CHEMISTRY

M. M. KOTON and O. K. SURNINA

1957

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

CHEMISTRY

M. M. KOTON and O. K. SURNINA

POLYMERIZATION OF 2-VINYLPYRIDINE AND 2-VINYLQUINOLINE

(Presented by Academician V. A. Kargin, December 10, 1956)

Despite the fact that vinyl derivatives of pyridine have in recent years found broad application (in the manufacture of SK, in the production of acrylonitrile fiber, in ion-exchange resins, etc.), the process of their polymerization and copolymerization has remained little studied (^{1}). Vinylquinoline is very close in its structure to vinylpyridine, but until recently had only limited application, apparently owing to insufficient knowledge of the polymerization process and of the properties of its polymers (^{2}). A study of the polymerization process of vinyl derivatives of pyridine and quinoline is of theoretical interest, since it makes it possible to assess the influence of the heteroatom included in the rings of vinyl monomers on their behavior in polymerization and copolymerization processes.

Fig. 1

2-vinylpyridine 2-vinylquinoline

in comparison with the structurally related styrene and vinylnaphthalene. At the same time it was also possible to study the influence of increasing the complexity of the molecule of the heterocyclic monomer, by introducing a second benzene ring, on the processes of polymerization and copolymerization.

For this purpose, monomers of 2-vinylpyridine and 2-vinylquinoline were synthesized by the interaction of picoline and quinaldine with paraform, followed by dehydration of the resulting carbinols over caustic potash. The physical properties of the monomers are presented in Table 1.

To study the ability of 2-vinylpyridine and 2-vinylquinoline to polymerize, the kinetics of polymerization of these monomers in bulk was studied by the dilatometric method in the presence of 0.135 mole % azodiisobutyric acid nitrile, at 50, 55, 60, 75, and 90°. The apparatus for filling the dilatometric ampoules consisted of a distillation flask, a condenser, and a receiver-desiccator containing ampoules with weighed initiator placed in it. Distillation of the monomers into the ampoules was carried out in a stream of specially

Table 1

Physicochemical properties of the monomers

Monomer	T_{boil}, °C/mm, found	T_{boil}, °C/mm, lit.	Refractive index n_D^{20}, found	Refractive index n_D^{20}, lit.	d_4^{20}, found	d_4^{20}, lit.	MR, found	MR, lit.	Elemental composition, %, C found	Elemental composition, %, C calcd.	Elemental composition, %, H found	Elemental composition, %, H calcd.	Elemental composition, %, N found	Elemental composition, %, N calcd.
2-Vinylpyridine	64.5/20	60/17	1.5497	1.5495	0.9757	0.9770	34.33	34.40	80.02	80.0	6.85	6.66	13.16	13.33
2-Vinylquinoline	104/3	120-125	1.6485	1.6439	1.0705	1.0692	52.79	–	85.50	85.15	6.00	5.80	9.19	9.03

purified nitrogen, which ensured the production of well-reproducible results.

In addition, the process of copolymerization of 2-vinylpyridine and 2-vinylquinoline with styrene, isoprene, and chloroprene in bulk at 60° in the presence of 0.2 wt.% azobis(isobutyric acid nitrile) was studied. The amount of copolymer formed was determined after threefold reprecipitation and drying at 40° under vacuum to constant weight. The composition of the copolymers was determined by nitrogen analysis by the Dumas micromethod. The copolymerization constants were determined from the integral equation for copolymer composition by the method of G. A. Shtraikhman (^{3}).

As can be seen from Fig. 1, 2-vinylpyridine (curve *I*), in contrast to 2-vinylquinoline (curve *II*), polymerizes very readily, beginning at a temperature of 50°.

With respect to the rate of polymerization, the monomers studied form the following series:

2-vinylpyridine (*I*) $\gg$ 2-vinylquinoline (*II*) $>$ styrene (*III*). On the basis of a study of the polymerization kinetics, the following values of the activation energy were obtained for 2-vinylpyridine and 2-vinylquinoline:

Monomer	k_0, sec^{-1}	u, kcal/mole
2-vinylpyridine	$1 \cdot 10^9$	20.4 ± 1.4
2-vinylquinoline	$1 \cdot 10^8$	18.3 ± 1.3

The slow polymerization process of 2-vinylquinoline proved unexpected; this, apparently, can be explained by steric hindrance occurring in the interaction of the radical with the monomer.

Comparison of the activation-energy values of 2-vinylpyridine and 2-vinylquinoline with those for styrene (21.5 kcal/mole) and 2-vinylnaphthalene (18.8 kcal/mole) shows that complication of the molecule of the vinyl compound by introduction of a second benzene ring leads to an increase in the reactivity of the monomer obtained, owing to an increase in the number of conjugated double bonds ([4]).

For a more complete characterization of the reactivity of the monomers 2-vinylpyridine and 2-vinylquinoline, the process of their copolymerization with a series of monomers was studied and the values of the copolymerization constants r_1 and r_2 were determined:

From the data presented it follows: 1) 2-vinylquinoline is more active in copolymerization processes than 2-vinylpyridine; 2) the monomers 2-vinylpyridine and 2-vinylquinoline are more active than the styrene monomer.

Monomer M_1	Monomer M_2	r_1	r_2
2-vinylpyridine	styrene	1.81 ± 0.05	0.55 ± 0.03
2-vinylpyridine	isoprene	0.46 ± 0.07	0.58 ± 0.05
2-vinylpyridine	chloroprene	0.064 ± 0.001	5.195 ± 0.003
2-vinylquinoline	styrene	2.69 ± 0.55	0.49 ± 0.14
2-vinylquinoline	isoprene	1.882 ± 0.002	0.534 ± 0.001
2-vinylquinoline	chloroprene	0.38 ± 0.03	2.10 ± 0.13

Thus, it has been shown that the introduction of a nitrogen heteroatom into the aromatic ring of a vinyl monomer, as well as an increase in the number of fused benzene rings in the monomers, increases the reactivity of vinyl derivatives.

Institute of High-Molecular Compounds
Academy of Sciences of the USSR

Received
6 XII 1956

REFERENCES

[1] Ch. Price, Ch. Greene, *J. Pol. Sci.*, **6**, 111 (1951); D. Maclay, R. Fuoss, *J. Pol. Sci.*, **6**, 511 (1951).
[2] B. Bachman, D. Micussi, *J. Am. Chem. Soc.*, **70**, 2381 (1948).
[3] G. A. Shtraikhman, Candidate’ s dissertation, LTI, 1950.

[4] M. M. Koton, T. M. Kiselyova, DAN, **88**, 465 (1953).
[5] R. Frank, C. Adams, *Ind. and Eng. Chem.*, **40**, 879 (1948).
[6] R. Mariella, L. Peterson, R. Ferris, *J. Am. Chem. Soc.*, **70**, 1494 (1948).
[7] A. A. Petrov, V. Lyudvig, ZhOKh, **25**, 739 (1955).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.