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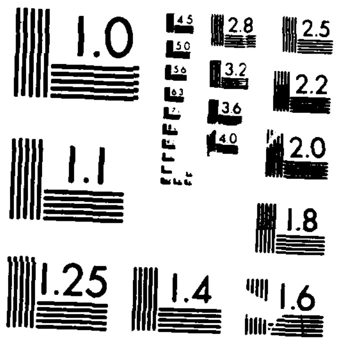

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FOREIGN TECHNOLOGY DIVISION

HIGH-MOLECULAR COMPOUNDS

(Selected Articles)

PARTIALLY EDITED MACHINE TRANSLATION

FTD-ID(RS)T-0881-87 9 October 1987

MICROFICHE NR: FTD-87-C-000905

HIGH-MOLECULAR COMPOUNDS (Selected Articles)

English pages: 14

Source: Vysokomolekulyarnyye Soyedineniya, Seriya B,
Kratkiye Soobshcheniya, Vol. 10, Nr. 1,
January 1968, pp. 6-8; 57-60

Country of origin: USSR
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Incorrect word/phrase: ____

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Foreign page numbers occur in the English text and may be found anywhere along the left margin of the page as in this example:

In them occurs the state named "night blindness" - hemeralopia, which, according to the current point of view, is a result of damage of the rod-shaped apparatus of the eye.

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However, in recent years it has been shown that with the hereditary pigment degenerations in animals the biochemical changes are observed in all celluar elements of the retina.

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А а	*А а*	A, a	Р р	*Р р*	R, r
Б б	*Б б*	B, b	С с	*С с*	S, s
В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
Ж ж	*Ж ж*	Zh, zh	Ц ц	*Ц ц*	Ts, ts
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К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
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М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

*ye initially, after vowels, and after ъ, ь; e elsewhere.
When written as ё in Russian, transliterate as yё or ё.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	$\sinh^{-1}$
cos	cos	ch	cosh	arc ch	$\cosh^{-1}$
tg	tan	th	tanh	arc th	$\tanh^{-1}$
ctg	cot	cth	coth	arc cth	$\coth^{-1}$
sec	sec	sch	sech	arc sch	sech^{-1}
cosec	csc	csch	csch	arc csch	csch^{-1}

Russian	English
rot	curl
lg	log

GRAPHICS DISCLAIMER

All figures, graphics, tables, equations, etc. merged into this translation were extracted from the best quality copy available.

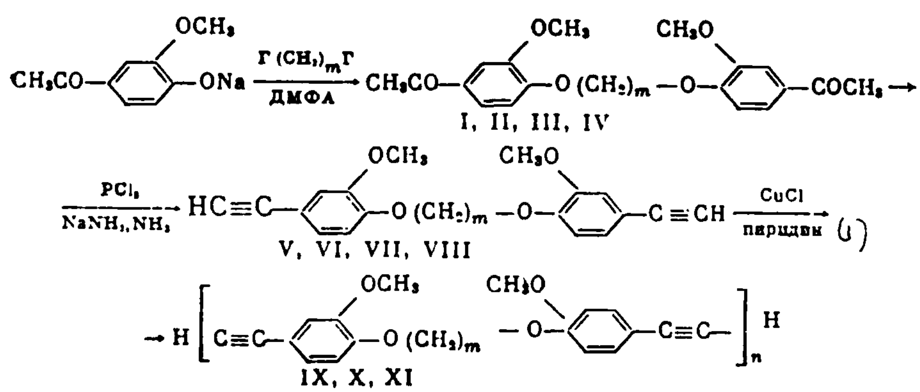
Page 6.

SYNTHESIS AND POLYCONDENSATION OF SOME ACETYLENE POLYESTERS.

T. G. Shishmakova, M. I. Bardamova, Z. P. Trotsenko, I. L. Kotlyarevskiy.

Electric and magnetic properties of oligomers of type $H[C\equiv C-Ar-C\equiv C]_nH$ depend on structure of arylene part of Ar - basic link of oligomer. The introduction of the aliphatic chain/network between the aromatic nuclei in the arylene part interrupts/breaks conjugation, and oligomer acquires dielectric properties. In this case their solubility plays especially large role, since the possibility of obtaining of them the films is determined. Therefore for increasing the solubility and for the break of conjugation we introduced alkoxyl groups into diethynylarenes, it is analogous how hydroxide groups were previously introduced into monoethynylarenes [1, 2].

All transformations are carried out according to overall diagram:



I, V, IX — $m=1$; II, VI — $m=2$; III, VII, X — $m=3$; IV, VIII, XI — $m=4$

Key: (1). pyridine.

