocopolymer also show a tendency toward increasing viscosity with time, which is especially noticeable in the case of the 5% solution.

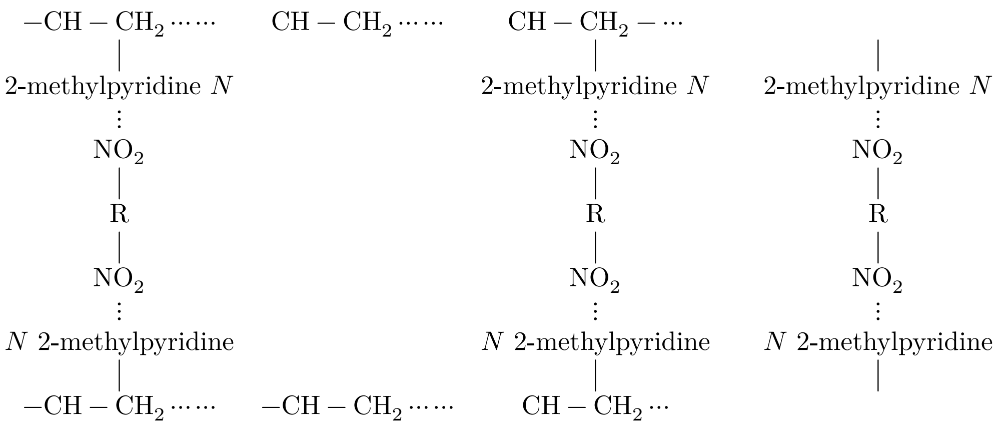
The interaction of polymers and copolymers of MVP, as well as of the nitrocopolymer, with the mixture of dinitro compounds (DNT and DNX), in addition to an increase in vis-

viscosity was accompanied by a noticeable coloration of the solution red and by a subsequent deepening of the color with time. In order to clarify the properties of the 2-methyl-5-vinylpyridine polymer after its reaction with nitro compounds, polymer samples were subjected to extraction with benzene for 18 h. In this process only the solvent could be extracted. The results of extraction of two polymer samples after reaction with nitro compounds are given in Table 3. The remaining polymer was dark brown in color and, upon further heating in benzene, did not dissolve. When heated in a capillary to 250°, no melting of the polymer was observed.

Table 3

Sample No.	Composition, wt.%	Polymer content in the charge, g, before extraction	Polymer content in the charge, g, after extraction
1	25% PMVP75% (DNT + DNK)	4.17	5.2
2	40% PMVP60% (DNT + DNK)	3.3	3.7

These data indicate the formation of crosslinked structures, possibly of the following type:



Effect of the addition of TNT

In a number of experiments, a mixture of nitro compounds (DNT and DNK), previously purified by distillation, was used to dissolve the 2-methyl-5-vinylpyridine polymer. It was found that the increase in viscosity of a 5% PMVP solution in the distilled solvent occurred more slowly than when an undistilled solvent was used. Apparently, polynitro compounds, as a possible impurity in the initial DNT + DNK mixture, lead to the formation of additional bonds between PMVP macromolecules. To test the influence of polynitro compounds, the dependence of the viscosity of PMVP solutions in a solvent (a DNT + DNK mixture) containing various amounts of trinitrotoluene was investigated. Figure 3 gives curves for the viscosity dependence of a 2.5% PMVP solution in the distilled solvent. With increasing TNT addition, the viscosity of the system increases. The influence of TNT, as well as of dinitrotoluene and dinitrobenzene, was also investigated in a system containing cyclohexanone as solvent. Figure 4 shows the change in the relative viscosity of a solution containing 3.2% PMVP, 64.5% TNT, DNT, or DNB, and 32.3% cyclohexanone (composition given in weight percent).

The observed increase in viscosity depends on the polymer concentration. For example, a solution containing 1.4% PMVP, 53.8% TNT, and 44.8% cyclohexanone showed no change in viscosity at 100° over 3 h.

The addition of dinitrotoluene has a similar effect. The change in viscosity with time is represented by curve *II* in Fig. 4. The same figure gives the straight line *III* for a solution containing dinitrobenzene. Comparison of curves *I* and *II* shows that, in the presence of TNT, the increase in the viscosity of the solution occurs more intensively than in the case of the addition of DNT. With dinitrobenzene, no interaction of the polymer is observed.

Fig. 3. Dependence of η_{rel}^{100} on heating time for 2.5% solutions of poly-2-methyl-5-vinylpyridine with addition of TNT. *I* –1.5%, *II* –6.3%, *III* –37.5%

Fig. 4. Dependence of η_{rel}^{100} on heating time for solutions of poly-2-methyl-5-vinylpyridine in cyclohexanone with additives: *I* –TNT, *II* –DNT, *III* –DNB

Experiments were also carried out on the interaction of MVP polymer with dinitro compounds and trinitro compounds in solutions of mononitro compounds. The compositions of the solutions used are given in Table 4. Mononitrotoluene was used as the solvent.

Table 4

No.	Solution composition	MNT content, %
1	1 g MNT + 18.5 g mixture of DNT + DNK	5.1
2	10 g MNT + 9.5 g mixture of DNT + DNK	51
3	20 g MNT + 20 g DNT	50
4	45 g MNT + 3 g TNT	96

Solutions prepared on the basis of mixtures Nos. 2, 3, and 4, containing 2.5% polymer of 2-methyl-5-vinylpyridine, showed absolutely no increase in viscosity. A slight increase in viscosity was observed only for a 2.5% solution of PMVP in a mixture of nitro compounds containing 5.1% MNT. The results of measuring the relative viscosity of the solution obtained at a temperature of 100° are given below.

Time, min.	0	35	65	95	290	350	410	470
η_{rel}^{100}	3.04	3.17	3.4	3.5	3.6	4.1	4.4	4.9

The inhibiting effect of the addition of mononitrotoluene can, in our opinion, be explained by the blocking of the active centers of the polymer (nitrogen atoms) by molecules of the mononitro compound.

Institute of Petrochemical Synthesis
Academy of Sciences of the USSR

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1. A. A. Berlin, A. G. Kronman et al., *Vysokomolek. soed.*, **2**, 1839 (1960).

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