

Chemical Modification of Poly(N-vinylcarbazole)

J. PIELICHOWSKI and E. MORAWIEC, *Instytut Chemii i Technologii Organicznej, Politechnika Krakowska, Kraków, Poland*

Synopsis

Investigation of the phosphorylation reaction of poly(vinylcarbazole) was carried out using different phosphorylating reagents and in the presence of various catalysts. PCl_3 , PBr_3 , P_2S_5 , and $\text{H}_3\text{PO}_4 + \text{P}_2\text{O}_5$ were examined, and it was noticed that PCl_3 and PBr_3 were the most effective phosphorylating reagents. The best results for the phosphorylation process of poly(vinylcarbazole) were obtained at 76°C when PCl_3 was used and at 140°C when PBr_3 was used. It was confirmed that the percentage of phosphorus which was introduced into the polymer can be expressed by the following formula:

$$\%P = 7.35 \sqrt[5]{t}.$$

The optimal value of the reaction time for both these phosphorylating reagents PCl_3 and PBr_3 amounts to 6 hr. The phosphorylated poly(vinylcarbazole) obtained under these conditions shows ion exchange behavior—the value of ion-exchange capacity amounts 3.2 mval/g. The pH-metric titration curve indicates two stages of dissociation. The DTA curve shows that there is no decomposition of the phosphorylated poly(vinylcarbazole) up to a temperature of 300°C ; at 550°C , there is 37.5% loss of weight. Spectrophotometric IR studies of phosphorylated poly(vinylcarbazole) indicate that the maximal quantity of phosphorus in the polymer is 11.3% P, that means one phosphone group in each monomer unit.

INTRODUCTION

Owing to its thermal and chemical stability poly(vinyl carbazole) is an interesting species. The studies on the synthesis of some new polymers are being developed into two directions: on one hand, by synthesis of some monomer vinylcarbazole derivatives; and on the other hand, by chemical modification of poly(vinylcarbazole). Among works done on the poly(vinylcarbazole) modification, the following reactions are to be mentioned: halogenation,¹⁻⁷ nitrosation,⁸ nitration,⁹ and chloromethylation.¹⁰

The thermal behavior of the modified poly(vinylcarbazole) has been shown before.¹¹ There has been a lack of information in the literature on the phosphorylation reaction of poly(vinylcarbazole). This problem is interesting in so far that an ion exchange resin and a polymer with increased thermal stability and fire retardancy can thus be obtained. The phosphorylation reaction of polystyrene has been described in detail in the literature.¹²⁻¹⁵ Out of the number of phosphorylating reagents and catalysts which have been examined, PCl_3 and AlCl_3 gave the most satisfactory results.

In this work, we intended to obtain polymers with high thermal stability and ion exchange properties. Polymers of vinylcarbazole were chosen for in-

vestigations because of their chemical structure—two aromatic rings in one molecule of vinylcarbazole. The introduction of phosphone groups into the polymer causes that the obtained products have ion exchange and also complex-forming properties, thus the possibilities of application are wider. The problem of phosphorylation of poly(vinylcarbazole) is the subject of the present paper.

EXPERIMENTAL

General Procedure

The phosphorylation reaction was carried out using 20% solution of poly(N-vinylcarbazole) in ethylene chloride. The molar ratio of polymer:catalyst:phosphorylating reagent was 1:2.5:10. The reaction mixture was maintained at the temperature of 70–80°C during 6 hr.

To a three-necked flask fitted with a stirrer, a reflux condenser, and a thermometer, 5 g (0.026 mole) poly(vinylcarbazole) in ethylene chloride, 0.065 mole catalyst, and 0.26 mole phosphorylating agent were introduced. The reaction mixture was then warmed up to a temperature of 76–80°C and kept at this temperature for 6 hr. After that time the mixture was cooled down to room temperature. Then 200 ml water containing 20 ml methanol was added to the mixture. The reaction product was washed with water and acetone and dried.

