Research Square

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Facile method for synthesis and polymerization of 1-allenyl-3-methyl- and 1- allenyl-5-methylpyrazoles

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Abstract

It is well known that imputing of allenyl group into heterocyclic systems, particularly in pyrazole structure allows to obtain modified and applied compounds with practically interesting properties.

In this research we have synthesized methyl group substituted allenyl pyrazoles, aiming to obtain conjugated and novel polymers with azole fragment in the side chain, the radical polymerization of those were carried out.

1-Allenyl-3-methyl and 1-allenyl-5-methylpyrazoles were synthesized by isomerization of 1-propargyl-3-methyl and 1-propargyl-5-methylpyrazoles, respectively, using KOH dissolved in the isopropanol, as a result yielding 50-55% of allenyl pyrazoles. Obtained allenyl pyrazoles have been easily polymerized using azobisisobutyronitrile (AIBN) as radical initiator, thermal polymerization was also performed, resulting of linear oligomers with η= 0,015–0,025 dl/g viscosity.

Polymerization of some isomers of 1-allenyl pyrazoles has been studied by gas-liquid chromatography, the structures of obtained polymers were identified by IR and NMR spectroscopy methods. It was found out that in the case of radical polymerization, when methyl group was located at the 3-position of the pyrazole ring, it polymerized faster under the same conditions compared to the isomer with the methyl group at the position 5. We have showed dependence of polydispersity of obtained poly(1-allenyl-3-methylpyrazole) samples from the synthesis route using the light scattering method.

Introduction

Allene monomers are of considerable interest for the development of functionalized polymer systems [1–3]. However, the synthesis of allenylpyrazoles directly from propargyl pyrazoles has received limited attention in the literature. This compounds have primarily been reported as products formed during the alkylation of azoles with propargyl bromide [4–6].

In contrast to the radical polymerization of 1-allenyl-3(5)-methylpyrazoles (compounds **3** and **4**), the polymerization behavior of their analogues, 1-vinyl-3(5)-methylpyrazoles, has been extensively investigated [7, 8]. Nevertheless, these studies did not address the influence of the methyl group position on the pyrazole ring with respect to the polymerization behavior within this series. Only recently the radical polymerizations of the separate isomers were examined [9], demonstrating that the isomer bearing the methyl group at the position 5 polymerizes more rapidly than its 3-methyl counterpart.

In the present work, we report a facile method for the synthesis of 1-allenyl-3-methyl- and 1-allenyl-5-methylpyrazoles from the corresponding 1-propargyl-3-methyl- and 1-propargyl-5-methylpyrazoles. The radical polymerization of compounds **3** and **4** in dimethylformamide (DMF) was investigated, and the results have been compared with previously reported procedure [9].

Experimental

Characterization

The solvents were initially purified by distillation, AIBN was recrystallized from methanol. Relative activity of monomers has been monitored by gas-liquid chromatography using known method.

Equipment

IR spectrums were obtained on *Nicolet AVATAR 330 FTIR* spectrometer. ^{1}H and ^{13}C NMR (300 and 75 *MHz*, respectively) spectrums were recorded on a *Varian Mercury VX 300* spectrometer in DMSO-d_6:CCl_4 using 1:3 ratio. Measurements of distribution of particle size of have been performed by *Litesizer 500* in ethanol.

Method

Synthesis of allenyl pyrazoles

10g of 1-propargyl-3-methyl- or 1-propargyl-5-methylpyrazoles was added to the solution of 2g of potassium hydroxide dissolved in 20 ml of isopropyl alcohol. The reaction was carried out under vigorous stirring within 24 hours at room temperature. Gas-liquid chromatography was used for monitoring of the reaction process. It was found out that propargyl pyrazoles undergoes conversion to 1-allenyl pyrazoles within 24 hours. Then, isopropyl alcohol was evaporated under vacuum, 10 ml of distilled water was added to the residue and extracted by dichloromethane.

