

Performance of metathesis reactions using different nano-sized ferrite-type catalysts

S. S. Dimova^{1*}, K. L. Zaharieva², F. S. Ublekov¹, H. P. Penchev¹

¹ Institute of Polymers, Bulgarian Academy of Sciences, "Acad. G. Bonchev" St., Bl.103A, 1113 Sofia, Bulgaria

² Institute of Catalysis, Bulgarian Academy of Sciences, "Acad. G. Bonchev" St., Bl. 11, 1113 Sofia, Bulgaria

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This paper represents a comparative study of our research on metathesis reaction, performed in the presence of different nano-sized ferrite-type catalysts. The obtained products – substituted polyphenylacetylenes, have been characterized by FTIR and ¹H-NMR spectroscopy, Size exclusion chromatography (SEC) and Scanning electron microscopy. The monomers used were – 1-phenylacetylene or 1-phenyl-1-propyne, co-monomer – isobutyraldehyde and various nanostructured ferrite-type catalysts – Ni_xFe_{3-x}O₄, Mg_xFe_{3-x}O₄, Co_xFe_{3-x}O₄ (x=0.25, 0.5, 1). The results obtained show that varying of alkyne – carbonyl metathesis reaction conditions – starting monomers, reaction time, temperature and ferrite-type catalysts used, lead to the formation of polyphenylacetylenes with a carbonyl- or olefin end groups. The alkyne – carbonyl metathesis is promising method for preparation of organic compounds and polymers with specific properties.

Keywords: alkyne - carbonyl metathesis, polyphenylacetylenes, ferrite catalysts.

INTRODUCTION

The metathesis carbon-carbon bond forming reactions mediated by transition metal catalysts (all variants of olefin metathesis, metathesis polymerization of alkynes, σ -bond metathesis, etc.) are powerful tools in organic synthesis. Over the last decade, it became an efficient tool to accomplish the synthesis of many complex molecules [1, 2].

The spinel ferrites are interesting materials as they can be used in various fields - catalysts, gas sensors, biomedical applications, targeted drug delivery, hyperthermia treatment. Spinel ferrites exhibit many advantages as catalyst - they are cheap, efficient, reusable and recyclable [3]. In their review I. Bauer et al. [4] report the application of various ferrites as catalysts in different reactions. The metathesis reactions have been studied also in [5–7].

The aim of this present paper is a comparative study of our research concerning the synthesis of polyphenylacetylenes with a carbonyl- or olefin end groups, using metathesis reactions and their physicochemical characterization. A new synthetic route for synthesis of substituted polyphenylacetylenes using different ferrite-type catalysts was developed.

The influence of different synthesis conditions - varying the monomer, co-monomer and the nano-sized ferrite-type catalyst on the products obtained in the alkyne-carbonyl metathesis reactions is discussed.

EXPERIMENTAL

Synthetic procedure

The polymerization was performed under nitrogen in a Schlenk flask, equipped with a three way stopcock placed in an oil bath. Starting materials for each synthesis: isobutyraldehyde (C₄H₈O) (Alfa Aesar), 1-phenyl-1-propyne (C₉H₈) (Alfa Aesar) or 1-phenylacetylene (C₈H₆) (Fluka AG), 4 ml solvent 1,2-dichloroethane (C₂H₄Cl₂) and nano-sized ferrite-type catalysts with average crystallite size in 6.5–10 nm. The following co-precipitated ferrite-type materials – Ni_xFe_{3-x}O₄, Mg_xFe_{3-x}O₄ and Co_xFe_{3-x}O₄ (x=0.25, 0.5, 1) – were tested as catalysts. The presence of ferrite and additional iron oxyhydroxide phase has been determined for nickel ferrite-type samples. In the Mg_xFe_{3-x}O₄ (x=0.25) sample non-stoichiometric ferrite phase and additional iron oxyhydroxide were registered. For the materials Mg_xFe_{3-x}O₄ (x=0.5; 1) the ferrite and additional phases iron oxyhydroxides, as well as

* To whom all correspondence should be sent:

E-mail: dimova@polymer.bas.bg

double layered hydroxides have been established. The single non-stoichiometric ferrite $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ ($x=0.25$) and cobalt ferrite-type materials $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ ($x=0.5;1$) containing additional phases – iron oxyhydroxide and double layered hydroxide were also used as catalysts. The synthesis conditions used, according to the end groups of the product, are summarized in Table 1 and Table 2.

