

## Synthesis of polyphenylacetylene by iron(III) chloride catalyzed carbonyl olefin metathesis polymerization of chalcone

H. Penchev<sup>1</sup>, S. S. Dimova<sup>1,\*</sup>, K. L. Zaharieva<sup>2</sup>, F. S. Ublekov<sup>1</sup>, Ch. Novakov<sup>1</sup>, V. Sinigersky<sup>1</sup>

<sup>1</sup> Institute of Polymers, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 103A, 1113 Sofia, Bulgaria

<sup>2</sup> Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 11, 1113 Sofia, Bulgaria

Received: January 15, 2018; Revised, March 22, 2018

Carbon-carbon bond formation is a fundamental reaction in organic synthesis, one of its most important applications being synthesis of polymers and copolymers. Studies of the olefin metathesis reaction have resulted in extensive knowledge regarding synthesis of molecules applied in agricultural, petroleum, and pharmaceutical industries. The most commonly used catalysts for this purpose are ruthenium, molybdenum, and tungsten-based complexes.

Recently, Ludwig et al. have successfully conducted iron(III)-catalysed carbonyl-olefin metathesis reaction for synthesis of low molecular weight compounds.

In this study, we demonstrate for the first time that the carbonyl-olefin metathesis reaction, catalysed by anhydrous iron(III) chloride, can also be effectively applied in polymerization mode by using a single bifunctional monomer as chalcone. Polymerization was performed in a simple and efficient way under mild reaction conditions in solvents of various polarity, such as 1,2-dichloroethane and toluene. The average molecular mass of the synthesized oligomers reached 5000 g.mol<sup>-1</sup>, which was higher than reference values so far reported. In situ doping of the as synthesized polyphenylacetylenes with FeCl<sub>3</sub> represents another advantage of selected synthetic approach.

Obtained products were characterized by gel permeation chromatography, <sup>1</sup>H NMR, and FTIR spectroscopy. The structure of the obtained oligomers was studied by X-ray diffraction analysis.

**Key words:** carbonyl olefin metathesis polymerization, Iron(III) chloride, polyphenylacetylenes, chalcone, catalyst dopant.

### INTRODUCTION

During the last decade, a new synthetic route for the preparation of oligomeric products based on carbonyl-olefin exchange reaction and reductive coupling of conjugated compounds has been developed using novel catalyst systems. The control over the polymer structure provided by metathesis polymerization makes fine-tuning of polymer properties and functionality possible.

Carbonyl olefin metathesis (COM) has been reported for the first time by Schopov *et al.* [1]. COM has been applied for polymerization of  $\alpha,\beta$ -unsaturated carbonyl compounds in the presence of WCl<sub>6</sub> [2]. It has been shown that treatment of  $\alpha,\beta$ -unsaturated carbonyl compound as 1,3-diphenyl-prop-2-en-1-one (chalcone) with WCl<sub>6</sub> resulted in the formation of polyphenylacetylene. Using this procedure several substituted  $\alpha,\beta$ -unsaturated carbonyl compounds were polymerized. A series of substituted polyacetylenes (polyphenylacetylene, polydiphenylacetylene, polymethylacetylene, polycamphor, etc.) was obtained. The most commonly used catalysts for this purpose are ruthenium,

molybdenum, and tungsten-based complexes. Until now, COM has not been widely applied. The requirement of stoichiometric amounts of transition metals with concurrent formation of inert metal oxo species, which preclude regeneration of the active metal catalyst, has probably been the main reason for obscurity of the carbonyl-olefin metathesis reaction [3]. Finding mild catalytic conditions to perform carbonyl olefin metathesis has always been a significant challenge.

Remarkable innovations have been made in the field of olefin metathesis concerned with design and preparation of new catalysts. Considerable breakthrough has been achieved exploring iron(III)-catalysed carbonyl-olefin metathesis reactions. This approach is characterized by operational simplicity, high functional group compatibility, and region-selectivity using anhydrous FeCl<sub>3</sub> as a cheap, non-toxic, and environmentally friendly compound. Ludwig and co-workers have successfully demonstrated iron(III)-catalysed carbonyl-olefin ring-closing metathesis reaction for synthesis of low-molecular cyclic compounds [4, 5].