Thermal Properties

The thermal properties of the product were studied by means of a Paulik-Paulik Erday derivatograph system, OD 102 Type (MOM Budapest, Hungary). The measurements were made over a temperature range of 20–500°C, in an atmosphere of air, the heating rate being 5°C/min. Alumina calcined at 1000°C was used as a reference material.¹¹

pH-Metric Titration

pH-Metric titration was carried out in the following way: a sample (about 15 g) of phosphorylated poly(vinylcarbazole) was washed with deionized water to obtain a neutral reaction, and then 0.5*N* NaOH solution was added. After 24 hr, the polymer was washed again to neutrality. Thereafter, a sample was converted to the H⁺ form by treating it with 2*N* HCl solution for 24 hr and then washed with deionized water to remove the sorbed HCl until the wash water is free of Cl⁻. Then the sample was dried to constant weight. Fourteen samples (about 1 ± 0.001 g each) were weighed into 100-ml flasks and 10 ml 1*N* NaCl solution was added to each flask. To these samples, incremental quantities of 0.1*N* NaOH solution were added (2, 4, 6, 8, . . . 28 ml). The content of the measuring flasks was filled up to 100 ml with deionized water. Equilibrium is established by shaking the stoppered flasks until the pH of the solution attains a constant level (about five days). The solutions of the polymer were titrated. The measurements were carried out using an LBS-66 type pH-meter (Poland).

Ion Exchange Capacity

The ion exchange capacity of the phosphorylated poly(vinylcarbazole) was found using a static method.¹⁶

IR Spectra

IR spectra were obtained in Nujol with a UR-20 (GDR) instrument.

RESULTS and DISCUSSION

Effect of Individual Parameters on the Phosphorylation Process

Effect of Type of Phosphorylating Reagent. Effect of phosphorylating reagents types studies were carried out to establish the effect of the individual phosphorylating reagents and to determine their usability for the phosphorylating process of poly(vinylcarbazole). The results are shown in Table I. AlCl_3 was used as a reaction catalyst in an amount of 2.5 times that of poly(vinylcarbazole). On the base of the presented results, it could be confirmed that PCl_3 is the best phosphorylating reagent for poly(vinylcarbazole). As a consequence of the reaction which was carried out in the presence of PCl_3 up to one phosphone group can be introduced into each monomer unit of poly(vinylcarbazole). The other reagents proved to be less effective. The lowest conversion level was obtained with a mixture of H_3PO_4 and P_2O_5 and POCl_3 . In the case P_2S_5 was used as phosphorylating reagent, a higher conversion level, i.e., approx. 5% P was obtained; however, there are many difficulties in removing the recovered sulfur. A more satisfactory ion exchange ability was obtained for a polymer which was phosphorylated by means of P_2S_5 , this fact being caused by the presence of sulfur bonded with polymer, this sulfur providing, some ionogenic groups upon oxidation.

Effect of Type of Catalyst. The generally accepted mechanism of the phosphorylation reaction is the Friedel-Crafts reaction mechanism. Hence, this type of catalyst is preferred for use. The usefulness of three catalysts was examined in this work. AlCl_3 , SnCl_4 , and ZnCl_2 were used as catalysts for the two most effective phosphorylating reagents, i.e., PCl_3 and PBr_3 . The

TABLE I
Results of Phosphorylation of Poly(N-vinylcarbazole) in the Presence of Various Phosphorylating Reagents

Sample no.	Phosphorylating agent	Catalyst	Temp., °C	Ion exchange capacity, mval/g	% P	Number of $\begin{array}{c} \text{O} \\ \parallel \\ \text{P} \\ \diagup \quad \diagdown \\ \text{OH} \quad \text{OH} \end{array}$ groups per 10 monomer units
1	PCl_3	AlCl_3	76	2.91	10.84	9.55
2	PBr_3	AlCl_3	80	2.48	7.9	6.96
3	P_2S_5	AlCl_3	82	3.65	5.08	4.48
4	$\text{H}_3\text{PO}_4 + \text{P}_2\text{O}_5$	AlCl_3	80	0.2	0.6	0.53
5	POCl_3	AlCl_3	82	0.4	1.78	1.57

TABLE II
Results of Phosphorylation of Poly(N-vinylcarbazole) in the
Presence of Various Catalysts