1,2-Dichloroethane was dried over CaH_2 then distilled and stored under nitrogen. All starting organic materials were characterized by TLC analysis. The reaction mixture was heated at 80–120 °C and stirred at 400–600 rpm for 4 or 24 hours. After cooling the crude mixture was purified using column chromatography with a mixture hexane:ethyl

acetate = 1:10. After evaporating the solvent viscous liquids (yellow to brown) were obtained [5–7].

Characterization

The FTIR spectra were recorded from thin films on KBr plates, using Fourier infrared spectrometer Bruker-Vector 22 in the region 400–4000 cm^{-1} .

$^1\text{H-NMR}$ analysis was performed on Bruker Avance DRX 250 spectrometer, 250 MHz. The peak of the solvent CDCl_3 ($\delta = 7.25$ ppm) was used as internal standard.

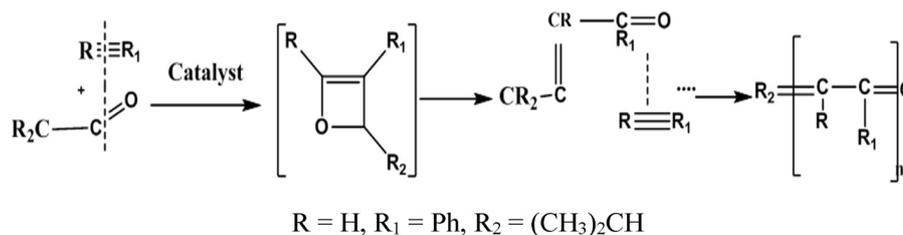
Size exclusion chromatography was used for the determination of the average molecular weight (M_w), number average molecular weight (M_n) and

Table 1. Synthesis conditions of polyphenylacetylene with a carbonyl end group

Name	Monomer	Co-monomer	Catalyst	Yield,%
P1-CO	1-phenylacetylene 0.007 mmol	isobutyraldehyde 0.005 mmol	CoFe_2O_4 0.0001mmol	70
P2-CO	1-phenylacetylene 0.007 mmol	isobutyraldehyde 0.005 mmol	$\text{Co}_{0.5}\text{Fe}_{2.5}\text{O}_4$ 0.0001mmol	80
P3-CO	1-phenylacetylene 0.007 mmol	isobutyraldehyde 0.005 mmol	$\text{Co}_{0.5}\text{Fe}_{2.5}\text{O}_4$ 0.0001mmol	65
P4-CO	1-phenylacetylene 0.007 mmol	isobutyraldehyde 0.005 mmol	$\text{Co}_{0.25}\text{Fe}_{2.75}\text{O}_4$ 0.0001mmol	60
P5-CO	1-phenylacetylene 0.1 mmol	isobutyraldehyde 1 mmol	NiFe_2O_4 0.000011mmol	65
P6-CO	1-phenylacetylene 7 mmol	isobutyraldehyde 5 mmol	$\text{Ni}_{0.5}\text{Fe}_{2.5}\text{O}_4$ 0.000011mmol	76
P7-CO	1-phenylacetylene 7 mmol	isobutyraldehyde 1 mmol	$\text{Ni}_{0.5}\text{Fe}_{2.5}\text{O}_4$ 0,000011 mmol	80
P8-CO	1-phenylacetylene 7 mmol	isobutyraldehyde 5 mmol	$\text{Ni}_{0.25}\text{Fe}_{2.75}\text{O}_4$ 0.000011mmol	Only for analyses
P9-CO	1-phenylacetylene 0.07 mmol	isobutyraldehyde 0.011 mmol	$\text{Mg}_{0.5}\text{Fe}_{2.5}\text{O}_4$ 0.00001mmol	75