Diketones I-IV are formed with good output/yield during condensation of sodium phenolate of 2-methoxy-4-acetylphenol with α, ω-dihaloidalkyls in dimethyl formamide (DMFA). The sequential effect/action on the diketones of phosphorus pentachloride and amide of sodium obtained acetylenes V-VIII, moreover V and VIII are obtained with the satisfactory output/yield, VI and VII - with the low.

Polycondensation, carried out by oxidation of diacetylenes by oxygen in presence of cuprous chloride in pyridine solution, leads to formation of oligomers with quantitative output/yield. Diacetylene VI as a result of a small solubility does not enter into the oxidative polycondensation under these conditions.

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All oligomers are yellowish powders, soluble in series/number of organic solvents (dioxane, DMFA, tetrahydrofuran, cyclohexanone, anisole). IX during the deposition on the glass in the form of the solution in the chloroform, carbon tetrachloride and dioxane and subsequent solvent elimination clear sheet is formed, whereas X and XI settle in the form of powders. During the heating the oligomers are melted, while with further increase in the temperature they darken and harden as a result of cross-linking due to the disclosure/expansion of triple bonds.

In IR-spectrum I-XI are strips, characteristic for all basic atomic groups.

Measurement of molecular weights by method of isothermal distillation of solvent does not succeed as a result of high boiling point of cyclohexanone, in which it is possible to obtain sufficiently concentrated solutions of polymers. Because of this for the approximate estimation of molecular weight of oligomers was used the comparison of the intensity of the absorption bands of terminal acetylene hydrogen in the IR-spectrum of monomers and polymers, taken/removed in the identical conditions as this was earlier made in the work of Japanese chemists [3]. Value n, determined by this method, is equal to 10 for XI, 5 - for X and XI.

Experimental part.

Ketones I-IV are obtained according to described by Japanese authors method [4]. 10 g of 2-methoxy-4-acetylphenol is mixed with the methanol solution 2.41 g NaOH and after the removal/distance of methanol are boiled 3 hours in 50 ml DMFA with 8.07 g CH_2J_2 and 20-30 mg KJ, they pour out into the water, they filter precipitate and they wash in water. Output/yield I 67.6%, melting point of 153-154° (from acetone). It is found, %: C 66.41; H 6.19. $C_{19}H_{20}O_6$. It is calculated, %: C 66.27; H 5.85.

It is analogous from 2-methoxy-4-acetylphenol even 1, 2-dibromoethane is obtained by II, output/yield 44%, melting point of

162-163° (from acetone). It is found, %: C 67.07; H 6.32. $C_{20}H_{22}O_6$. It is calculated, %: C67.02; H 6.19.

From 2-methoxy-4-acetylphenol even 1, 3-dibromopropane is obtained by III, output/yield 82.35% melting point of 121-122° (from acetone). It is found, %: C 67,68; H 6.52. $C_{21}H_{24}O_6$. It is calculated, %: C 67.73; H 6.50.

From 2-methoxy-4-acetylphenol even 1, 4-dibromobutane is synthesized IV, output/yield 92.6%, melting point of 156° (from acetone). It is found, %: C 68.21; H 7.02. $C_{22}H_{26}O_6$. It is calculated, %: C 68.38; H 6.78.

Diacetylene V. The mixture 3 g of diketone I, 50 ml of benzene and 8.1 g PCl_5 is boiled before the dissolution of precipitate, solution in 35 min. is introduced into sodium amide in liquid ammonia (of 8.5 g Na and 500 ml NH_3), are added 100 ml of benzene and 450 ml of ether/ester, mixed 3 hours, is removed ammonia and they mix already 2.5 hours at 20°. Decompose/expand 20 g NH_4Cl, organic layer wash in water and after the distillation/removal of solvents separate/liberate diacetylene V; output/yield 58.2%, melting point of 126° (from methanol). It is found, %: C 74.14; H 5.46. $C_{19}H_{16}O_4$. It is calculated, %: C 74.01; H 5.23.

Diacetylene VI. The mixture of chlorides, obtained during boiling 5.91 g of diketone II, 15.5 g PCl_5 and 60 ml of benzene, in 20 minutes introduce into suspension $NaNH_2$ in liquid ammonia (of 15.5 g Na and 700 ml NH_3), add 150 ml of benzene, vaporize ammonia and after addition 400 additional ml of benzene are mixed 6 hours at 20° and 5 hours at 50°; they decompose/expand 36 g NH_4Cl, they wash in water, they remove benzene and separate/liberate diacetylene VI with output/yield 10.6%, melting point of 225-227° (from dioxane). It is found, %: C 74.36; H 5.88. $C_{20}H_{18}O_4$. It is calculated, %: C 74.52; H 5.63.

