Polymerization of Aromatic and Heterocyclic Vinyl Compounds

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A considerable quantity of substituted ethylenes and the wide possibilities of their application for practical usage made them of extensive interest for the investigator. The study of the influence of chemical structure of vinyl series monomers upon their polymerization ability is both interesting from the scientific point of view and important for practical purposes. However, by reviewing the bibliography on the polymerization of vinyl compounds, one observes that the number of systematic investigations in comparable conditions that enable evaluation of the influence of the properties of substituting groups in ethylene molecules on the polymerization process, is not all sufficient. Among the great number of ethylene series derivatives, its aromatic derivatives have long been drawing the attention of investigators. The studies of Shorygin,[1] Marvel,[2] Wiley,[3] as well as our data[4] show that within the series of substituted styrene there is interrelation between the structure of monomers and their ability for polymerization. The rate of polymerization of substituted styrenes differs, depending on the chemical nature of the substituents, the number of substituents, and their position in the styrene benzene ring as related to the vinyl group. We[5] have studied some substituted styrenes (halogen- and methylstyrenes) and have shown the influence of isomerism of substituents in the styrene benzene ring upon the rate of polymerization which increases from mono- to di- and tri-substituted styrenes. Polymerization of substituted styrenes, when such substituents as halogen atoms and the cyanogen group are introduced, proceeds with greater speed because the process of polymerization continues less actively (8–18 cal./mole) compared to unsubstituted styrene (22 cal./mole). The study of the polymerization ability of other aromatic and heterocyclic substituents of ethylene encounters many difficulties, mostly because it is rather complicated to isolate these monomers in their pure form since they polymerize very easily.

POLYMERIZATION OF VINYL COMPOUNDS OF THE NAPHTHALENE SERIES

We thought that it would be most interesting to connect the high reactibility of vinyl compounds of multinuclear hydrocarbons with the existence

of coupling double bonds in the rings, giving as examples certain vinyl compounds of the naphthalene series.

With this purpose we have synthesized: (*1*) vinylnaphthalene (1-VN), b.p. 86–88°C. (2 mm.), n_D^{25} 1.6405; (*2*) vinylnaphthalene (2-VN), m.p. 65–66°C. dibromide melting point 83.4°C., 6-vinyl-1,2,3,4-tetrahydro-naphthalene (VT), b.p. 96–98°C. (2 mm.), n_D^{25} 1.5690.

The content of monomer in all these compounds was 96.6–99.8%.

Vinyldecahydronaphthalene (VD) was isolated for the first time, in the same way as VT, as a colorless liquid, b.p. 103°C. (3 mm.), n_D^{25} 1.5443.
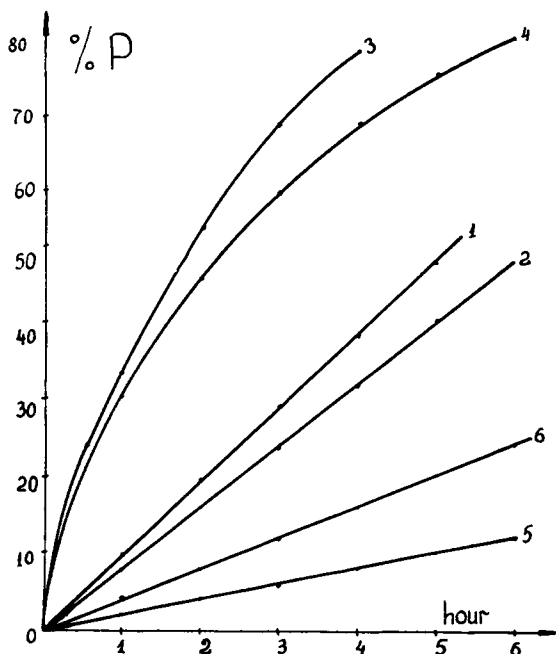

Fig. 1. The polymerization rate of vinyl derivatives of naphthalene. (*1*) 1-VN at 100°C. (*2*) 2-VN at 100°C. (*3*) 1-VN at 110°C. (*4*) 2-VN at 100°C. (*5*) 6-VT at 100°C. (*6*) 6-VT at 110°C.