Synthesized 1-allenyl-3-methyl pyrazole and 1-allenyl-5-methyl pyrazole were distillated under 1 mm Hg vacuum at 50 and 55^{0}C temperatures. Obtained compounds have 1,542 and 1,570 refractive indexes, respectively. It was noticed that within distillation process allenyl pyrazoles could be polymerized.

1-Allenyl-3-methylpyrazole

^{1}H NMR (CCl_4), *δ*, *ppm*: (1 Hz), 2.26 (3H, 3- CH_3), 5.59 (2H, =CH_2, J- 6.51), 6.09 (1H, 4H, J- 1.7), 7.06 (1H, N-C = C, J- 1.7), 7.39 (1H, 5-H, J- 1.7).

^{13}C NMR, *δ*, *ppm*: 11.6, 88.1, 101.3, 107.1, 128.4, 150.1, 203.4.

IR spectrum (KBr, cm^{-1}): 1540 (ring); 1950, 2000 (C = C=C).

$C_7H_8N_2$ Found %, C 69.87, H 6.59, N 13.00, calculated %, C 70.0, H 6.66, N 23.33.

1-Allenyl-5-methylpyrazole

^{1}H NMR (CCl_4), δ, *ppm*: (1 Hz), 2.29 (3H, 5-CH_3), 5.54 (2H, =CH_2, J- 6.7), 6.025 (1H, J- 1.7), 7.04 (1H, N-C = C, J- 1.7), 7.44 (1H, 3-H, J- 1.7).

^{13}C NMR, δ, *ppm*: 11.53, 88.2, 101.7, 107.1, 149.2, 202.3.

IR spectrum (KBr, cm^{-1}): 1532 (ring), 1950, 2000 (C = C=C).

$C_7H_8N_2$ Found %, C 69.81, H 6.42, N 23.15, calculated %, C 70.0, H 6.66, N 23.33.

Polymerization of allenyl pyrazoles

Radical polymerization of compounds **3** and **4** have been carried out in DMF at 70^0C temperature in ampoule using 1 *mol/l* for monomers and 0.01 *mol/l* concentrations for AIBN. Separation of unreacted monomers from obtained polymers has been carried out by precipitation in DMF/hexane mixture. Synthesized polymers were dried at 55^0C under 10 mm Hg vacuum. Relative viscosity of polymeric samples has been determined at 20 ^{0}C in DMF, for poly(1-allenyl-3-methylpyrazole) (**5**) and poly(1-allenyl-5-methylpyrazole) (**6**) it was η = 0,032 and 0.018 *dl/g*, respectively.

RESULT AND DISCUSSION

We have developed a facile method of isomerization of 1-propargy-3-methyl- and 1-propargyl-5-methylpyrazoles in the solution of KOH in isopropyl alcohol within 24 hours at room temperature yielding 50–55% of compounds **3** and **4** (Scheme 1). It should be noted that if the precipitate forms after 24 hours, it was filtered, dried over magnesium sulfate, the solvent was removed and the product was purified by distillation technique.

Isomerization of 1-propargy-3-methyl- and 1-propargy-5-methyl pyrazoles resulting of compounds **3** and **4** and further polymerization procedure

Monomers **3** and **4** exhibit different activity within radical polymerization reaction (Fig. 1).

Our findings reveal that, in the case of allenyl pyrazoles (**3**,**4**), the polymerization behavior is reversed compared to reported in the literature [9]. Specifically, the isomer with the methyl group at the position 3 of pyrazole ring is being polymerized more readily than the corresponding 5-methyl isomer. Allenyl pyrazoles could be easily polymerized by AIBN resulting of soluble oligomers with linear structure ([η] = 0.032–0.018 *dl/g*) in contrast to 1-vinylpyrazoles.

The polymerization process of **3** and **4** isomers was studied by gas-liquid chromatography using known method [10]. Initial concentrations of the monomer and initiator were [M] = 1 and [I] = 0.01, respectively.