Sample no.	Phosphorylating agent	Catalyst	Temp., °C	Ion exchange capacity, mval/g	% P	Number of $\begin{matrix} \text{O} \\ \text{P} \begin{matrix} \diagup \text{OH} \\ \diagdown \text{OH} \end{matrix} \end{matrix}$ groups per 10 monomer units
1	PCl_3	AlCl_3	76	2.91	10.84	9.55
2	PCl_3	SnCl_4	76	3.20	6.87	6.05
3	PCl_3	ZnCl_2	76	1.02	2.93	2.58
4	PBr_3	AlCl_3	90	2.3	8.2	7.22
5	PBr_3	SnCl_4	90	3.07	7.65	6.74
6	PBr_3	ZnCl_2	90	3.05	6.25	5.50

results are compiled in Table II. The obtained results prove that, according to our expectation AlCl_3 is the most efficient catalyst for these two phosphorylating reagents. Moreover, in case of phosphorylation in the presence of PBr_3 , the effectiveness of all these three catalysts is similar and is increased for ZnCl_2 : it amounts to 2.93% P when PCl_3 is used and to 6.25% P when PBr_3 is used. AlCl_3 seems to be the most reasonable catalyst for the phosphorylation process.

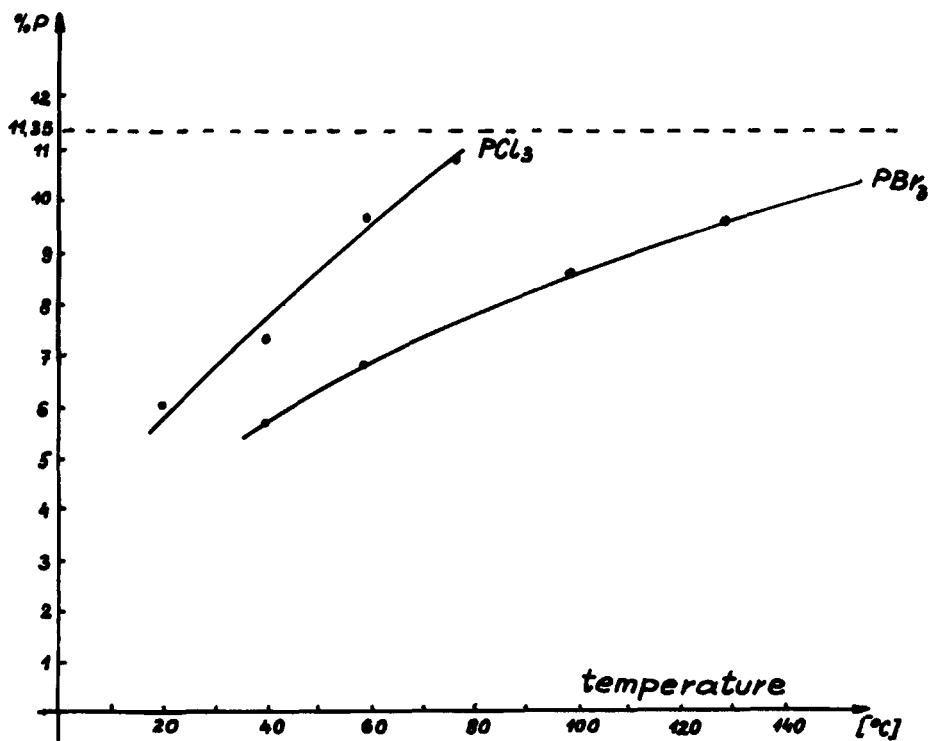


Fig. 1. Dependence of degree of phosphorylation of poly-N-vinylcarbazole on temperature.

