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АЛКИЛИРОВАНИЕ 3(5)-МЕТИЛПИРАЗОЛА ПРОПАРГИЛ БРОМИДОМ И ИЗУЧЕНИЕ ТЕРМИЧЕСКОЙ И КАТАЛИТИЧЕСКОЙ ПОЛИМЕРИЗАЦИЙ ПОЛУЧЕННЫХ ПРОДУКТОВ

А.А. Сукоян, Л.А. Бичахчян, Т.Г. Мовсисян, А.Г. Шахатуни, Р.М. Акопян, О.С. Аттарян

Астхик Акоповна Сукоян (ORCID 0009-0002-9266-3591), Лилит Ашотовна Бичахчян (ORCID 0000-0002-8713-3724)*, Татевик Гарегиновна Мовсисян (ORCID 0009-0007-5579-3932), Роберт Мамиконович Акопян (ORCID 0000-0002-4318-3172), Оганес Саркисович Аттарян (ORCID 0000-0001-9790-2577)

Лаборатория проблем прикладной химии Института органической химии Научно-технологического центра органической и фармацевтической химии, пр. Азатутян, 26, Ереван, Республика Армения, 0014
E-mail: astghik.sukoyan@gmail.com, lilitbichakhchyan@mail.ru*, tatevikmovsisyan86@gmail.com, robahakob@gmail.com, hovelenatt@mail.ru

Алексан Геворкович Шахатуни (ORCID 0000-0002-2506-1091)

Лаборатория ядерного магнитного резонанса Центра исследований строения молекулы Научно-технологического центра органической и фармацевтической химии, пр. Азатутян, 26, Ереван, Республика Армения, 0014
E-mail: shahkhatuni@gmail.com

Известно, что почти все реакции с атомом азота 3(5)-метил пиразола неизбежно приводят к образованию N-замещенных 3-метил и 5-метил пиразолов. Это касается также 1-пропаргил 3(5)-метил пиразола. В данной работе нам удалось разделить эти изомеры и идентифицировать их методами ^{1}H и ^{13}C ЯМР спектроскопии. С целью синтеза индивидуальных изомеров 3-метил-1-(проп-2-ил)-1H- и 5-метил-1-(проп-2-ил)-1H-пиразолов нами было изучено алкилирование 3(5)-метил пиразола пропаргил бромидом в условиях межфазного катализа в системе жидкость-жидкость изопропиловый спирт-вода при температуре 0-5° С, что обеспечивает 75-80% выход пропаргил пиразолов. Нам впервые удалось идентифицировать полученные изомеры. В продуктах алкилирования всегда преобладает 3-метил изомер, но это не затрудняет их разделение. Представлялось интересным выявить влияние местоположения метильной группы пиразольного кольца в процессах термической и каталитической полимеризации. Данные, полученные при термической полимеризации отдельных изомеров, показали, что изомер, где метильный заместитель находится в третьем положении пиразольного кольца, при температуре 120-130 °С за 20 ч практически не полимеризуется, тогда как у изомера, в котором метильный заместитель находится в пятом положении пиразольного кольца, выход при полимеризации пиразолов составляет 40,0%. Совершенно иная картина наблюдается при каталитической полимеризации. Так, при температуре 120-130 °С за 20 ч в присутствии каталитического количества $PdCl_2$ оба изомера полимеризуются на 50,0%. Так как при алкилировании 3(5)-метилпиразола получаем смеси изомеров-3-метил-1-(проп-2-ил)-1H-пиразол (2а) и 5-метил-1-(проп-2-ил)-1H-пиразол (2б), целесообразно изучать их поведение при термической и каталитической полимеризации совместно. Результаты термической полимеризации показали, что 3-метил-1-(проп-2-ил)-1H-пиразол (2а)-изомер почти полностью подавляет процесс полимеризации, и выход полимера составляет лишь 8,0%, а в присутствии $PdCl_2$ при полимеризации смеси изомеров 3(5)-метил-1-(проп-2-ил)-1H-пиразол (2а, 2б) выход полимера составляет ~40%. Термогравиметрический анализ (ТГА) полученных полимеров проводился в условиях динамического нагревания и показано, что интенсивная потерия массы образцов 3, 4 и 5 начинается при температуре около 195 °С, 200 °С и 215 °С соответственно. Значения удельной электропроводности полипропаргил пиразолов (10^{-3}- 10^{-5} $Ом^{-1}. см^{-1}$) указывают на то, что они могут найти применение в качестве органических полимерных полупроводников.