Table 2. Synthesis conditions of polyphenylacetylene with an olefin end group

Product	Monomer	Comonomer	Catalyst	Yield, %
P10-OL	1-phenyl-1-propyne 0.007 mmol	isobutyraldehyde 0.005 mmol	$\text{Co}_{0.5}\text{Fe}_{2.5}\text{O}_4$ 0.0001mmol	75
P11-OL	1-phenyl-1-propyne 7 mmol	isobutyraldehyde 1 mmol	$\text{Ni}_{0.5}\text{Fe}_{2.5}\text{O}_4$ 0.000011 mmol	72
P12-OL	1-phenyl-1-propyne 7 mmol	isobutyraldehyde 1 mmol	$\text{Ni}_{0.25}\text{Fe}_{2.75}\text{O}_4$ 0.000011 mmol	Only for analyses
P13-OL	1-phenyl-1-propyne 0.07 mmol	isobutyraldehyde 0.011 mmol	$\text{Mg}_{0.5}\text{Fe}_{2.5}\text{O}_4$ 0.00001mmol	56
P14-OL	1-phenylacetylene 0.07 mmol	isobutyraldehyde 0.011 mmol	MgFe_2O_4 0.00001mmol	65
P15-OL	1-phenylacetylene 0.07 mmol	–	$\text{Mg}_{0.5}\text{Fe}_{2.5}\text{O}_4$ 0.00001mmol	80
P16-OL	1-phenylacetylene 0.07 mmol	isobutyraldehyde 0.011 mmol	$\text{Mg}_{0.25}\text{Fe}_{2.75}\text{O}_4$ 0.00001mmol	72



Scheme 1. Alkyne – carbonyl metathesis polyaddition reaction between phenylacetylene and isobutyraldehyde.

molar mass dispersity of products. The SEC system used (Waters, Millipore Corp., USA), was equipped with a double detection – differential refractometer RI M410 and a UV M490 detector. Three different columns were used – Phenogel 50 A; + Phenogel 100 A; + Phenogel 10000 A) calibrated with PS standards, mobile phase – THF, flow rate – 1 ml/min, pressure – 500 psi and temperature – 40 °C [5–7].

The SEM images were recorded on scanning electron microscope JEOL JSM-T200.

RESULTS AND DISCUSSION

The newly developed one-step route for the preparation of substituted polyphenylacetylene

with a carbonyl or olefin end group is presented in Scheme 1. The products obtained are stable in air, well soluble in common volatile solvents like chlorinated hydrocarbons and exhibit the physical properties of conjugated polymers. The yield of polyphenylacetylenes with a carbonyl or olefin end groups is 60–80% (Table 1 and Table 2).

Another advantage of the reaction is that cheap catalysts are used instead of the well-known ones (Ru, W, Mo).

The FTIR spectra of the products are presented in Fig. 1 and Fig. 2. The FTIR spectra of polyphenylacetylenes with a carbonyl end group, prepared using 1-phenylacetylene as monomer and co-monomer – isobutyraldehyde and nano-sized ferrite-type catalysts – samples $M_xFe_{3-x}O_4$ (M – nickel, cobalt

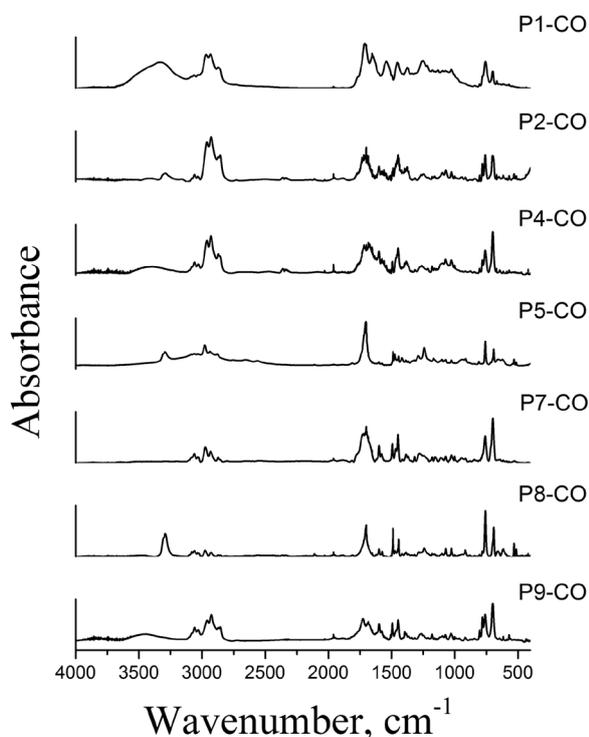


Fig. 1. FTIR spectra of polyphenylacetylene with a carbonyl end group.