The goal of the present work was to synthesise polyphenylacetylene by iron(III)-catalysed carbonyl olefin metathesis polymerization of chalcone. Struc-

\* To whom all correspondence should be sent  
E-mail: dimova@polymer.bas.bg

ture and chemical composition of the obtained products were studied by GPC,  $^1\text{H}$  NMR, FTIR, and XRD analysis.

## EXPERIMENTAL

### Materials and methods

Chalcone  $\geq 98.0\%$  (Sigma-Aldrich) was used as received. Anhydrous  $\text{FeCl}_3$  (98%) was purchased from Alfa Aesar. 1,2-Dichloroethane and toluene *ppa* grade were purchased from Valerus company, Bulgaria. 1,2-Dichloroethane was dried over  $\text{CaH}_2$  and distilled; toluene was dried over  $\text{CaH}_2$  and stored with metal sodium wire.

### Characterization

The products prepared by metathesis polymerization were studied by several analytical techniques.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , dioxane) spectroscopy was performed on a Bruker Avance DRX 600 spectrometer, 600 MHz. FTIR spectra were recorded by means of a Bruker-Vector 22 spectrometer using thin films applied on KBr discs. GPC analysis was carried out on a Shimadzu Nexera XR LC20ADXR liquid chromatograph equipped with a DGU-20A5R degasser, a SIL-20ACHT auto sampler, a RID-20A refractive index detector, and a set of PLgel GPC columns: 5  $\mu\text{m}$  50 A, 500 A, and 10  $\mu\text{m}$  Mixed-B. Tetrahydrofuran (THF) was used as eluent at a flow rate of 1  $\text{ml}\cdot\text{min}^{-1}$  at 40  $^\circ\text{C}$ . Samples were prepared as solutions in THF. Molecular weight characteristics as number average and weight average molecular masses and polydispersity index of the copolymers were calculated using a calibration curve constructed with monodisperse polystyrene standards. Data acquisition and processing were performed using LabSolutions v.5.54 GPC software.

Morphology of the obtained oligomers was studied by X-ray diffraction analysis. X-ray diffraction patterns were recorded on a Bruker D8 Advance ECO diffractometer in reflection mode with Ni-filtered  $\text{Cu K}\alpha$  radiation over the  $2\theta$  range of 10–60 $^\circ$  at 40 kV. ICDD database was used to establish the phases.

### Synthetic procedure

Polymerization was conducted in a Schlenk flask equipped with a three-way stopcock under argon, chalcone being dissolved at room temperature. Then the solution was heated according to applied medium: 60  $^\circ\text{C}$  for 1,2-dichloroethane and 90  $^\circ\text{C}$  for toluene. Almost immediately after addition of the  $\text{FeCl}_3$  catalyst, a distinguished benzaldehyde smell was perceived. Best results were obtained for reaction time within 12–24 hours. At the first step 10

wt.% chalcone solutions in 1,2-dichloroethane ( $\text{C}_2\text{H}_4\text{Cl}_2$ ) or toluene were obtained. Then anhydrous  $\text{FeCl}_3$  preliminary dissolved in an appropriate amount of solvent was added. The solution immediately turned brown-reddish in colour as the viscosity was increased. Synthesis conditions are summarized in Table 1.

**Table 1.** Preparation conditions of polyphenylacetylenes

Sample	Solvent	$\text{FeCl}_3$ , mole%	Yield, %
PA-1	1,2-dichloroethane	7.5	43
PA-2	1,2-dichloroethane	15	76
PA-3	Toluene	15	81
PA-4	Toluene	45	68

All experiments were carried out for 24 h.

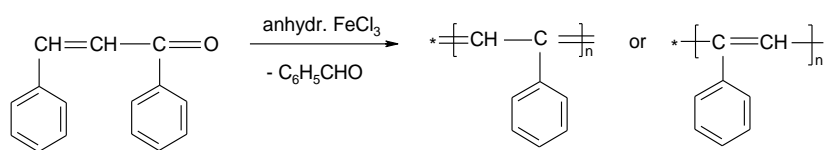
The products were purified by precipitation in methanol, filtering and abundant washing with conc. HCl, washing with distilled water, neutralization with 0.1M  $\text{NaHCO}_3$ , and final washing with water to neutral pH of the filtrate (removal of catalyst and reaction rests). Purified polyphenylacetylene powder was pale yellow in colour while the  $\text{FeCl}_3$ -doped product was reddish-brown.