Ключевые слова: алкилирование, пропаргилбромид, полимеризация, 3(5)-метилпиразол

ALKYLATION OF 3(5)-METHYLPYRAZOLE WITH PROPARGYL BROMIDE AND STUDY OF THERMAL AND CATALYTIC POLYMERIZATION OF THE PRODUCTS OBTAINED

A.H. Sukoyan, L.A. Bichakhchyan, T.G. Movsisyan, A.G. Shakhatuni, R.M. Hakobyan, O.S. Attaryan

Astghik H. Sukoyan (ORCID 0009-0002-9266-3591), Lilit A. Bichakhchyan* (ORCID 0000-0002-8713-3724), Tatevik G. Movsisyan (ORCID 0009-0007-5579-3932), Robert M. Hakobyan (ORCID 0000-0002-4318-3172), Hovhannes S. Attaryan (ORCID 0000-0001-9790-2577)

Laboratory of Applied Chemistry Problems, Institute of Organic Chemistry, Scientific and Technological Center for Organic and Pharmaceutical Chemistry, Azatutyan ave., 26, Yerevan, Republic of Armenia, 0014
E-mail: astghik.sukoyan@gmail.com, lilitbichakhchyan@mail.ru*, tatevikmovsisyan86@gmail.com, robahakob@gmail.com, hovelenatt@mail.ru

Aleksan G. Shakhatuni (ORCID 0000-0002-2506-1091)

Laboratory of Nuclear Magnetic Resonance, Center for Research on the Structure of the Molecule, Scientific and Technological Center for Organic and Pharmaceutical Chemistry, Azatutyan ave., 26, Yerevan, Republic of Armenia, 0014
E-mail: shahkhatuni@gmail.com

It is known that almost all reactions involving the nitrogen atom of 3(5)-methylpyrazole inevitably lead to the formation of N-substituted 3-methyl and 5-methyl pyrazoles. This also applies to 1-propargyl 3(5)-methylpyrazole. In this work, we succeeded in separating these isomers from each other and identifying them using ^{1}H and ^{13}C NMR spectroscopy methods. To synthesize individual isomers of 3-methyl-1-(prop-2-yl)-1H- and 5-methyl-1-(prop-2-yl)-1H-pyrazoles, we studied the alkylation of 3(5)-methylpyrazole with propargyl bromide under conditions of interphase catalysis in a liquid-liquid system of isopropyl alcohol-water at a temperature of 0-5°C, which provides a 75-80% yield of propargyl pyrazoles. For the first time, we were able to identify the obtained isomers. In the alkylation products, the 3-methyl isomer always predominates, but this does not complicate their separation from each other. It was of interest to determine the influence of the position of the methyl group in the pyrazole ring during the process of thermal catalytic polymerization. The data obtained from the thermal polymerization of the individual isomers showed that the isomer with the methyl substituent in the third position of the pyrazole ring does not polymerize practically at a temperature of 120-130 °C over 20 h, whereas the isomer with the methyl substituent in the fifth position of the pyrazole ring has a yield of 40.0% in the polymerization of pyrazoles. A completely different picture is observed during catalytic polymerization. At a temperature of 120-130 °C over 20 h, in the presence of a catalytic amount of $PdCl_2$, both isomers polymerize at a rate of 50.0%. Since the alkylation of 3(5)-methylpyrazole yields mixtures of the 3-methyl-1(prop-2-yl)-1H-pyrazole (2a) and 5-methyl-1(prop-2-yl)-1H-pyrazole (2b) isomers, it is advisable to study their behavior during thermal and catalytic polymerizations together. The results of thermal polymerization showed that the 3-methyl-1(prop-2-yl)-1H-pyrazole (2a) isomer almost completely suppresses the polymerization process, with a polymer yield of only 8.0%, and in the presence of $PdCl_2$ during polymerization of a 3(5)-methyl-1-(prop-2-yl)-1H-pyrazole (2a, 2b) isomer mixture, the polymer yield is ~40%. Thermogravimetric analysis (TGA) of the obtained polymers was carried out under dynamic heating conditions and it was shown that intensive weight loss of samples 3, 4 and 5 begins at a temperature of about 195 °C, 200 °C and 215 °C, respectively. The specific conductivity values of polypropargyl pyrazoles (10^{-3}-10^{-5} $Ohm^{-1}.cm^{-1}$) indicate that they can find application as organic polymer semiconductors.