Vinyl substituents of naphthalene were polymerized in a block at 100, 110, and 125°C.

The studies of Koton and Kiseleva[6] showed that 1-VN and 2-VN have the greatest rate of polymerization, the 1-VN being the easiest to polymerize. VT is much slower to polymerize, being more like unsubstituted styrene (Fig. 1). VD, which has no double bonds in the monomer molecule ring, did not polymerize during thirty days at 100°C. The obtained polymers were of low molecular weight and had the following value of [η]: 1-VN, 0.06; 2-VN and VT, 0.22.

The study of polymerization kinetics provided data for the calculation of the value of activation energy of polymerized vinyl derivatives in the naphthalene series: 1-VN, 16.9 ± 0.5 kcal./mole; 2-VN, 18.8 ± 0.3

kcal./mole; and VT, 20.9 ± 0.5 kcal./mole. Thus, vinyl derivatives of the naphthalene series showed that there is a relationship between the number of coupling double bonds in the monomer molecule ring and the polymerization ability.

POLYMERIZATION OF VINYL DERIVATIVES OF PYRIDINE AND QUINOLINE

To acquire more data on the polymerization process of vinyl compounds which contain different cyclic radicals as substituents in ethylene molecule, we have studied 2-vinylpyridine (VP) and 2-vinylquinoline (VQ). We have chosen these particular monomers because they enabled us to compare the data on their polymerization with those of styrene and 2-vinylnaphthalene we had obtained before, and thus to evaluate the influence of a heteroatom (nitrogen), which is a part of the cyclic radical, upon polymerization ability. Besides this, the polymerization of VQ has been studied very little until now.[8] VP was isolated according to the Winterfeld and Heinen method;[8] its properties are b.p. 64.5°C. (2 mm.); n_D^{20} 1.5497; d_4^{20} 0.9757.

VQ was isolated by means of the Bachman and Micucci method.[7] Its properties are b.p. 104°C. (3 mm.); n_D^{20} 1.0705.

The polymerization process of these monomers was studied by Surnina,[15] and was carried out in a block in the presence of azobisisobutyronitrile (0.135 mole-%) as the initiator in a nitrogen atmosphere. Polymerization was carried out dilatometrically at 50, 55, 60, 75, and 90°C.
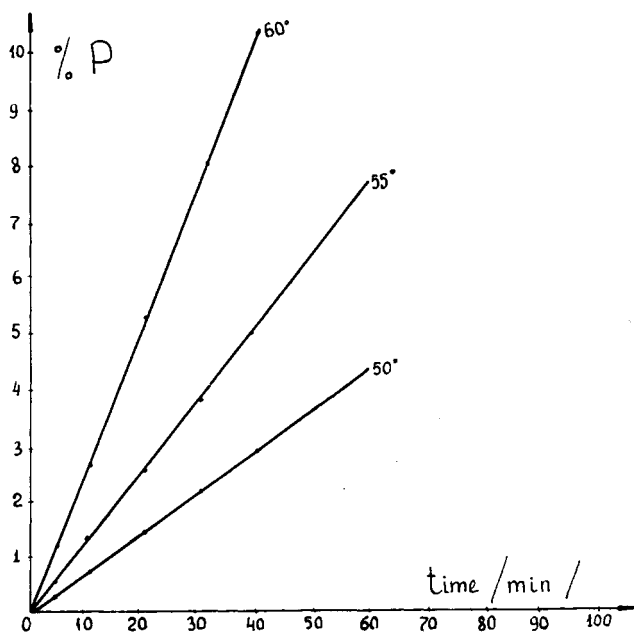