## RESULTS AND DISCUSSION

The aim of this study was to use anhydrous  $\text{FeCl}_3$  as a cheap and widely available catalyst for metathesis polymerization of chalcone and to characterize the obtained product – oligomeric polyphenylacetylene. Resonance structures of the synthesized oligomeric polyphenylacetylene are given in Scheme 1.

The products are stable in air, well soluble in common volatile solvents like chlorinated hydrocarbons, and exhibit the physical properties of conjugated polymers. GPC analysis of PA-4 sample showed a multimodal molar mass distribution with dispersity index of 2.5. Representative GPC traces are displayed in figure 1. It should be pointed out that the molar mass of the obtained oligomers strongly depended on the polarity of solvent used as polymerization medium. The polymerization carried out in 1,2-dichloroethane resulted in formation of predominantly trimeric product, irrespective of catalyst amount and polymerization time, while when performing the reaction in solvent of lower polarity like toluene, fractions of molecular masses up to 5000  $\text{g}\cdot\text{mol}^{-1}$  were registered.

FTIR spectra of the products are presented in figure 2. All oligomers showed a band at 1656  $\text{cm}^{-1}$  assigned to  $\text{C}=\text{O}$  bond (conjugated ketone end group). In the spectrum of PA-2 sample, the double bond for  $-\text{C}=\text{C}-$  from the phenylene ring appeared around 1597  $\text{cm}^{-1}$ , the  $=\text{C}-\text{H}$  aromatic vibrations



Scheme 1. Fe(III) chloride catalyzed carbonyl olefin metathesis polymerization of chalcone.

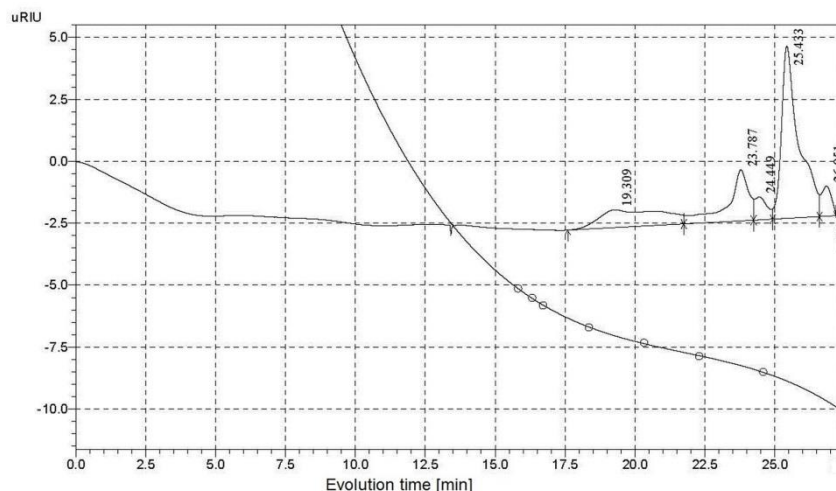


Fig. 1. GPC traces of sample PA-4 (eluent THF).

were in the range of  $1180\text{--}1029\text{ cm}^{-1}$ , while the  $=\text{CH}$ - vibration from the polymer backbone was at  $1448\text{ cm}^{-1}$  [6].

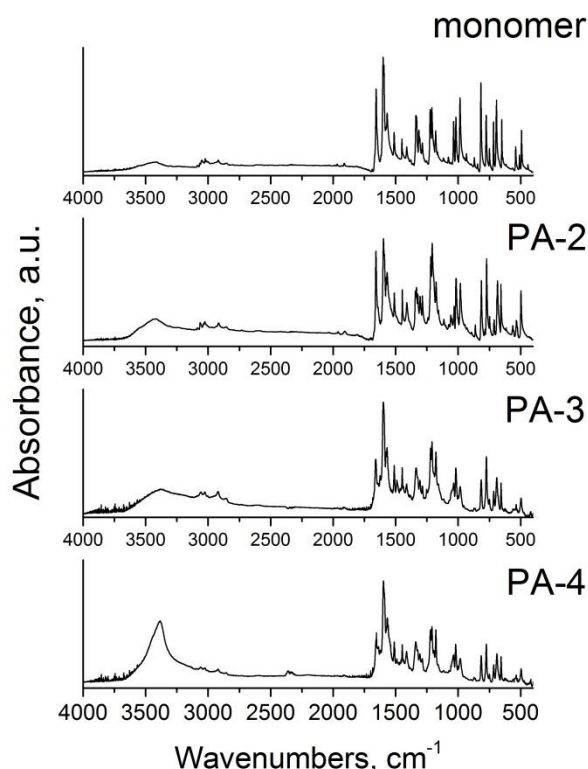


Fig. 2. IR spectra of monomer, PA-2, PA-3, and PA-4.