Keywords: alkylation, propargyl bromide, polymerization, 3(5)-methylpyrazole

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INTRODUCTION

All reactions involving the nitrogen atom of 3(5)-methylpyrazole inevitably lead to the simultaneous formation of N-substituted 3-methyl and 5-methyl isomers, due to the tautomerism present in 3(5)-methylpyrazole.

Only in cases where the mobile hydrogen on nitrogen is replaced by relatively less mobile substituents is it possible to separate and identify these isomers.

With the aim of synthesizing individual isomers of 3-methyl- and 5-methyl-1-propargyl pyrazoles, we studied the alkylation of 3(5)-methylpyrazole **(1)** with propargyl bromide under phase-transfer catalysis (PTC) conditions and the subsequent separation of the resulting isomers by rectification.

The task of this work, namely the separation of the resulting isomeric products of alkylation, was successfully solved by alkylation of 3(5)-methylpyrazole **(1)** with propargyl bromide in the presence of phase transfer catalysts (benzyltriethylammonium chloride, TEBAC) at a temperature of 0-5 °C to exclude the formation of 1-allenyl-3(5)-methylpyrazoles.

Polymerization of 3(5)-methyl-1-(prop-2-yl)-1H-pyrazole, as well as individual isomers of 3-methyl-1-(prop-2-yl)-1H and 5-methyl-1-(prop-2-yl)-1H-pyrazoles was carried out at a temperature of 120-130 °C, in the catalytic presence of $PdCl_2$.

From the obtained data it is easy to see that the isomer with a methyl group in position **5** in the ring exhibits greater activity in the process of thermal polymerization.

The obtained polypropargylpyrazoles are powders from dark brown to black colors, well soluble in many solvents (acetone, chloroform, DMF). They exhibit a specific electrical conductivity in the range of $2.2\text{-}2.4\cdot10^{-4}$ $Ohm^{-1}\cdot cm^{-1}$.

EXPERIMENTAL PROCEDURE

Alkylation of 3(5)-methylpyrazole with propargyl pyrazole was carried out under PTC conditions in the presence of isopropyl alcohol: water solution. The separation of the obtained isomers was done by the rectification method. The composition and structure of the synthesized isomers have been proven by NMR and IR spectroscopy methods and confirmed by elemental analysis data. Polymerization of individual isomers and their mixtures was carried out in the presence of a catalytic amount of $PdCl_2$ and thermally at a temperature of 120-130 °C. Thermal properties of the polymers were studied, as well as electrical conductivity of the obtained polymers.

EXPERIMENTAL PART

3(5)-methyl-1-(prop-2-yn-1-yl)-1H-pyrazole (2a, b)

a) A mixture of 16.4 g (0.2 mol) of 3(5)-methylpyrazole, 12.0 g (0.3 mol) of sodium hydroxide, 2.0 g of TEBAC, 5 ml of water and 60 ml of isopropyl alcohol was stirred under reflux at 25 °C for 30 min. After cooling to 5 °C, 22.8 ml (0.3 mol) of propargyl bromide were added dropwise to the reaction mixture. The mixture was stirred for 2 h. The reaction mixture was filtered, the resulting precipitate was washed with methylene chloride and left overnight. After removing the solvent and isopropyl alcohol, the residue was distilled under reduced pressure. Yield 20.2 g (84.0%), b. p. 85-90 °C/15 mm Hg, n_D^{20} 1.500. IR spectrum, υ, cm^{-1}: 1526 (ring), 2124 (C≡C). Found, %: C 67.95; H 5.84; N 26.58; $C_7H_8N_2$. Calculated, %: C 67.90; H 5.70; N 26.40.

b) The result is similar to the previous example, with the difference that 22.8g (0.3 mol) of propargyl bromide was added directly. Yield 18.2 g (75.8%).

c) It is analogous to the first example, with the difference that after adding 22.8 g (0.3 mol) of propargyl bromide, stirring was continued for 1 h. Yield 17.5 g (73.0%).