Diacetylenes VII and VIII are obtained analogously with V (they mix at 20° 7 hours). VII: melting point of 112-113° (chromatography in ether/ester), output/yield 21%. It is found, %: C 75.25; H 5.96%. $C_{21}H_{20}O_4$. It is calculated, %: C 74.98; H 5.99. VIII: melting point of 189-190° (from dioxane), output/yield 30.5%. It is found, %: C 76.63; H 6.48. $C_{22}H_{22}O_4$. It is calculated, %: C 75.41, H 6.33.

Oligomers IX-XI. 0.6 g of diacetylene V, 20 ml of pyridine and 0.1 g CuCl shake in the atmosphere of oxygen before the absorption of the calculated quantity of gas, pour out into the water, wash clean precipitate from Cu^+ and Cl^-, is obtained oligomer IX with quantitative output/yield, melting point 150-160°. It is found, %: C 75.48; H 5.68. $C_{105}H_{92}O_{20}$. It is calculated, %: and harden. It is found, %: C 74.00; H 4.96. $C_{190}H_{142}O_{40}$. It is calculated, %: C 74.45; H 4.67, oligomer X is obtained in presence 0.1 ml of tetramethylenediamine with the quantitative output/yield, melting point of 150-160°. It is found, %: C 75.48; H 5.68. $C_{105}H_{92}O_{20}$. It is calculated, %: C 75.34; H 5.54. Analogously IX is obtained oligomer XI with quantitative output/yield, melting point ~200°. It is found, %: C 74.10; H 7.01. $C_{110}H_{102}O_{20}$. Calculated, %: C 75.80; H 5.90.

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Conclusions.

During introduction of methoxy groups to benzene nuclei of oligomers, which are obtained by oxidative polycondensation α, ω-bis-(ethynylphenylhydroxy) alkanes, solubility of oligomers strongly is increased.

Institute of chemical kinetics and SO AN SSSR [- Siberian Department of the Academy of Sciences of the USSR] burning.

It was received by the editorial staff 7 JULY 1966.

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CONNECTION OF REACTIVITY OF VINYLPYRIDINES WITH THEIR STRUCTURE DURING COPOLYMERIZATION IN ACETIC ACID.

Yu. D. Semchikov, A. V. Ryabov, V. N. Kashayeva.

Previously we showed that during homogeneous radical copolymerization of some monomers of addition of substances, which generate hydrogen bonds with one of monomers, they influence values of constants of relative activities [1, 2]. In the present work the data about the effect of acetic acid on the homogeneous radical copolymerization of vinylpyridines (VP) of different structure with styrene (St) and methylmethacrylate (MMA) are cited. For investigation were selected the 2-vinylpyridine (2VP), 4-vinylpyridine (4VP) and 5-vinyl-2-methylpyridine (5V2MP), were studied kinetics of their copolymerization, and also composition of the forming copolymers. According to the data about the composition by Joshi-Kapoor method through five points are found relative activities of monomers. The obtained values, which correspond to copolymerization of VP with MMA and with St in the mass and in acetic acid, are given in Table 1.

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Acetic acid was taken in a quantity of 2 moles to 1 mole VP. Using values of r_1 and r_2, we determined graphically parameters Q, e of vinylpyridines, which characterize them at copolymerization in the mass and acetic acid. These data are cited in Table 2.

From Table 1 it follows that acetic acid dissimilarly influences copolymerization of VP of different structure. In all cases, except the latter the introduction of acetic acid leads to the decrease of values r_1 and r_2, and also $r_1 \cdot r_2$. However, this fact is much more brightly expressed for 4VP or 2VP, than for 5V2MP. Thus, acetic acid causes in the system St - 4VP decrease $r_1 \cdot r_2$ 25 times in comparison with the copolymerization in the mass, in the system St - 2VP - 14 times, and in the system St - 5V2MP - only 1.8 times. This attests to the fact that acetic acid very considerably raises tendency toward alternating of structural links St 2VP or 4VP and only several - 5V2MP. From Table 2 it follows that acetic acid causes the significant positive polarization of double bond 2VP and 4VP (from -0.7 to +1.3) and only insignificantly is changed the state of double bond 5V2MP. The so/such differentiated effect/action of acetic acid on VP of different structure can be explained by different polarization of the atoms of urethane of pyride ring. With the formation of the hydrogen bond of acetic acid with the pyridine or VP as a result of the reaction of proton with the unshared vapor of nitrogen the latter acquires a certain positive charge, which leads to the polarization of entire aromatic ring. Let us examine the possible results of polarization on the structures of Kekule and D'yuar, by which the real pyridine is described.