$^1\text{H}$  NMR spectra of the synthesized polyphenylacetylenes are shown in figures 3 and 4.  $^1\text{H}$ -NMR (in  $\text{CDCl}_3$ ) of PA-2 manifested a characteristic chemical shift for double bonds at 5.37 ppm. Signals in the region 7.3–8 ppm are assigned to protons characteristic of aromatic rings. The chemical shifts between 1.8–2.5 ppm are attributed to  $=\text{CH}$ - protons from the backbone.

In the  $^1\text{H}$  NMR spectrum of dominating *cis*-polyphenylacetylene PA-2, the peak characteristic of proton attached to the *cis*-conformation of the double bond was observed at 5.4 ppm. It is known that if W, Mo, and Rh catalyse the polymerization of arylacetylenes a *cis*-transoidal structure is mainly obtained [7–9]. Sample PA-2 showed a singlet at  $\delta = 5.37$  ppm that has to be assigned to olefinic protons in the *cis*-transoidal main chain.

X-ray diffraction pattern of the polymerization product in toluene is displayed in figure 5. The diffractogram shows a broad maximum around  $2\theta \sim 12.5^\circ$ , which confirms predominant amorphous structure of the sample. However, sharpening of two peaks at  $26.6^\circ$  and  $32.8^\circ$  was observed. This indicates that synthesized oligomer is susceptible to some structural ordering. [10]. The area of these two peaks is negligible in comparison with the amorphous halo. For this reason, the crystallinity is close to zero.

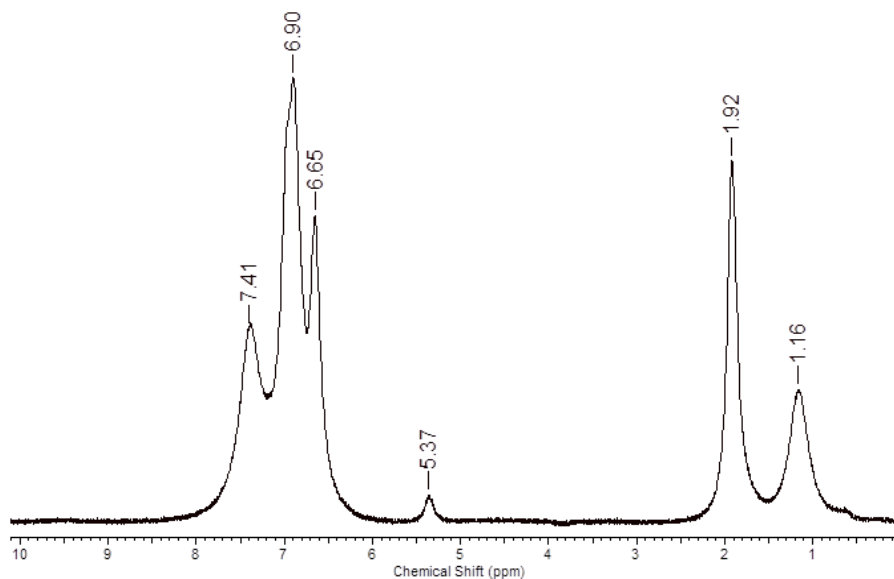


Fig. 3.  $^1\text{H}$  NMR spectrum of PA-2.