To separate the mixture of isomers, a reactivation column 30 cm long, 4 cm in diameter, filled with a ceramic packing (0.5×0.1 cm) was used. The top temperature is 70-72 °C, and the temperature of the cube is 94 °C, and the pressure is 3 mm Hg. R = 10 (reflux ratio). 100 g of the mixture of 1-propargyl-3(5)-methylpyrazole isomers are loaded into the cube, the ratio is 3Me:5Me-3:1, respectively. After separation, it was obtained:

a) **3-methyl-1-(prop-2-in-1-yl)-1H-pyrazole (2a)** (25.0g), b. p. 75 °C/10mm Hg, n_D^{20} 1.4906, purity according to ^{1}H NMR spectrum - 98.3%. ^{1}H NMR spectrum (400 MHz, DMSO-d_6/CCl_4/1:3), δ, ppm, Hz: 2.21s (3H, 3-CH_3), 2.90t (1H, *J* = 2.6, C≡CH), 4 .84d (2H, *J* = 2.6, N-CH_2), 5.97d (1H, *J* = 2.2, 4-H), 7.49d (1H, *J* = 2.2, 5-H). ^{13}C NMR spectrum (100 MHz, DMSO-d_6/CCl_4/1:3), δ, ppm: 12.96; 40.25; 74.84; 77.48; 104.74; 128.97; 147.34.

b) **5-methyl-1-(prop-2-in-1-yl)-1H-pyrazole (2b)** (10.0g), b. p. 80 °C /10 mm Hg, n_D^{20} 1.5040, purity according to ^{1}H NMR spectrum – 98 %. ^{1}H NMR spectrum (400 MHz, DMSO - d_6/CCl_4/1:3), δ, ppm, Hz: 2.39s (3H, 5-CH_3), 2.85t (1H, *J* = 2.6, C≡CH), 4.84d (2H, *J* = 2.6, N-CH_2), 5.97d (1H, *J* = 2.2, 4-H), 7.20d (1H, *J* = 2.2, 3-H). ^{13}C NMR spectrum (100 MHz, DMSO-d_6/CCl_4/1:3), δ, ppm: 10.34; 30.27; 74.10; 77.46; 129.88; 105.15; 137.43.

During the separation, an intermediate fraction of approximately 30.0 g (3Me:5Me-4:1) was obtained. During the separation of isomers, a resinous mass of 25.3 g was also formed.

3(5)-methyl-1-allenyl pyrazole (2c, d). A mixture of 16.4 g (0.2 mol) of 3(5)-methylpyrazole, 12.0 g (0.3 mol) of sodium hydroxide, 2.0 g of TEBAC, 5 ml of water and 60 ml of isopropyl alcohol was stirred under reflux at 20 °C for 30 min, 22.8 ml (0.3 mol) of propargyl bromide were added dropwise to the reaction mixture. Stirred for 2 h. The reaction mixture was filtered, the resulting precipitate was washed with methylene chloride and left overnight. After the solvent and isopropyl alcohol were removed, the residue was distilled under reduced pressure. Yield 12.1 g (50.5%) b. p. 80 °C/15 mm Hg, n_D^{20} 1.5430. IR spectrum, υ, cm^{-1}: 1950 cm^{-1}, two absorption bands C=C=C and 1050 cm^{-1} respectively. ^{1}H NMR spectrum (400 MHz, DMSO-CCl_4/1:3), δ, ppm, Hz: 2.21s (3H, 3-CH_3), 2.61s (3H, 5-CH_3), 5.51m (4H, 2C=CH_2), 6.15d (1H, *J* = 2.4, 4-H), 6.22d (1H, *J* = 2.4, 4-H), 7.41-7.43m (2H, 2N-CH=C), 7.45d (1H, *J* = 2.4, 3H), 7.65d (1H, *J* = 2.4, 5H).