TABLE III
Results of Phosphorylation of Poly(N-vinylcarbazole) at Various Reaction Times

Sample no.	Phosphorylating agent	Catalyst	Time, hr	Ion exchange capacity, mval/g	% P	Number of $\begin{array}{c} \text{O} \\ \text{P} \\ \text{OH} \\ \text{OH} \end{array}$ groups per 10 monomer units
1	PCl_3	AlCl_3	0.5	1.70	4.70	3.68
2	PCl_3	AlCl_3	1	2.07	6.66	5.87
3	PCl_3	AlCl_3	2	2.54	8.65	7.62
4	PCl_3	AlCl_3	3	2.60	9.12	8.02
5	PCl_3	AlCl_3	5	2.77	10.30	9.06
6	PCl_3	AlCl_3	6	2.91	10.84	9.55
7	PCl_3	AlCl_3	8	2.99	11.27	9.90
8	PCl_3	AlCl_3	11.5	3.17	11.70	10.3

Effect of Temperature. Among the phosphorylating reagents for poly(vinylcarbazole), PCl_3 and PBr_3 are the most effective ones, however, their boiling points are different (76°C and 175°C). This is the reason for limited application of PCl_3 at higher temperatures. In order to find the effect of temperature on the phosphorylating process of poly(vinylcarbazole), PCl_3 and PBr_3 were examined as phosphorylating agents. The results of these investigations are shown in Figure 1. On the basis of the presented data, it is evident that the phosphorylation degree increases with temperature. As the reaction temperature gets nearer to the boiling point of the reaction mixture,

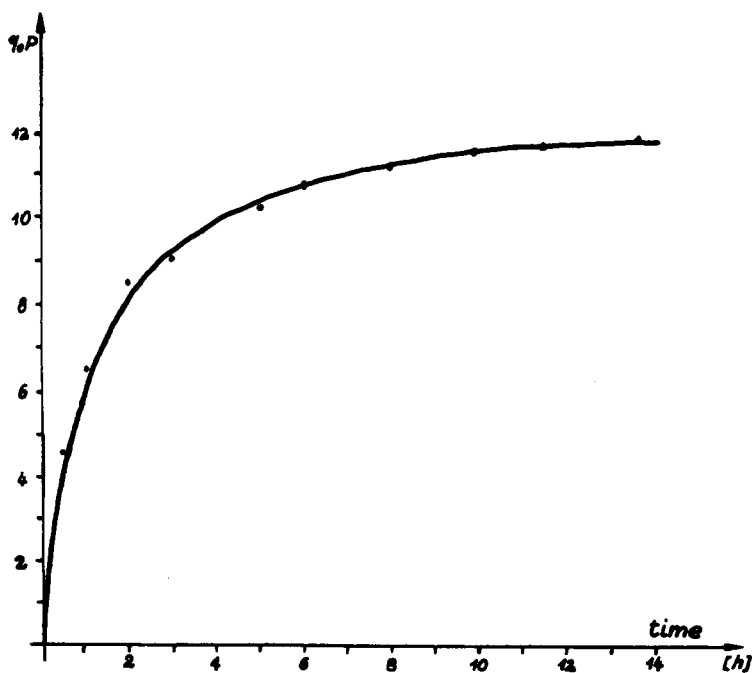


Fig. 2. Dependence of degree of phosphorylation of poly(N-vinylcarbazole) on reaction time.

the content of phosphorus in the polymer approaches 11.36% P, this value proving that there is one single phosphone group in each carbazole ring of the polymer. Since the same results may be obtained at a temperature of 76°C for PCl_3 and 140°C for PBr_3 , it is obvious that PCl_3 is more preferred for the phosphorylation reaction of poly(vinylcarbazole) than PBr_3 .

Effect of Time. The studies on the effect of time on the course of the reaction were helpful in finding kinetic dependences of the reaction. In this work, the problem was limited to the calculation the equation which describes the dependence between conversion degree (the percentage of introduced P) and reaction time. We found that $\%P = 7.35 \sqrt[5]{t}$. This equation works in the case of introducing one phosphone group into the carbazole ring. The results of our studies on the effect of phosphorylation time of poly(vinylcarbazole) on the quantity of the phosphorus introduced into the molecule are shown in Table III and Figure 2. From the presented data it is evident that the prolongation of the reaction time results in an increase of the proportion of the accepted phosphone groups. The optimum phosphorylation time was found to be 6 hr. Prolongation of the reaction time up to 11.5 hr results in additional increase of phosphorus in the polymer by as little as 0.84%. Moreover, it should be concluded that, under the described conditions, it was possible to introduce only one single phosphone group into the carbazole ring.