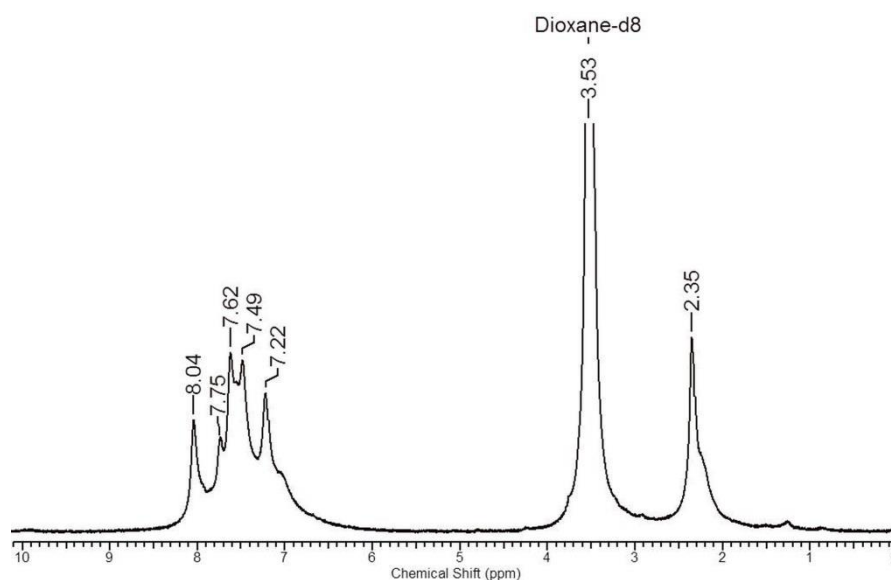


Fig. 4.  $^1\text{H}$  NMR spectrum of PA-4.

In previous pioneering studies, Jossifov *et al.* performed carbonyl-olefin exchange reaction of chalcone using  $\text{WCl}_6$  as catalyst and obtained polyphenylacetylenes, however, the  $\text{WCl}_6$  catalyst is expensive and toxic [11,12]. Binary systems like  $\text{WCl}_6 + \text{AlCl}_3$ ,  $\text{WOCl}_4 + \text{AlCl}_3$  and others were also used as Friedel-Crafts type catalysts [11,12]. In our study, we performed polymerization of chalcone in solution using anhydrous  $\text{FeCl}_3$ . Iron(III) chloride was selected as a cheap and green catalyst alternative to traditionally used tungsten-based catalyst systems. Another advantage that could be emphasized is conducting the metathesis polymerization in common volatile organic solvents and using low concentrations of  $\text{FeCl}_3$ .

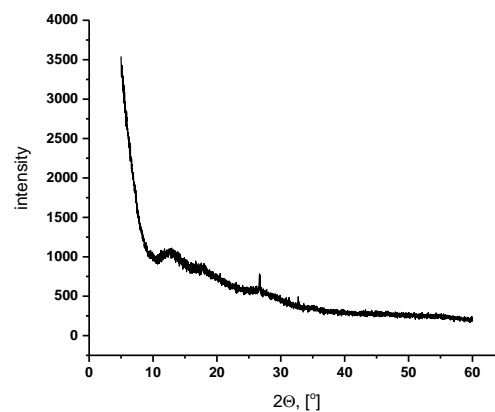


Fig. 5. XRD pattern of the polymerization product in toluene.

## CONCLUSIONS

A simple and efficient procedure for synthesis of polyphenylacetylene by iron(III)-catalysed carbonyl olefin metathesis polymerization of chalcone is described for the first time. This procedure could be applied to prepare a broad range of functionalized benzalacetophenone derivatives with high chemo- and regioselectivity. High selectivity, mild reaction conditions, and easy available starting materials can be pointed out as considerable advantages.

The catalytic carbonyl-olefin metathesis reaction enables direct carbon-carbon bond formation between carbonyl and olefin entities by using anhydrous iron(III) chloride as catalyst. Depending on the polarity of the reaction medium, oligomeric products with different molecular mass can be obtained. The procedure can render *in situ* FeCl<sub>3</sub>-doped conjugated oligomers. The chemical structure of the synthesized polyphenylacetylenes was studied by <sup>1</sup>H-NMR, FTIR spectroscopy, XRD analysis, and GPC. The proposed procedure provides *in situ* FeCl<sub>3</sub>-doped polyphenylacetylene.