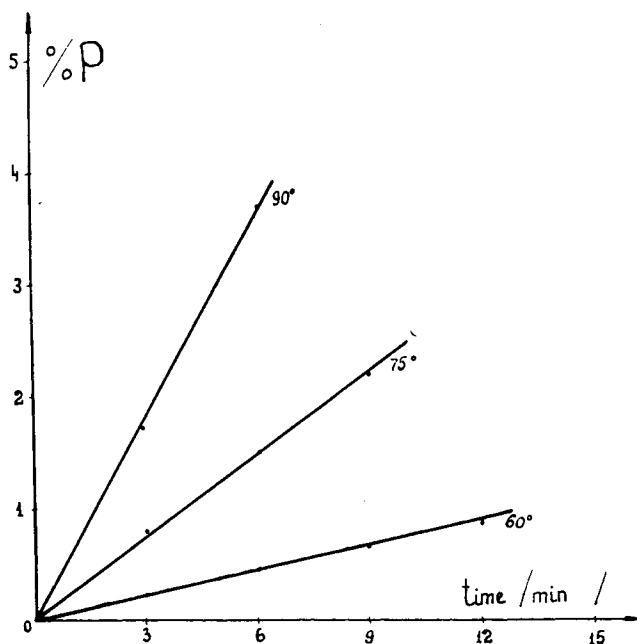Fig. 2. The polymerization rate of 2-vinyl pyridine.

Fig. 3. The polymerization rate of 2-vinyl quinoline.

As Figures 2 and 3 show, VP is polymerized faster than styrene and VQ. In 30 minutes at 60°C. the yield of VP was 10.6% and of styrene, 1.7%. VQ yielded 6.4% in 15 minutes at 90°C.

The determined $[\eta]$ values were: VP, 0.5; VQ, 0.1. The data on polymerization kinetics were used to calculate the activation energy of polymerization: VP, 20 ± 1 kcal./mole; VQ, 18 ± 1 kcal./mole. For a more thorough evaluation of the reactability of VP and VQ, we have studied their polymerization with unlimited monomers. Copolymerization was effected in the presence of azo-bis-isobutyronitrile (0.2%) at 60°C.

The composition of copolymers was determined by the Dumas micro-determination of nitrogen.

Copolymerization constants were determined with the help of integral equation of copolymer composition; the data are shown in Table I.

TABLE I

Constants of Copolymerization of 2-Vinyl Pyridine and 2-Vinyl Quinoline with Some Monomers

No.	M_1	M_2	r_1	r_2
1	2-Vinyl pyridine	Styrene	1.81 ± 0.05	0.55 ± 0.03
2	" "	Isoprene	0.47 ± 0.07	0.59 ± 0.05
3	" "	Chloroprene	0.06 ± 0.01	5.19 ± 0.03
4	" "	Acrylonitrile	21.88 ± 5.52	0.05 ± 0.01
5	2-Vinyl quinoline	Styrene	2.09 ± 0.55	0.49 ± 0.14
6	" "	Isoprene	1.88 ± 0.02	0.53 ± 0.01
7	" "	Chloroprene	0.38 ± 0.03	2.10 ± 0.02

The system VP–isoprene allows isolation of azeotropic copolymer. We must also point out the system VP–acrylonitrile which is like the well-known system vinyl styrene–acetate. Monomer VP couples with both types of radicals 20–22 times faster than with acrylonitrile.

The determined constant values of copolymerization allowed calculation of the activity of VP and VQ monomers as related to styrene, isoprene, chloroprene, and acrylonitrile radicals as shown in Table II.

TABLE II

Activity of 2-Vinyl Pyridine and 2-Vinyl Quinoline as Related to Different Radicals

	Radicals					
Monomers	2-vinyl pyri- dine	2-vinyl quino- line	Sty- rene	Iso- prene	Chloro- prene	Acrylo- nitrile
2-Vinyl pyridine	1.0	—	1.8	1.7	0.2	21.7
2-Vinyl quinoline	—	1.0	2.0	1.8	0.5	—
Styrene	0.5	0.5	1.0	0.5^a	0.14^a	20.0^a
Isoprene	2.1	0.5	0.7^a	1.0	0.27^a	33.3^a
Chloroprene	15.6	2.6	20.0^a	7.5^a	1.0	100^a
Acrylonitrile	0.05	—	2.7^a	2.2^a	0.17^a	1.0

[a] Data obtained by other authors.