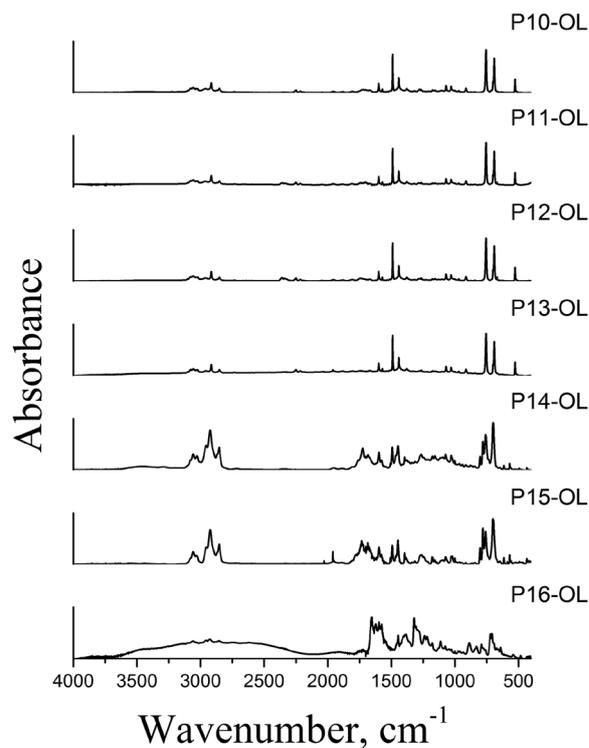


Fig. 2. FTIR spectra of polyphenylacetylene with an olefin end group.

and magnesium; $x=0.25, 0.5, 1$) at different reaction time – 4 or 24 hours are shown in Figure 1. All oligomers showed a band at 1656 cm^{-1} assigned to C=O bond (conjugated ketone end group). Characteristic peaks observed: about 3058 cm^{-1} (=C-H), 2925 cm^{-1} , 2860 cm^{-1} (CH_2 and CH_3). The double bond -C=C- from the phenylene ring appears around 1597 cm^{-1} , the =C-H aromatic vibrations are in the range of $1180\text{--}1029\text{ cm}^{-1}$, while the =CH- vi-

bration from the polymer backbone is at 1448 cm^{-1} . Figure 2 shows the FTIR spectra of polyphenylacetylenes with an olefin end group. The presence of conjugated -C=C- bonds corresponding to the bands at around 1600 cm^{-1} is observed [5–7, 8].

The $^1\text{H-NMR}$ spectra of the synthesized polyphenylacetylenes are shown in Figures 3 and 4. The $^1\text{H-NMR}$ (in CDCl_3) of P2-CO and P9-CO showed characteristic chemical shift for double bonds