## REFERENCES

1. I. Schopov, C. Jossifov, L. Mladenova, *Makromol. Chem., Rapid Commun.*, **6**, 659 (1985).
2. C. Jossifov, R. Kalinova, in: Green Metathesis Chemistry (Dragutan V., Demonceau A., Dragutan I., Finkelshtein E. S., eds.), NATO Science for Peace and Security Series A: Chemistry and Biology, Springer, Dordrecht, 2010, p. 305
3. C. Sa, *Angew. Chem. Int. Ed.*, **55**, 2 (2016).
4. J. R. Ludwig, P. M. Zimmerman, J. B. Gianino, C. S. Schindler, *Nature*, **533** (7603), 374 (2016).
5. J. R. Ludwig, S. Phan, C. C. McAtee, P. M. Zimmerman, J. J. Devery III, C. S. Schindler, *J. Am. Chem. Soc.*, **139** (31), 10832 (2017).
6. S. Dimova, K. Zaharieva, V. Sinigersky, Z. Cherkezova-Zheleva, I. Mitov, *Materials, Methods & Technologies*, **8**, 233 (2014).
7. T. Masuda, *J. Polym. Sci. Part A: Polym. Chem.*, **45**, 165 (2007).
8. T. Masuda, N. Sasaki, T. Higashimura, *Macromolecules*, **8** (6), 717 (1975).
9. M. Shiotiuki, F. Sanda, T. Masuda, *Polym. Chem.*, **2**, 1044 (2011).
10. R. Kamashi, B. S. R. Reddy, *J. Polym. Sci. Part A: Polym. Chem.*, **46**, 1521 (2008).
11. C. Jossifov, in: Ring Opening Metathesis Polymerisation and Related Chemistry (Khosravi E., Szymanska-Buzar T., eds.), NATO Science Series (Series II: Mathematics, Physics and Chemistry), vol. 56, Springer, Dordrecht, 2002, p. 425.
12. C. Jossifov, R. Kalinova, in: Metathesis Chemistry: From Nanostructure Design to Synthesis of Advanced Materials (Y. İmamoglu, V. Dragutan, eds.), Springer, 2007, p. 461.

## СИНТЕЗ НА ПОЛИФЕНИЛАЦЕТИЛЕНИ ПОЛУЧЕНИ ЧРЕЗ КАРБОНИЛ ОЛЕФИНОВА МЕТАТЕЗНА ПОЛИМЕРИЗАЦИЯ НА ХАЛКОН КАТАЛИЗИРАНА ОТ ЖЕЛЕЗЕН(III) ХЛОРИД

Хр. П. Пенчев<sup>1</sup>, С. С. Димова<sup>1\*</sup>, К. Л. Захариева<sup>2</sup>, Ф. С. Ублеков<sup>1</sup>, Хр. Новаков<sup>1</sup>, В. Синигерски<sup>1</sup>

<sup>1</sup> Институт по полимери, Българска академия на науките, ул. „Акад. Г. Бончев“, бл. 103А, 1113 София, България

<sup>2</sup> Институт по катализ, Българска академия на науките, ул. „Акад. Г. Бончев“, бл. 11, 1113 София, България

Постъпила на 15 януари 2018 г.; Преработена на 22 март 2018 г.

(Резюме)

Образуването на въглерод-въглеродна връзка е фундаментална реакция в органичния синтез като едно от най-важните приложения е получаването на полимери и съполимери. Изследването на реакцията на олефиновата метатеза води до задълбочени познания по отношение на синтеза на молекулите, прилагани в селското стопанство, нефтената и фармацевтичната промишленост. Най-често използваните катализатори за тази цел са комплекси на базата на рутений, молибден и волфрам.

Лудвиг и сътр. успешно осъществяват карбонил олефин метатезна реакция, катализирана от желязо(III), за синтез на нискомолекулни съединения.

В това изследване ние показваме за първи път, че карбонил олефинова метатезна реакция, катализирана от безводен желязо(III) хлорид, може успешно да се прилага и в полимеризационен режим чрез използване на бифункционален мономер - халкон. Полимеризацията се извършва по прост и ефективен начин при умерени реакционни условия в разтворители с различна полярност като 1,2-дихлороетан и толуен. Средната молекулна маса на синтезираните олигомери достига 5000 g.mol<sup>-1</sup>, което е по-високо от посоченото в литературата досега. *In-situ* дотирането на получените полифенилацетилени с FeCl<sub>3</sub> е друго предимство на избора от нас синтетичен подход.