Properties and Structure of Phosphorylated Poly(vinylcarbazole)

Ion Exchange Capacity. The obtained phosphorylated products of poly(vinylcarbazole) showed some ion exchange behavior. The ion exchange capacities of these products were determined. The ion exchange capacity is defined as the amount of ionogenic groups per mass unit which are capable of

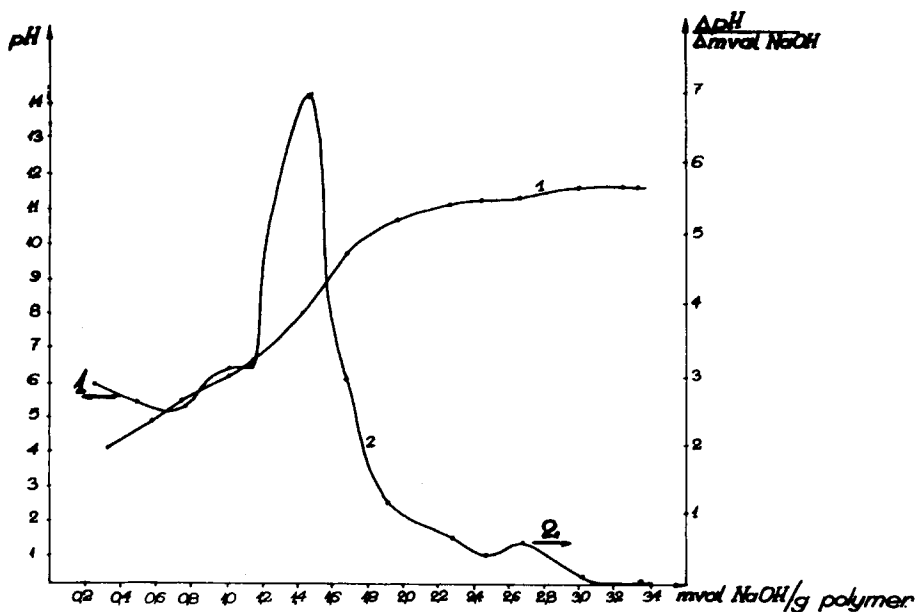


Fig. 3. Results of pH-metric titration: (1) pH-metric titration curve; (2) differential curve.

ion exchange process. The value of static ion exchange capacity is determined for ion exchanger which is in equilibrium with the electrolyte solution.

The ion exchange capacity values for phosphorylated polymers were remarkably lower than those estimated theoretically on the basis of phosphone group content in the polymer, e.g., for the polymer containing 9.80% P, the calculated ion exchange capacity amounts to 6.31 mval/g; the value determined by a static method is 2.88 mval/g; the values determined by pH-metric titration are 2.70 mval/g.

The behavior of this polymer at various pH levels was observed using pH-metric titration. Results are compiled in Figure 3, where curve 1 is the pH-metric curve and curve 2 is the corresponding differential curve. On the pH-metric titration curve, a significant inflection is observed in the pH range of 6–11, this range referring to the first degree of dissociation. This fact is also evident in the differential curve. The second degree of dissociation is very weak and can be observed in the pH range of 11.4–14.5 but is practically invisible on the pH-metric titration curve; it can be observed on the differential curve. This low level of ion exchange capacity of some modified polymers is caused by a hindered accessibility of the phosphone groups by ions and also by the fact that some phosphone groups are bonded with two molecules of vinylcarbazole, this fact resulting in the disactivity of these groups in ion exchange process.

Thermal Properties. The thermal examination of the obtained polymers reveals their high stability. The thermal properties of poly(vinylcarbazole)