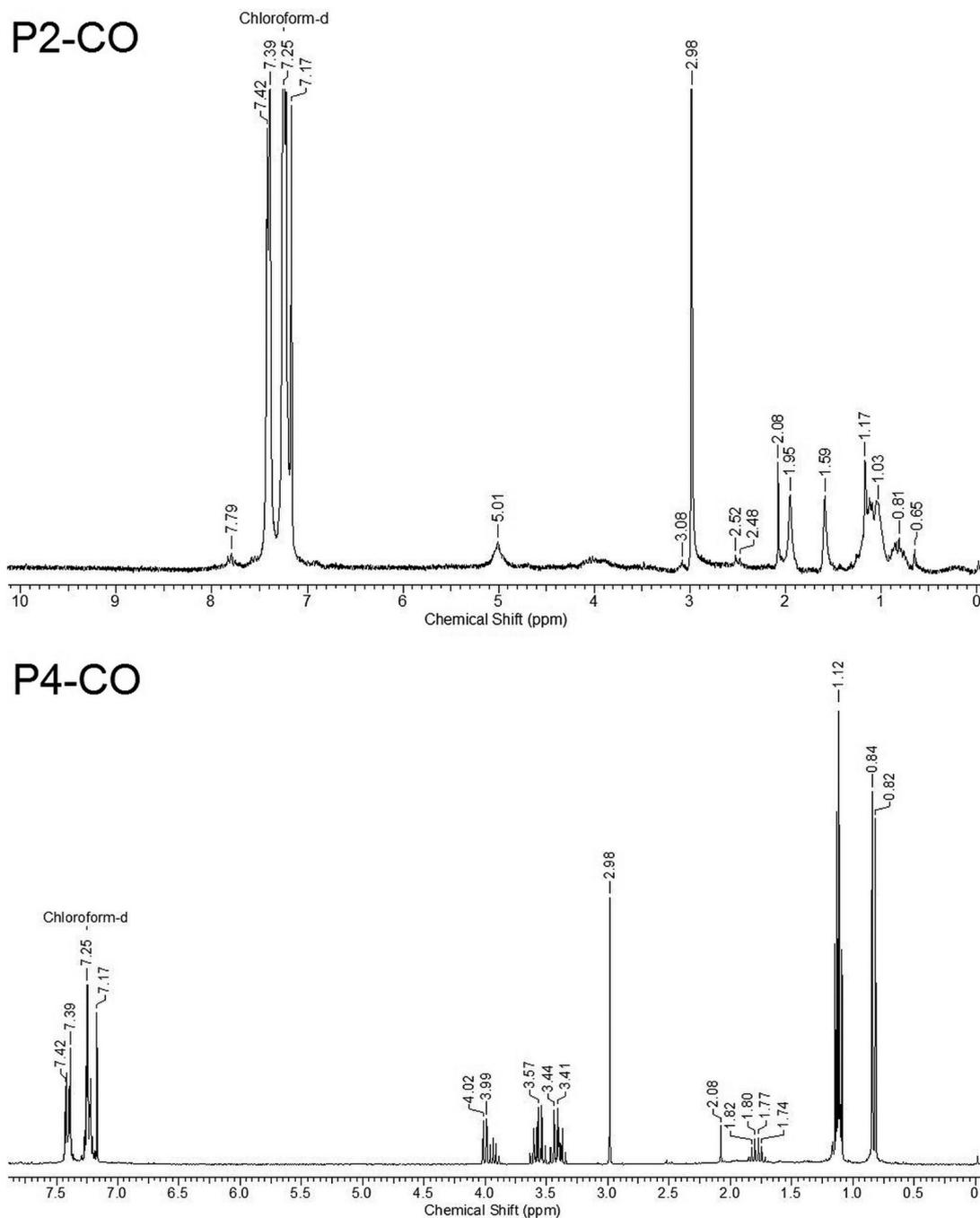
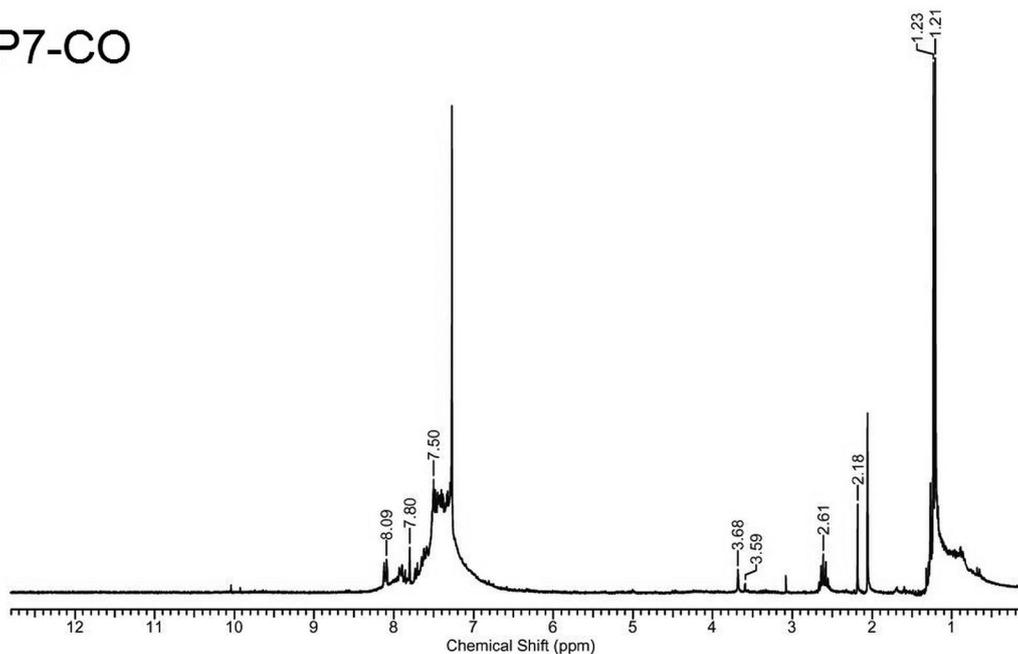