Table 1. Values r_1, r_2 and $r_1 \cdot r_2$ the corresponding copolymerizations of vinylpyridines with styrene and methylmethacrylate in mass and acetic acid (Temperature of 22°, 1% of dicyclohexylperoxydicarbonate, M_2+VP).

Мономеры (1)	Условия сополимеризации (2)	r_1	r_2	$r_1 \cdot r_2$
Ст — 4ВП	В массе (3)	0,78±0,02	1,1 ±0,03	0,857
	В CH_3COOH	0,1 ±0,04	0,34±0,03	0,034
ММА — 4ВП	В массе (3)	0,42±0,07	0,65±0,06	0,27
	В CH_3COOH	0,24+0,06	0,55±0,07	0.132
Ст — 2ВП	В массе (3)	0,57±0,04	1,33±0,08	0,76
	В CH_3COOH	0,16±0,04	0,33±0,07	0,053
ММА — 2ВП	В массе (3)	0,48±0,03	0,68±0,04	0,33
	В CH_3COOH	0,43±0,08	0,30±0,06	0,130
Ст — 5В2МП	В массе (3)	0,88±0,03	1,1 ±0,02	0,97
	В CH_3COOH	0,73±0,04	0,76±0,03	0,55
ММА — 5В2МП	В массе (3)	0,42±0,05	0,58±0,06	0,25
	В CH_3COOH	0,47±0,05	0,75±0,06	0,35

Key: (1). Monomers. (2). Conditions of copolymerization. (3). In mass.

Table 2. Values Q, e of vinylpyridines and their complexes with acetic acid.

Мономер (1)	Условия сополимеризации (2)	e	Q
4ВП	В массе (3)	—0,72	1,12
	В CH_3COOH	1,35	3,1
2ВП	В массе (3)	—0,7	1,35
	В CH_3COOH	1,3	1,80
5В2МП	В массе (3)	—0,8	1,1
	В CH_3COOH	—0,2	1,0

Key: (1). Monomer. (2). Conditions of copolymerization. (3). In mass.

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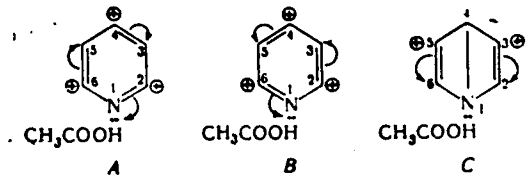
Kekule's structures (A, B), statistical weight of which in the real pyridine reaches 78% [3], they indicate



the presence of equal charge in the para- and orthopositions, and only the structure of Dewar flask (C), to which is 7%, it indicates the possibility of the appearance of a charge in the meta position. If double bond will be connected in the ortho-(2VP) or para-(4VP) position with respect to nitrogen, then it will be polarized to a considerable degree positively, if in the meta position (5V2MP), then weakly.

From preceding it becomes obvious, that 2VP and 4VP must have close reactivity in acetic acid, since it exerts identical polarizing effect/action on double bonds of both monomers (Table 2). However, in the processes of copolymerization and polymerization these monomers show a deep difference.

Thus, from Table 1 it follows that acetic acid causes in system St - 4VP decrease r_1 7.8 times, in system St - 2VP - altogether only 3.5 times. Since $r_1 = k_{11} / k_{12}$ and k_{11} (m_1-St) acetic acid does not influence, it is possible to conclude that complex 4VP - acetic acid interacts with the polystyrene radical 2 times more active than complex 2VP - acetic acid.

Acetic acid accelerates radical homogeneous copolymerization of equimolar mixtures St - 4VP and retards it in the case St - 2VP (Fig. 1). Acetic acid also accelerates radical polymerization 4VP and retards polymerization 2VP (Fig. 2).