The data of Table II show that VQ is more active than VP, while the latter is more active than styrene. Thus the results of the studies of VP and VQ polymerization are in the same relation as the results obtained for styrene and 2-vinyl naphthalene.

POLYMERIZATION OF VINYL DERIVATIVES OF FURAN AND THIOPHENE

To obtain more detailed data on the influence of the nature of heteroatoms which constitute cyclic radicals of substituted ethylenes upon the polymerization process, Andreeva and Koton[9] have studied some vinyl derivatives of the furan and thiophene series which up till now have been but little studied. For this purpose they synthesized: 2-vinyl furan (VF), b.p. 96–97°C., n_D^{28} 1.4994; 2-vinyl thiophene (VT), b.p. 66.5°C. (48 mm.), n_D^{20} 1.5722; 2-vinyl benzofuran (VBF) b.p. 52°C. (0.5 mm.), n_D^{25} 1.6020; 2-vinyl dibenzofuran (VDBF), b.p. 130°C. (0.5 mm.), m.p. 31°C.; and 2-vinyl dibenzothiophene (VDBT), m.p. 42°C. These compounds had 99.7–99.9% of monomer.

Andreeva and Koton have studied the polymerization process for all monomers of the furan and thiophene series in the presence both of peroxides (0.5 mole-% of benzoyl peroxide) and ion catalysts (lithium butyl, boron trifluoride etherate). Polymerization has been carried out in block in benzene and toluene solutions by means of the dilatometric method in the temperature range of 0 to 100°C.

The obtained data on the VF polymerization kinetics at 80, 90, and 100° C. allowed the calculation of activation energy of polymerization process: 17 ± 1 kcal./mole. The observation was made while studying the VF polymerization that molecular oxygen plays an important role in formation of properties of synthesized polymers. In the absence of ambient oxygen, the VF polymerizes with the benzoyl peroxide to form a hard and non-fuzible polymer which is obtained in the form of grains of the "ω-polymer" type; this type of polymer had been observed by Carothers with co-workers[10] and by Pravednikov and Medvedev[11] when studying diene polymerization.

The formation of the three-dimensional polymer leads us to believe that the double bonds in the ring of the VF polymer take part in the polymerization reaction. In the presence of oxygen, instead of these polymers, VF polymers are formed which are a soft mass. Their temperature of softening after resettling is 60–80°C.

Polymerization of VBF has been little studied; there is only one work by Elliott[12] which states that this polymer is able to polymerize and co-polymerize.

Polymerization of VDBF has not been studied at all. Investigations into the polymerization kinetics of these monomers at 60, 80, 90, and 100°C. permitted calculation of activation energy of the VBF polymerization process, 16.5 ± 0.5 kcal./mole, and of VDBF, 12.4 ± 0.60 kcal./mole. The determined values show that the VDBF have a very high reactibility in the polymerization process. These monomers also easily polymerize in the presence of ion catalysts. The VBF in the presence of BF_3 at 0°C. gave a 42% yield of polymer after 3 hours; the VDBF, 70% after 1 hour. The VBF polymers had an intrinsic viscosity, $[\eta]$, of 0.02–0.2, the value depending on polymerization conditions. The VDBF polymers had an $[\eta]$ of 0.05–0.40; while the polymers synthesized in the presence of the initiator of azo-bis-isobutyronitrile had high values of $[\eta]$: 1.44.

Polymerization of 2-vinyl thiophene (VT) and 2-vinyl dibenzthiophene (VDBF) have been but little studied.[13,14] These monomers polymerize very easily both in the presence of radical initiators and ion-type catalysts. The VDBF polymerizes more quickly than VT (Fig. 4). The energy of activation of the polymerization process of VT is 16.5 ± 0.5 kcal./mole VT, together with etherate BF_3 at 0°C., gave a yield of 74% of polymer in 50 minutes, the intrinsic viscosity of VT polymers was 0.08, and the temperature of softening was 70–85°C. The polymers of the VDBT showed $[\eta]$ of 0.13–0.20 and a softening point of 144°C.