Polymerization of N-propargylpyrazoles

a) Catalytically: 0.5 g (0.0042 mol) of N-propargylpyrazole and 0.0083 g (0.000047 mol) of $PdCl_2$ were loaded into a glass ampoule. The ampoule was sealed after degassing under vacuum and a nitrogen atmosphere: placed in an oil bath at 120-130 °C and kept for 20 h. After opening, the obtained dark brown mass was dissolved in acetone and the polymer was precipitated in hexane, the precipitate was filtered and dried to constant weight at 50 °/10 mm Hg. The yield of polypropargyl pyrazoles of sample **3** and sample **4** is 50.0%, respectively, the yield of polypropargyl pyrazoles of sample **(5a, b)** is 39.0%.

b) Thermally: similar to example a), only the polymerization is carried out without palladium chloride at 120-130 °C for 20 h. The yield of polypropargylpyrazole **(3)** is practically zero, and in the case of a mixture of polypropargylpyrazole isomers **(5a, b)** it is 8.3%.

The electrical conductivity of polymer samples **3, 4** and **5a, b** was determined in the AT-512 device (China). The obtained samples were pre-doped with 0.1N hexane solution J_2, after which they were dried to constant weight. The doped polymer was converted into tablets and the electrical conductivity was measured on the device.

RESULT AND DISCUSSION

Propargyl compounds, along with other acetylene compounds, are used in the synthesis of polyconjugated polymers with semiconductor properties. These compounds are promising reagents for constructing molecular building blocks of natural azole derivatives [1-8]. For the synthesis of propargyl compounds of the azole series, azoles containing a mobile hydrogen atom are usually used [9].

The developed method for alkylation of azoles under conditions of phase-transfer catalysis [10-12] and in the NMO/H_2O system [13-16] opens up broad possibilities for the synthesis of N-propargylpyrazoles.

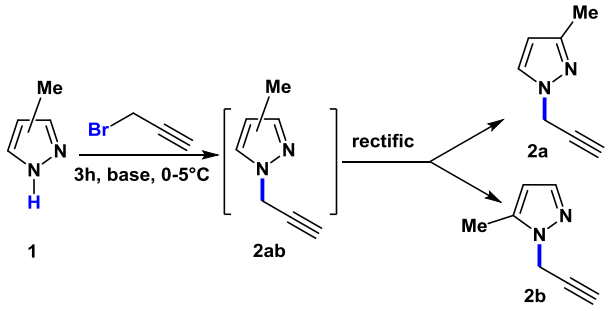
Direct alkylation of pyrazole with propargyl bromide under phase-transfer catalysis (PTC) conditions was first investigated in [17], where the authors showed that, using indicated method, instead of the expected 1-propargylpyrazole, the product of its isomerization, 1-allenylpyrazole, is obtained with a yield of 52%.

The essence of another method [18] for obtaining propargylpyrazole (yield 76%) and 1-propargyl-2,5-dimethylpyrazole (yield 35%) consists in alkylation of the corresponding sodium pyrazolates with propargyl bromide in absolute tetrahydrofuran. The duration of the process is 5 h, at the boiling point of the solvent (66 °C).

To avoid the aforementioned disadvantages, it was advisable to carry out the alkylation of pyrazoles with propargyl bromide in the NMO/H_2O system [13]. Using an aqueous solution of NMO and potassium hydroxide as a reaction medium allowed us to obtain N-propargylpyrazoles with a yield of 66-79%, while the formation of a side allene derivative was not observed.

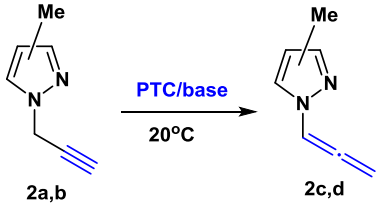
Considering the aforementioned works and their disadvantages, partially in the NMO/H_2O system of alkylation of azoles with propargyl bromide, high consumption of NMO and the associated high cost, in this work we investigated the alkylation of 3(5)-methylpyrazole with propargyl bromide under conditions of phase-transfer catalysis according to scheme 1.