Presented facts attest to the fact that complex 2VP - acetic acid is less reactive than complex 4VP - acetic acid; this can be explained by special features of stereoximi of both monomers. It is known that in the pyridine the unshared vapor of nitrogen occupies sp^2 trigonal orbit and is located in one plane with two bonds σ of nitrogen at angle of 120° to them. From this it follows that into 2VP the electron cloud of the unshared vapor elongated in the direction, parallel to the direction of its double bond, and it is located in one plane with the molecule 2VP. With the formation of hydrogen bond three atoms, by it connected (in our case $-O-H\ldots N\langle$), predominantly attempt to be arranged on one line [4]. Upon the achievement of a maximally possible value of energy of hydrogen bond this line coincides with the axis of orbit sp^2 of the electron cloud of the unshared vapor. From the diagram it is not difficult to see that with three-dimensional/space arrangement of complexer in accordance with these requirements is probable the shielding of double bond 2VP that, obviously, will lower its reactivity.

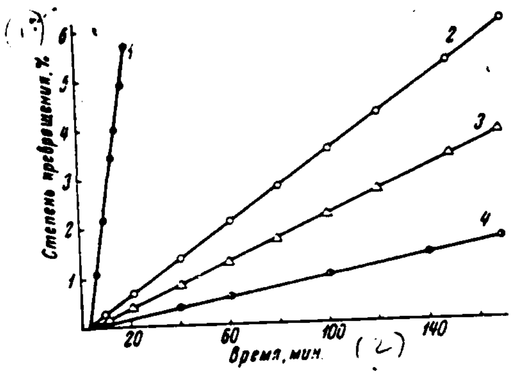


Fig. 1.

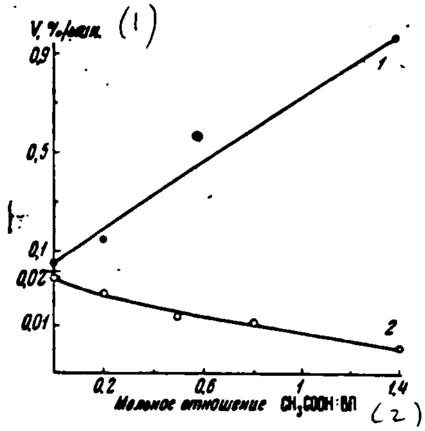


Fig. 2.

Fig. 1. Kinetics of copolymerization of equimolar mixtures 4VP and 2VP with St in mass and in acetic acid at 22° and in presence 1 wt.% of dicyclohexylperoxydicarbonate 1, 2 - St - 4VP; 3, 4 - St - 2VP; 1, 4 - in CH_3COOH; 2, 3 - in mass.

Key: (1). Degree of transformation. (2). Time, min.

Fig. 2. Dependence of speeds of polymerization 4VP (1) and 2VP (2) on quantity CH_3COOH temperature - 22°, initiator - 1 wt.% of dicyclohexylperoxydicarbonate.

Key: (1). min. (2). Molar relation.

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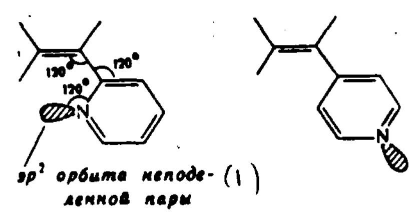
During the rotation of the plane of substituent on 180° steric difficulties during the reaction of the compound vinylpyridine radical become obvious.



2 ВП 4 ВП

Key: (1). orbit of the unshared vapor.

Increase in parameter Q 4VP and 2VP at copolymerization in acetic acid focuses attention, which, probably, testifies about additional stabilization of vinylpyridine radicals under these conditions.

Experimental part.

Vinylpyridines were dried by granulated KOH and they purified by double vacuum distillation. 2VP: boiling point 67-69°/20 mm, n_D^{20} 1.5491; 4VP: boiling point 65°/15 mm, n_D^{20} 1,5532; 5V2MP; boiling point 75°/15 mm, n_D^{20} 1,5454. Styrene was dried $CaCl_2$ and they purified analogously; boiling point 44°/20 mm, n_D^{20} 1,5462. MMA dried $CaCl_2$ and they distilled at the atmospheric pressure: boiling point of 99.8°, n_D^{20} 1,4135. Acetic acid - ice, initiator - dicyclohexylperoxydicarbonate, the temperature of polymerization of 22°. Monomeric mixtures degassed. The procedure of cleaning/decontamination and analysis of copolymer is analogous given earlier than [2].

Conclusions.

1. Effect of acetic acid on homogeneous radical copolymerization of 2-vinylpyridine, 4-vinylpyridine, 5-vinyl-2-methylpyridine with methylmethacrylate and styrene is investigated.

2. Acetic acid produces change in values of relative activities, and also parameters Q, e of vinylpyridines. The explanation of the observed effects is given.

Scientific research institute of chemistry with the Gor'kiy university.

It was received by the editorial staff 31 Jan. 1967.

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