The results that have been obtained by studying the polymerization of vinyl derivatives of furan and thiophene series show that by increasing the number of condensed rings in the monomer molecule, we can considerably increase the rate of the polymerization process (Fig. 5). The data for the monomers of the same structure of the furan and thiophene series have been compared and the results help to determine the influence of nature of the heteroatom (oxygen, sulfur) upon the ability to polymerize. It was proved
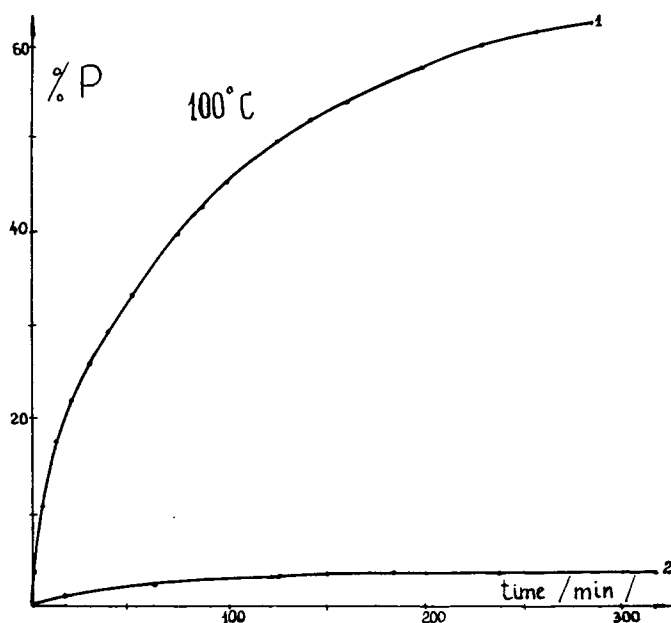
Fig. 4. The polymerization rate of vinyl derivatives of thiophene. (*1*) VDBT. (*2*) VT.   1 *M* solution in toluene, 0.5 mole-% peroxide.
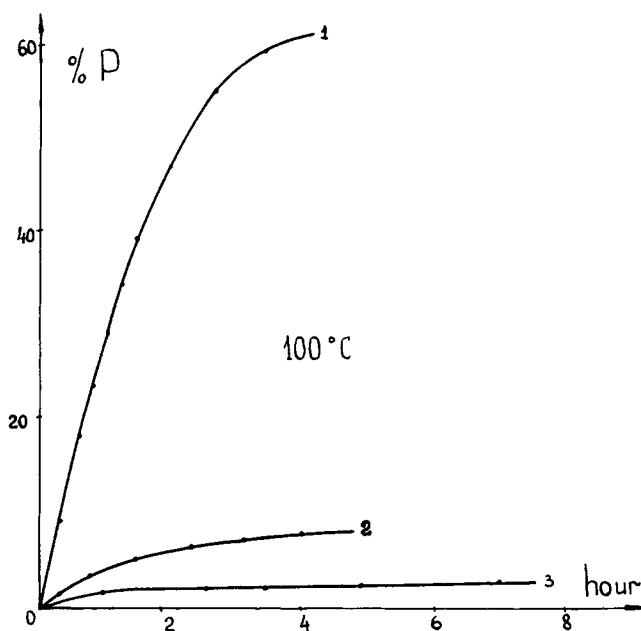