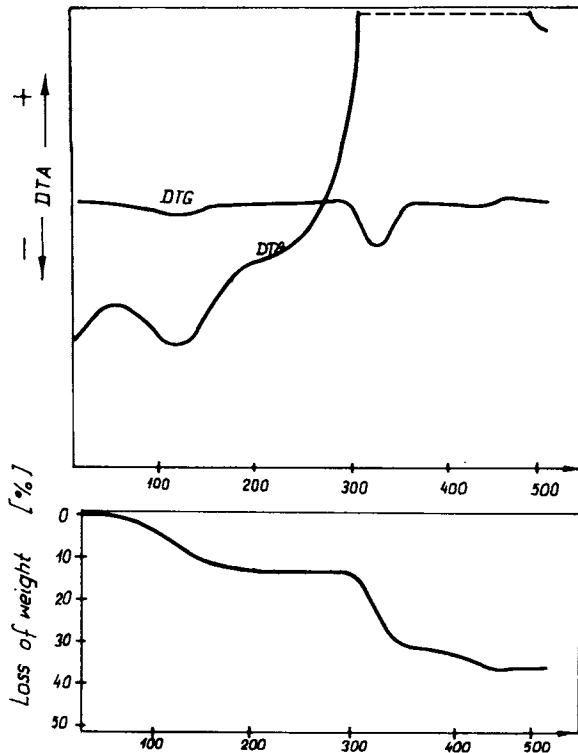


Fig. 4. Thermal analysis of phosphorylated poly(N-vinylcarbazole) (content 11.2% P).

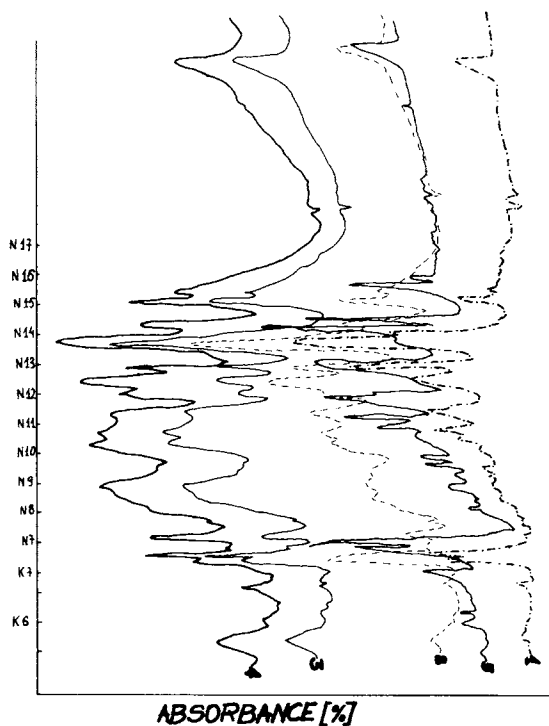


Fig. 5. IR spectra of poly(N-vinylcarbazole) and phosphorylated products: (1) 1.78% P; (2) 5.08% P; (3) 9.6% P; (4) 11.3% P.

containing 11.2% P are discussed below. The more detailed thermal studies of the other modified polymers containing the various content of phosphorus are described in reference 17.

For the phosphorylated polymer (11.2% P), a marked endothermic effect is observed on the DTA curve in the range of 60–180°C. Its minimum point is at 120°C. The TG curve shows a loss of weight of 12.5% in the same temperature range. The DTG curve also reveals a rise in weight loss. The described transformation occurring in the range of 60–180°C is due to the loss of water in the polymer. On the DTA curve, an increase in exothermic effects is observed below a temperature of 300°C, these effects ending at 500°C. A marked loss of weight with the transformation occurs in the TG curve, this loss being 31.9% at 375°C (Fig. 4).

The maximum point of degradation rate is at 382°C. As the temperature rises above 375°C, a slight loss of weight is observed, which amounts then up to 35.7%. This loss of weight ends at 476°C and remains unchanged up to 550°C. The conversion at the temperature above 305°C is caused by a destructive oxidation process. This is evidenced by the exothermic effect of those conversions, the effect probably being due to the splitting of the phosphoric acid the presence of which in the degradation product was stated.

Physical Properties. The color of the phosphorylated poly(vinylcarbazole) is dependent on phosphorus content in the polymer and ranges from yellow to brown. The modified polymer is insoluble in the typical organic solvents, but is soluble in concentrated sulfuric acid.

Analysis of IR Spectra. IR spectra of poly(vinylcarbazole) and of the product of phosphorylation with various phosphorus contents are shown in Figure 5. Based on the IR spectra of some individual modified products, the presence of phosphone group was demonstrated. In the wave number of $909\text{--}1040\text{ cm}^{-1}$, a distinct band can be observed, attributable to the presence of a P—O—H group. A remarkable wide band appearing in the range of $1100\text{--}1230\text{ cm}^{-1}$ seems to be caused by superposition of P—O band vibrations and asymmetric vibration of PO_2^- groups. The remaining bands are specific for poly(vinylcarbazole).