Fig. 3a. $^1\text{H-NMR}$ spectra of polyphenylacetylenes with a carbonyl end group (P2-CO, P4-CO).

P7-CO



P9-CO

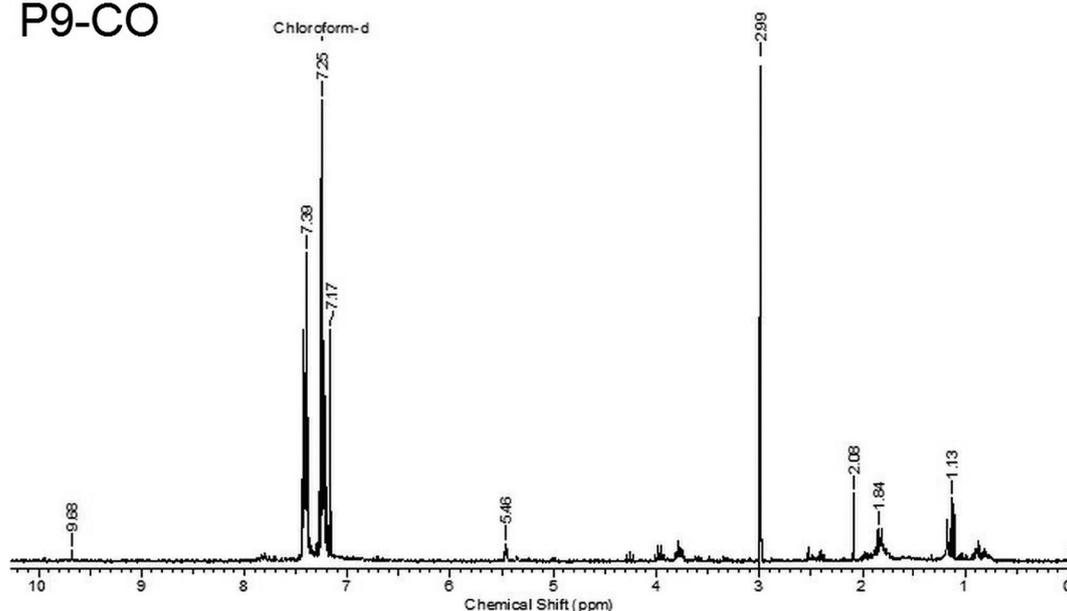


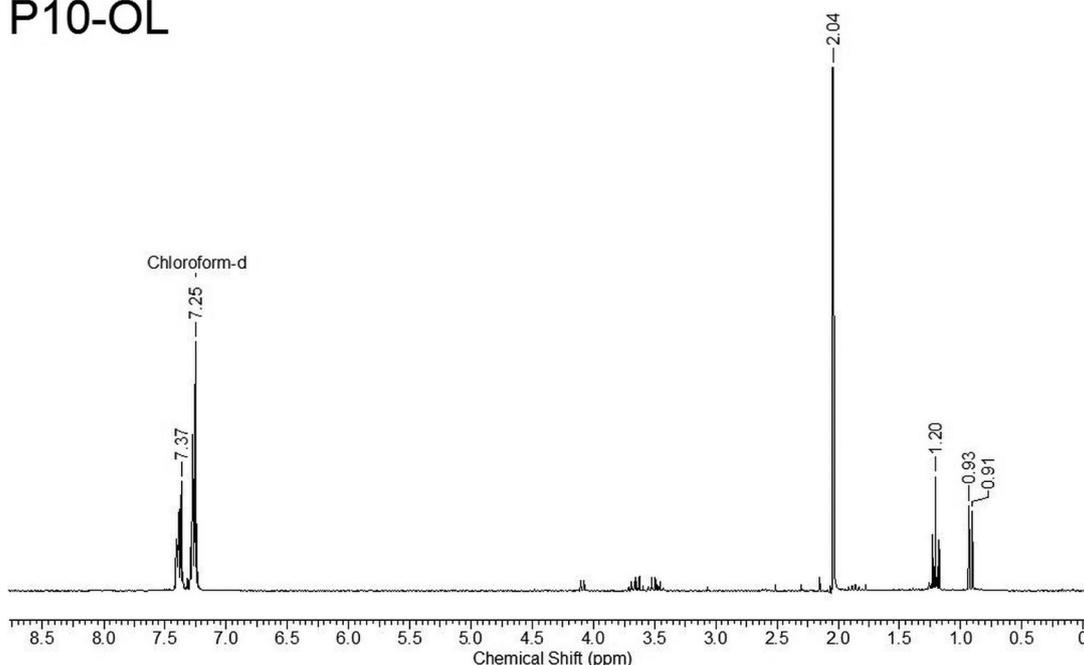
Fig. 3b. ¹H-NMR spectra of polyphenylacetylenes with a carbonyl end group (P7-CO, P9-CO).

around 5.07 and 5.4 ppm. The observed signals in the region 7.3–8 ppm are assigned to the protons characteristic for aromatic rings. The chemical shifts between 1.8–2.5 ppm are attributed to the =CH- protons from the backbone. In the ¹H-NMR spectrum of the predominantly cis-polyphenylacetylene P9-CO, the peak, characteristic for the proton, attached to the cis-conformation of the double bond, is observed at 5.4 ppm [5–7]. From the literature it is