When transitioning from the NMO/H_2O system to the isopropyl alcohol/water system, it was found that the determining factor in propargylation under PTC conditions is the process temperature. The optimum temperature is 0-5 °C, which allows chemoselective alkylation of 3(5)-methylpyrazole.



Scheme 1
Схема 1

The yields of the target products are 75-80%. At a temperature of 20 °C, an acetylene-allenyl rearrangement is observed with the formation of 1-allenyl-3(5)-methylpyrazole according to scheme 2.



Scheme 2
Схема 2

Alkylation of 3(5)-methylpyrazole **(1)** with propargyl bromide, as expected [19-22], led to the formation of a mixture of 3-methyl- (predominant) and 5-methylpyrazoles **(2a, b)**.

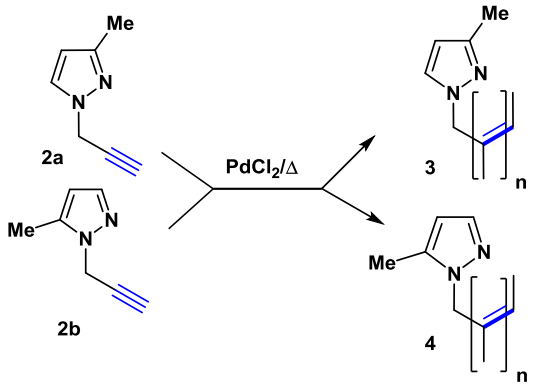
The isomeric forms 3Me and 5Me were identified by the cross peaks of the methylene group with the proton of the pyrazole ring (compound with 3Me) and with the methyl group (compound with the methyl group in the 5-position).

Polymerization of propargylpyrazoles

It was of interest to determine the influence of the position of the methyl group of the pyrazole ring during thermal and catalytic polymerization. In order to obtain reliable results, in this work individual isomers **2a** and **2b** were isolated by fractionation of their mixture **2a, b,** obtained by alkylation of 3(5)-methylpyrazole **(1)** with propargyl bromide.

For this purpose, individual isomers **2a** and **2b** were polymerized thermally at a temperature of 120-130 °C, as well as catalytically in the presence of palladium chloride according to scheme 3.

As a result, during thermal polymerization of individual isomers **2a** and **2b**, it was revealed that isomer **2a**, where the methyl substituent is in the third position of the pyrazole ring, did not polymerize in almost 20 h at a temperature of 120-130 °C.



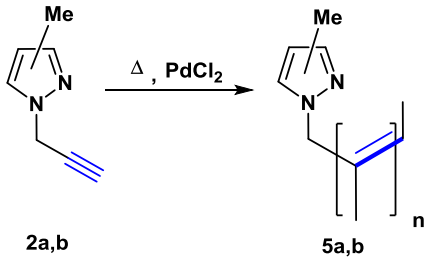
Scheme 3
Схема 3

At the same time, when the methyl substituent is in the fifth position of the pyrazole ring **2b**, the yield of polypropargylpyrazole is 40.0%.

A completely different picture is observed in catalytic polymerization. From the previously used catalytic system $PdCl_2$-pyridine-pyridine was excluded on the grounds that in the pyrazole ring itself the monomers have a pyridine atom (nitrogen in position 2 of the pyrazole ring).

Thus, at a temperature of 120-130 °C for 20 h in the presence of a catalytic amount of $PdCl_2$, both isomers **2a** and **2b** polymerize by 50.0%.

Since during the alkylation of 3(5) methylpyrazole **(1)** with propargyl bromide always results in mixtures of isomers **2a**, **b**, it was advisable to study their behavior in the mixture according to scheme 4.



Scheme 4
Схема 4

The first experiments showed that during thermal polymerization, the 3Me isomer almost completely inhibits the polymerization process and the yield of polymer **5a, b** is only 8.2%. However, in the presence of a catalytic amount of $PdCl_2$, the 3Me:5Me isomer mixtures polymerize by 40%.