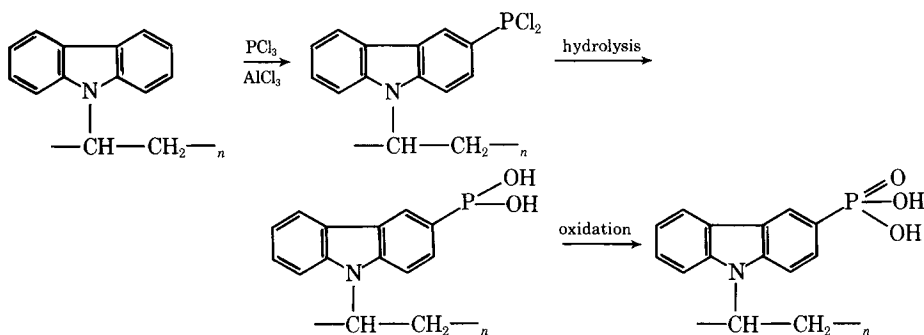
In IR spectra of some modified products of various phosphorus content, significant differences can be noticed, these differences being used to determine the degree of phosphorylation.

CONCLUSIONS

From the results of the phosphorylation reaction of poly(N-vinylcarbazole), it was found that PCl_3 was the best phosphorylating reagent and that AlCl_3 was the most adequate catalyst for this process. Under these conditions, up to one phosphone group can be introduced into each monomer unit of polymer.

The phosphorylation reaction product is flame retardant and has a high thermal stability; it is also chemically stable up to 300°C . Ion exchange capacity of the phosphorylated products is 3.2 mval/g for a phosphorus content of 11.3% , and hence these products may be used as ion exchangers.

From the experiments and the references concerning the phosphorylation reaction of the other polymers, we suggest the following scheme of phosphorylation reaction of poly(N-vinylcarbazole):



References

1. Y. Murakami and K. Morimoto, Brit. Pat. 1,186,658 (1970).
2. Y. Murakami and K. Morimoto, Jap. Pat. 7,005,385 (1970).
3. S. S. Rogachewa, E. E. Sirotkina, and W. P. Lopatiński, *Ural. Konf. Spektrosk.*, **2**, 54 (1971); *Ref. Žurn. Chim.*, **1313**, 1148 (1972).
4. French Pat. 2,118,612 (1970).
5. K. Morimoto and A. Monobe, Jap. Pat. 7,015,509 (1970).
6. K. Morimoto and Y. Murakami, Jap. Pat. 7,015,508 (1970).
7. J. Pielichowski, *Roczniki Chemii*, **45**, 497 (1971).
8. K. Tubuko, U.S. Pat. 3,595, 648 (1971).

9. K. Morimoto, A. Minami, and A. Minobe, Jap. Pat. 22,049 (1967).
10. E. E. Sirotkina and W. P. Lopatiński, USSR Pat. 275,396 (1970).
11. J. Pielichowski, *J. Therm. Anal.*, **4**, 339 (1971).
12. G. V. Samsonow and E. B. Trostiańska, *Vysokomol. Soedin.*, **3**, 41 (1969).
13. E. B. Trostiańska, *Jonnyj Obmien, i Jevo Primienienije*, Izd. A. N. USSR, Leningrad, 1959.
14. E. E. Ergożin, *Chimia Monomerow i Polimerow*, Izd. A. N. USSR, Leningrad 1956.
15. A. B. Nikolajew and J. N. Gribanowa, *Izv. Otd. Sib. A.N. USSR, Ser. Chim. Nauk*, **3**, 86 (1967).
16. F. Helfferich, *Ion Exchange*, McGraw-Hill, New York, 1962.
17. J. Pielichowski and E. Morawiec, 4th Bratislava IUPAC Intern. Conf. on Modified Polymers, Their Preparation and Properties, Polymer Institute of the Slovak Academy of Science, Bratislava, *Preprints*, 1975, p. 40.

Received September 3, 1975