The structures of obtained **5** and **6** polymers were verified by IR and ^{1}H, ^{13}C NMR spectrometry. Valence vibrations of allenyl bond (C = C=C) at the range of 1990 and 1960 cm^{-1} were disappeared in the both

obtained **5** and **6** polymer spectrums, meanwhile vibrations characteristic to azole ring at 1515–1523 cm^{-1} range were equable. IR spectrums of obtained polymers shows that only 1 kind of double bond is present which is characteristic to N = CH group (1641 and 2918 cm^{-1}). In addition, the vibrations at 1655 and 3100 cm^{-1} range characteristic to (C = CH) methylene group were not observed.

The signals of ^{1}H NMR spectrum of studied samples are broaden which is specific for polymers. Signals of olefin protons (N-CH = CH) are verified at 6.88-7.00 *ppm* and at 2.00-2.31 *ppm* range corresponded to methyl group (CH_3). Signal relevant to allene (CH_2) fragment at 5.35 *ppm* is not observed.

As continuation, the polydispersity of **PA-1**, **PA-2** and **PA-3** derivatives of poly(1-allenyl-3-methylpyrazole) has been studied by light scattering method.

Table 1
Conditions of the polymerization reaction of 1-allenyl-3-methyl pyrazole resulting of **PA-1**, **PA-2** and **PA-3** polymers

Sample	**AIBN**	**T ^{0}C**	**DMF**	**Reaction duration, hours**
PA-1	+	70	+	2
PA-2	-	25	-	30
PA-3	-	70	-	8

The distribution of the particles size of obtained samples has been carried out by two steps technique. Aiming to obtain more regular distribution of the polymer particles, the measurement has been proceeded before filtration, then second step has been done after treatment by ultrasonic and filtration process.

Before treatment with ultrasonic and filtration of the sample of **PA-1**, there has been observed distribution of polydisperse molecules and big agglomerates (~ 100–1000 nm).

Study shows that **PA-1** exhibits high polydispersity (Fig. 2), which means that particles tend to agglomerate even after filtration.

The distribution presented in Fig. 3 is also in multimodal type, because there are short (~ 1–10 nm) and long length particles (~ 100–1000 nm).

It has been shown that the distribution of the particles of **PA-2** is polytope type, as well, but the agglomeration is weaker compared to **PA-1** (Fig. 4). The medium length of the peaks is in the range of 10–30 nm. After treatment by ultrasonic (Fig. 5) and filtration of the sample of **PA-2** the distribution of the particles became more narrow and big agglomerates were completely disappeared resulting of distribution of monomodal type (Fig. 6). This proves the fact that after treatment, it has become stable and monodisperse system.

As shown in Fig. 7 and Fig. 8, the **PA-3** sample exhibits high polydispersity, because the distribution is polytope type and there are peaks of short (10 nm), medium (10–15 nm) and long (approximately 1000 nm) diameter of particles. After treatment with ultrasonic and filtration the system gets closer to monodisperse type, however, in these characteristics it is inferior to the **PA-2** sample (Fig. 5). As a result, **PA-3** takes an intermediate position between **PA-1** and **PA-2** samples: **PA-1** (widest dispersity), **PA-3** (medium), **PA-2** (monodisperse).

Conclusion

Synthesis of compounds **3** and **4** was performed by facile method of isomerization of 1-propargy-3-methyl- and 1-propargyl-5-methylpyrazoles. Polymer **5** was used as a representative example to demonstrate the dependence of dispersity of the particles of polymer on the synthesis method. Analysis of the obtained data indicates that the formation of monodisperse systems requires polymerization of allenyl pyrazoles to be conducted in bulk at room temperature, without the application of heat or usage of an initiator.

Declarations

Conflict of interests

The authors declare no conflict of interest.

Author Contribution

L. A. Bichakhchyan, M. L. Petrosyan and N. A. Mirakyan-performed data analysis, conducted of experimental part, N. A. Mirakyan , R. M. Hakobyan, H. S. Attaryan- conceptualization, methodology, writing of manuscript.

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Consent to Publish declaration: not applicable

Ethics and Consent to Participate declarations: not applicable

Data Availability

All data analyzed during this study are included in this article and its supplementary material file.

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Scheme 1

Scheme 1 is available in the Supplementary Files section.