The analysis of IR spectra of the obtained polymers showed that polymerization of compounds **2a** and **2b** occurs via the triple bond of propargylpyrazoles without affecting the pyrazole ring. Thus, according to

IR spectroscopy data, the absorption bands of valence vibrations characteristic of the triple bond at 2124 cm^{-1}, 2122 cm^{-1} are completely absent in the obtained polymers **3** and **4**, however, a new absorption band characteristic of the vinyl group appears in the region of 1638 cm^{-1}, and finally, the characteristic bands for valence vibrations of the pyrazole ring at 1524 cm^{-1} for compounds **3** and **4** are preserved in the IR spectra of polyvinylpyrazoles.

Some physicochemical characteristics of polypropargylpyrazoles are given in the table.

Table

Conditions of thermal and catalytic polymerization of 1-propargyl-3-methyl and 1-propargyl-5-methylpyrazoles and main physicochemical characteristics

***Таблица*. Условия термической и каталитической полимеризации 1-пропалгил-3-метил и 1-пропаргил-5-метилпиразолов и основные физико-химические характеристики**

Compound	Polymerization method	Polymer yield, %	Characteristic viscosity σl/g	Doping compound	Specific Electrical Conductivity $Ohm^{-1}\cdot cm^{-1}$	T. softenin, °C
2a	$PdCl_2$	50.0	0.042	0.1N J_2 in hexane	10^{-3}	115-120
	Thermal	-	-		-	-
2b	$PdCl_2$	50.0	0.052	-	10^{-3}	200-240
	Thermal	40.0	0.030	-	10^{-5}	-

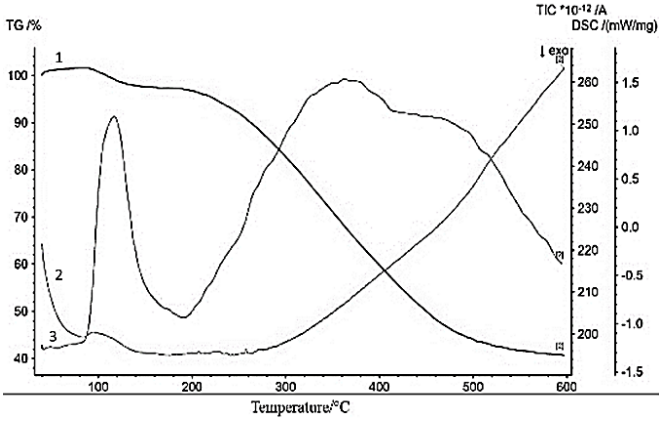


Fig. 1. Thermogravimetric analysis curves of polymer sample **3**. 1-mass loss curve, 2-thermodynamic curve, 3-potential change curve

Рис. 1. Кривые термогравиметрического анализа полимерного образца **3**. 1–кривая потери массы, 2-термодинамическая кривая, 3-кривая изменения потенцала

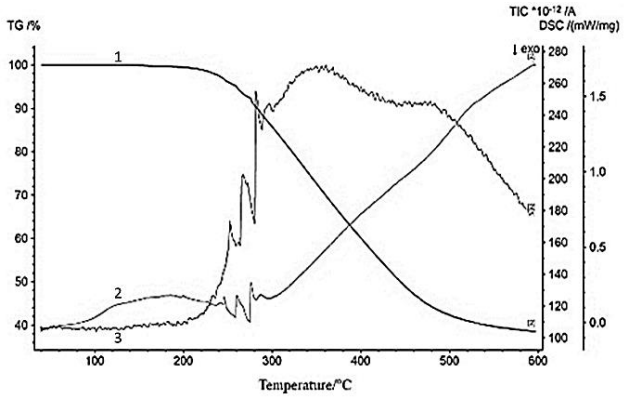


Fig. 2. Thermogravimetric analysis curves of polymer sample **4**. 1-mass loss curve, 2-thermodynamic curve, 3-potential change curve

Рис. 2. Кривые термогравиметрического анализа полимерного образца **4**. 1–кривая потери массы, 2-термодинамическая кривая, 3-кривая изменения потенцала