Fig. 5. The polymerization rate of vinyl derivatives of furan. (*1*) VDBF. (*2*) VBF. (*3*) VF.   1 *M* solution in toluene, 0.5 mole-% peroxide.
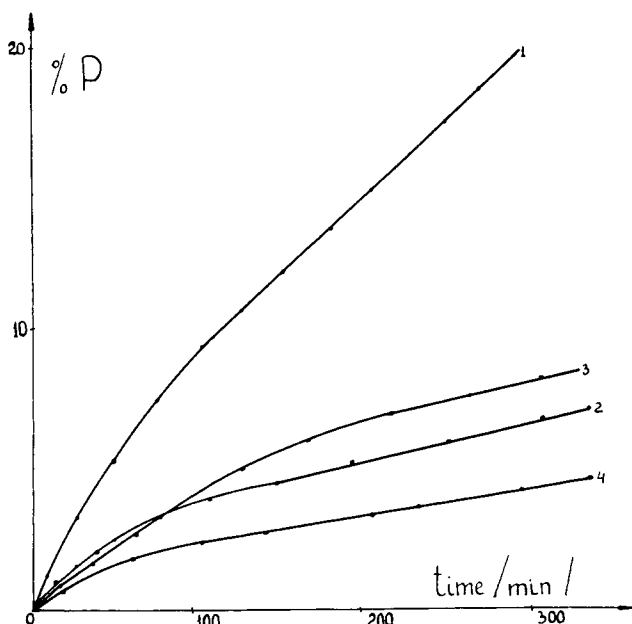
Fig. 6. The polymerization rate of 2-vinyl furan and 2-vinyl thiophene. (*1*) VT at 100°C. (*2*) VF at 100°C. (*3*) VT at 80°C. (*4*) VF at 80°C. 0.5 mole-% peroxide.
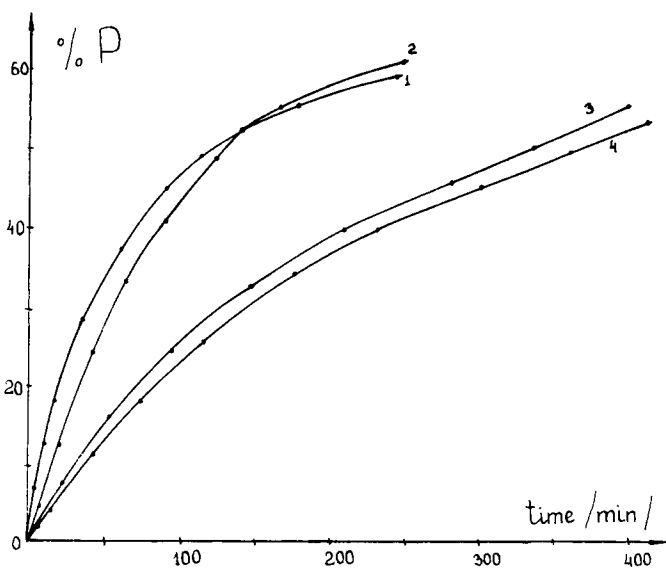

Fig. 7. Polymerization rate of 2-vinyl dibenzofuran and 2-vinyl benzothiophene. (*1*) VDBT at 100°C. (*2*) VDBF at 100°C. (*3*) VDBT at 80°C. (*4*) VDBF at 80°C. 0.5 mole-% peroxide; 1 *M* solution in toluene.

that the VT monomer is more reactive than the VF monomer, and under equal conditions it polymerizes twice as quickly as the latter (Fig. 6). The monomers VDBF and VDBT have the same tendency, the only difference being that the influence of the nature of the heteroatom is revealed much less distinctly (Fig. 7), as was observed before with pyridine and quinoline. The monomer studied form series according to their reactibility in polymerization: 2-vinyl dibenzfuran (thiophene) > 2-vinyl benzfuran > 2-vinyl furan (thiophene), and 2-vinyl thiophene > 2-vinyl furan.

Thus, the results of our investigations show that by increasing the number of condensed rings in the substituting radical of ethylene molecules, and by introducing heteroatoms (nitrogen, oxygen, sulfur) into them, we can heighten the ability of these compounds to polymerize.

References

1. P. P. Shorygin and N. V. Shorygina, *Zhur. Obhscheĭ Khim.*, **5,** 555 (1935); **9,** 845 (1939).

2. C. Marvel, *J. Am. Chem. Soc.*, **62,** 45 (1940); **66,** 475 (1944); **67,** 2250 (1945); **68,** 737, 1085, 1088, 1090, 2106 (1946); **70,** 1895 (1948).

3. R. Wiley, *J. Polymer Sci.*, **3,** 445 (1948); **5,** 483 (1950); *J. Am. Chem. Soc.*, **70,** 1560 (1948); **71,** 2429 (1949); **72,** 1822, 5198 (1950); **75,** 4519 (1953); **78,** 2169 (1956).