Figures

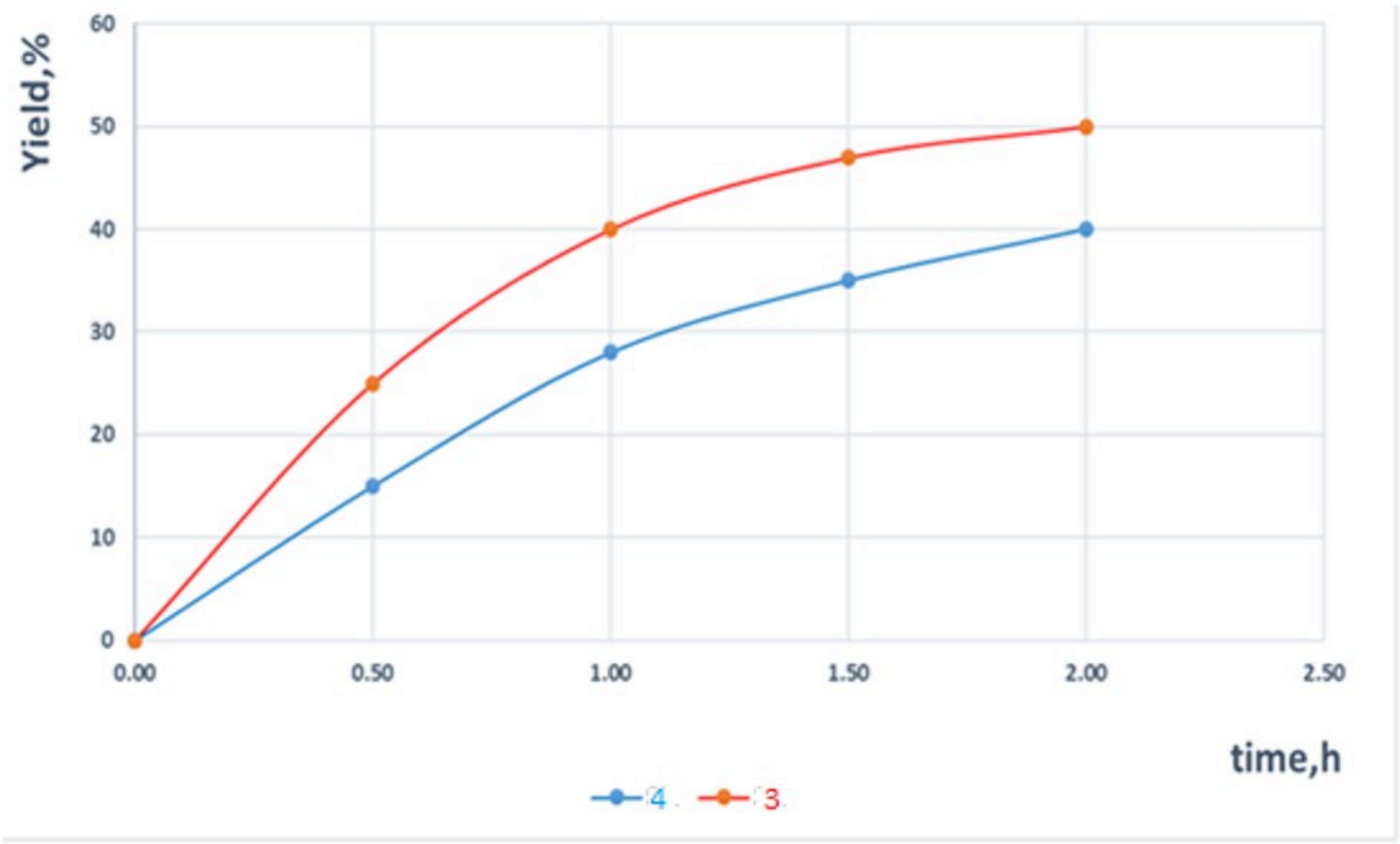


Figure 1

Kinetics of polymerization of the monomers **3**and **4**

Supplementary Files

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- SupplementaryMaterial.docx
- scheme1.jpg