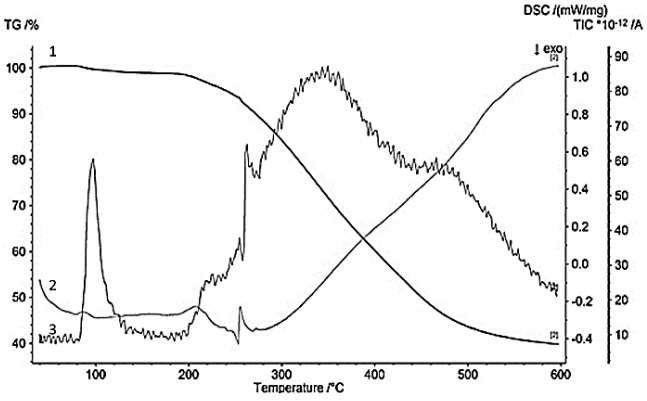


Fig. 3. Thermogravimetric analysis curves of polymer sample **5a**, b. 1-mass loss curve, 2-thermodynamic curve, 3-potential change curve

Рис. 3. Кривые термогравиметрического анализа полимерного образца **5a**, б. 1–кривая потери массы, 2-термодинамическая кривая, 3-кривая изменения потенцала

The specific conductivity values of polypropargyl pyrazoles (10^{-3}-10^{-5} Ohm^{-1} cm^{-1}) indicate that they can find applications as organic polymer semiconductors (table).

To assess the thermal stability and the possibility of decomposition of the polymer samples **3** (Fig. 1) and **4** (Fig. 2), as well as their mixture of isomers **(5a, b)** (Fig. 3), a thermal study was carried out under dynamic heating conditions using the [TG/MSNETZSHSTA499(TG)QSM403(MS)] device.

According to thermogravimetric analysis (TGA), intensive weight loss of samples **3, 4** and **5** begins at temperatures of about 195, 200 and 215 °C, respectively. The first stage of weight loss for sample **5** begins at 80 °C and ends at 140 °C, the weight loss is about 0.8%. This stage is manifested on the differential

thermogravimetry (DTG) curve as an intense peak, and on the differential scanning calorimetry (DSC) curve as a weak endothermic (endo) peak.

Probably, at the first stage of thermal destruction of sample **5**, adsorbed or weakly bound water is removed from the sample. At the beginning of intensive loss of sample mass, at 196 °C, another process begins in the form of an endo effect (ends at 206 °C), and residual monomer may be removed. At temperatures from 240 °C (beginning of the exo effect) to 270 °C, complex processes apparently occur in the sample with the formation of new chemical bonds.

The mass loss for sample **3** starts at 80 °C and ends at 180 °C, the mass loss is about 1.5%. According to DTG and DSC data, the subsequent thermal behavior of sample **3** is almost identical to the thermal behavior of sample **5**.

Sample **4** (according to TGA data), compared to samples **5**, **3**, is thermally stable and has no mass losses up to 200 °C. Intensive thermodestruction (onset at 215 °C) includes two exo processes with onsets temperatures of 245 °C and 260 °C, suggesting the formation of new structures, with their subsequent (with an increase in temperature above 260 °C) destruction.

The mass loss for samples **5, 3** and **4** with an increase in temperature to 600 °C is 60% of the original mass.

CONCLUSION

In the presented work, it is once again shown that 3Me and 5Me isomers differ not only in their physical but also chemical properties. Thus, during thermal polymerization at 120-130 °C, the 3Me isomer is hardly polymerized, while the 5Me isomer is polymerized by 50%. During catalytic polymerization, the two isomers polymerize in almost equal amounts, approximately 50 percent each. This suggests that during catalytic polymerization, $PdCl_2$ does not play a role for the 5Me isomer, whereas for the 3Me isomer, it promotes the cleavage of the triple bond. During the thermal polymerization of an isomer mixture, the 3Me isomer completely inhibits the polymerization of the 5Me isomer. This phenomenon is not observed during catalytic polymerization, which again suggests that the polymerization of the 3Me isomer proceeds under the influence of $PdCl_2$.

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