4. A. F. Dokukina, M. M. Koton, O. K. Mineyeva, and V. A. Paribok, *Zhur. Fiz. Khim.*, **30,** 190 (1956).

5. M. M. Koton, E. M. Moskvina, and F. S. Florinsky, *Zhur. Obshcheĭ Khim.*, **21,** 1847 (1951); **22,** 789 (1952); *Zhur. Priklad. Khim.*, **26,** 660, 666 (1953); *Doklady Akad. Nauk S.S.S.R.*, **102,** 305 (1955).

6. M. M. Koton and T. M. Kiseleva, *Doklady Akad. Nauk S.S.S.R.*, **88,** 465 (1953).

7. G. B. Bachman, and D. D. Micucci, *J. Am. Chem. Soc.*, **70,** 2381 (1948).

8. K. Winterfeld and C. Heinen, *Ann.*, **573,** 85 (1951).

9. I. V. Andreeva and M. M. Koton, *Doklady Akad. Nauk S.S.S.R.*, **110,** 75 (1956).

10. W. Carothers and J. Williams, *J. Am. Chem. Soc.*, **53,** 4214 (1931).

11. A. N. Pravednikov and S. S. Medvedev, *Doklady Akad. Nauk S.S.S.R.*, **103,** 461 (1955); **106,** 579 (1956).

12. D. Elliott, *J. Am. Chem. Soc.*, **73,** 754 (1951).

13. G. B. Bachmann and L. Heisey, *J. Am. Chem. Soc.*, **70,** 2378 (1948).

14. R. Flowers and L. Flowers, *J. Am. Chem. Soc.*, **71,** 3102 (1949); *U.S. Pat. 2,499,-187; Chem. Abstr.*, **44,** 5393 (1950).

15. M. M. Koton and O. K. Surnina, *Doklady Akad. Nauk S.S.S.R.*, **113,** 1063 (1957).

Synopsis

The polymerization of vinyl derivatives of naphthalene and of the heterocyclic series containing the atoms of nitrogen, oxygen, and sulfur has been investigated. It is proved that an increase in the number of condensed rings in the radicals replacing the hydrogen atoms in the ethylene molecule, as well as the introduction of heteroatoms (nitrogen, oxygen, sulfur) into these radicals increase the polymerization ability of the above compounds.

Résumé

La polymérisation de dérivés vinyliques du naphtalène et de hétérocycles contenant des atomes d'azote, d'oxygène et de soufre a été étudiée. Il a été prouvé qu'une augmentation du nombre des cycles remplaçant les atomes d'hydrogène dans la molécule d'éthylène, ainsi que l'introduction d'hétéroatomes (azote, oxygène, soufre) dans ces radicaux augmente la possibilité de polymérisation de ces composés.

Zusammenfassung

Die Polymerisation von Vinylderivaten des Naphthalins und von solchen von hetero-cyklischen Verbindungen, die Stickstoff-, Sauerstoff- und Schwefelatome enthalten, wurde untersucht. Es wird gezeigt, dass eine Zunahme der Zahl der kondensierten Ringe in den Radikalen, die die Wasserstoffatome der Äthylenmolekel ersetzen, ebenso wie die Einführung von Heteroatomen (Stickstoff, Sauerstoff, Schwefel) in diese Radikale die Polymerisationsfähigkeit der genannten Verbindungen erhöht.

Discussion

G. Hardy (*Budapest*): In our laboratory we have studied the reactivity of compli-cated vinyl esters in relation to the acid radical. In the course of this work the vinyl ester of furancarbonic acid was synthesized. This monomer could not be polymerized either with radical-type initiators or with ionic-type catalysts. Thus it is interesting to compare the increase in reactivity of 2-vinyl furan with the nonpolymerizable vinyl furancarbonate.

J. C. Bevington (*Birmingham*): Have the properties of these polymers been examined? The optical and photochemical properties might be particularly interesting.