known that if the polymerization of arylacetylenes is catalyzed by W, Mo, Rh, mainly cis-transoidal structure is obtained [9].

Polyphenylacetylene with a carbonyl end group can be prepared using monomer-1-phenylacetylene, co-monomer – isobutyraldehyde and ferrite-type catalysts – Mg_{0.5}Fe_{2.5}O₄, Ni_xFe_{3-x}O₄ and Co_xFe_{3-x}O₄ (x=0.25, 0.5, 1). The use of 1-phenylacetylene, isobutyraldehyde or only 1-phenylacetylene and

P10-OL



P14-OL

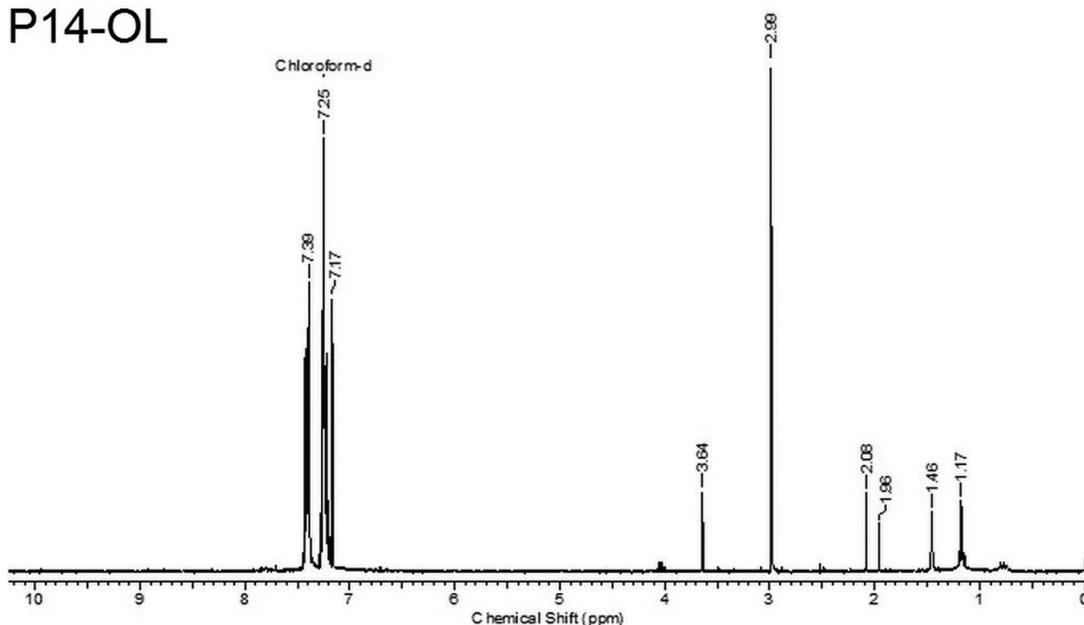


Fig. 4. $^1\text{H-NMR}$ spectra of polyphenylacetylenes with an olefin end group.