M. M. Koton (*Leningrad*): We have also worked with furylacrylic acid and its esters and also noticed that they did not polymerize. In reply to Prof. Bevington's question: The polymers are transparent thermoplastic materials having various values of char-acteristic viscosity, softening temperatures, and dielectric properties.

K. J. Ivin (*Leeds*): Prof. Koton reports that vinyl decahydronaphthalene does not polymerize, even if heated for many hours at high temperature. I should like here to make the general point that an increase in temperature is generally unfavorable toward polymerization in the thermodynamic sense and that the rate of polymerization (for addi-tion polymerization) will fall to zero at the temperature (the ceiling temperature T_c) at which the free energy of polymerization has fallen to zero (under the particular con-centration conditions used in the experiment).
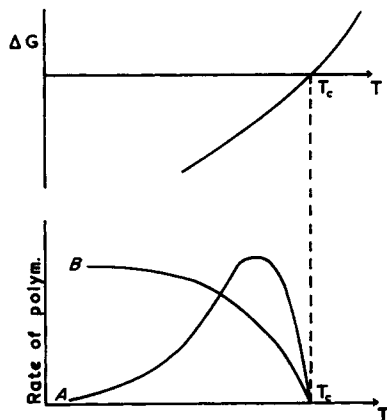
(*A*) Catalytic initiation. (*B*) Photochemical initiation.

In the case of vinyl decahydronaphthalene, it is unlikely that it will polymerize by free radicals at low temperature even if thermodynamically possible (for reasons given by Prof. Smets in a comment following my paper). However, the above considerations should be borne in mind when testing a compound for polymerizability, and a wide range of temperature, particularly below room temperature, should be tried.

M. M. Koton: I can say that we carried out the experiments over a wide temperature

range and that we calculated the activation energy. There is a great difference here. For vinyl furan it is 17 kcal./mole; for vinyl dibenzofurans, 12 kcal./mole. Even this is an indication of the polymerization tendency, to say nothing of the circumstance that the experiments were carried out in a wide range of 0–100°, in the presence not only of radical but also ionic catalysts.

G. Smets (*Louvain*): Have some determinations been carried out concerning the kinetics of polymerization of vinyl decaline? Does this compound behave "normally" with respect to the concentration of the initiator, *i.e.*, is the rate of polymerization proportional to the square root of the concentration of initiator?

M. M. Koton: We intended to elucidate why the vinyl derivatives of polynuclear hydrocarbons polymerize extraordinarily easily. Vinyl phenanthrene and vinyl anthracene cannot even be successfully isolated since they polymerize immediately during the dehydration of the corresponding carbinols. We therefore synthesized a series of hydrocarbons in which the vinyl group was conjugated with a larger or smaller number of double bonds. The polymerizations were carried out in a certain temperature range under the same conditions (without an initiator). I do not state that vinyl decalin does not polymerize, but only that under these conditions vinyl decalin did not show any sign of polymerization. Vinyl tetralin polymerized distinctly, and α- and β-vinyl naphthalenes particularly easily.

G. Smets: It is not correct to compare the polymerization rates if the kinetics of the polymerizations compared are not the same. In vinyl decaline there is an "allylic" hydrogen present and all the allylic monomers are different from the kinetic point of view, from, let us say, aromatic vinyl derivatives, (styrene, etc.).

A. L. Klebanskii (*Moscow*): I agree with Prof. Smets that the reason for the decrease in the polymerization rate of vinyl decaline might be the presence of the active α-methylene hydrogen in this compound which is absent in aromatic derivatives.

O. F. Solomon (*Bucharest*): I am not surprised by the polymerization tendency of the compounds investigated by Prof. Koton since we ourselves have carried out interesting experiments with vinyl-furans. When comparing their polymerization with other heterocyclic vinyl derivatives we investigated also the polymerization of chlorovinyl furan. Whether the conjugated compounds can or cannot be polymerized catalytically was proved by me in 1954 for cyclooctatetraene which polymerizes by Na in liquid ammonia and yields a polymer of a similar molecular weight as vinyl furan and chlorvinyl furan.