$\text{Mg}_x\text{Fe}_{3-x}\text{O}_4$ ($x=0.25, 1$) or $\text{Mg}_{0.5}\text{Fe}_{2.5}\text{O}_4$ as catalysts leads to the formation of polyphenylacetylene with an olefin end group. Polyphenylacetylene with an olefin end group can be obtained also in the presence of monomer-1-phenyl-1-propyne, co-monomer – isobutyraldehyde and ferrite-type catalysts – $\text{Mg}_{0.5}\text{Fe}_{2.5}\text{O}_4$, $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ ($x=0.25, 0.5$) and $\text{Co}_{0.5}\text{Fe}_{2.5}\text{O}_4$.

The SEC analysis of P16-OL and P14-OL showed various fractions with different molecular masses – 10^2 – 10^4 g/mol and multimodal molar mass distribution with dispersity index of 2.5.

The highest molecular masses of P16-OL and P14-OL are 548 and about 17000 g/mol [5–7]. The polymerization carried out in 1,2-dichloroethane results in formation of predominantly oligomer prod-

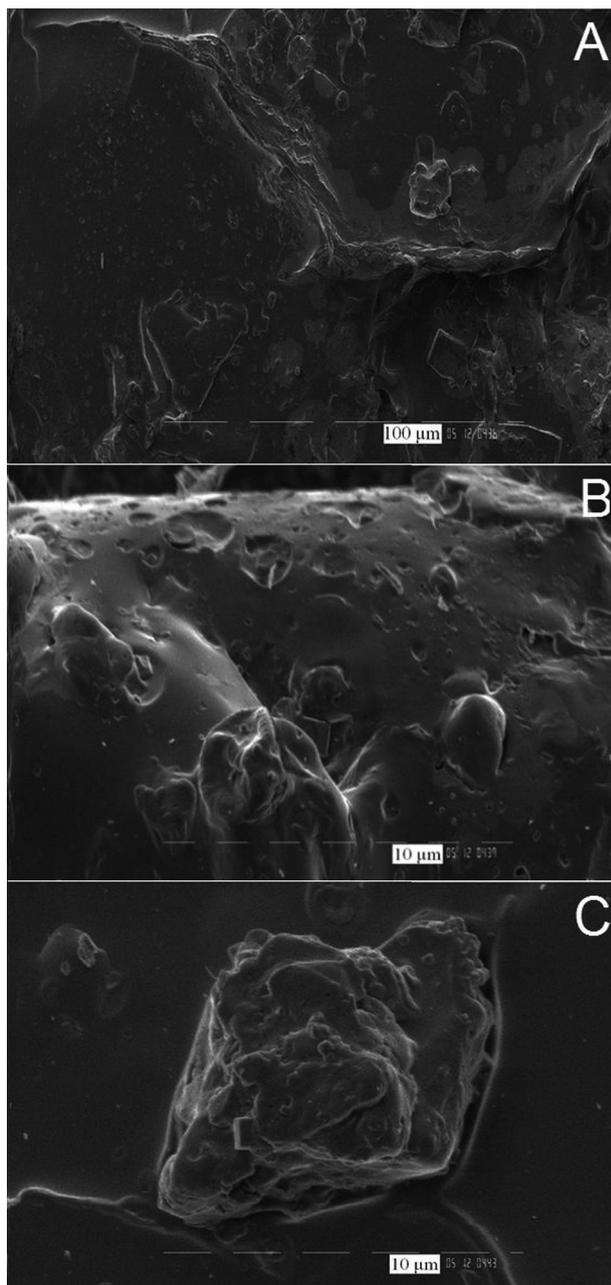


Fig. 5. SEM images of P1-CO at magnifications: 200x (A); 1000x (B); 1000x (C).

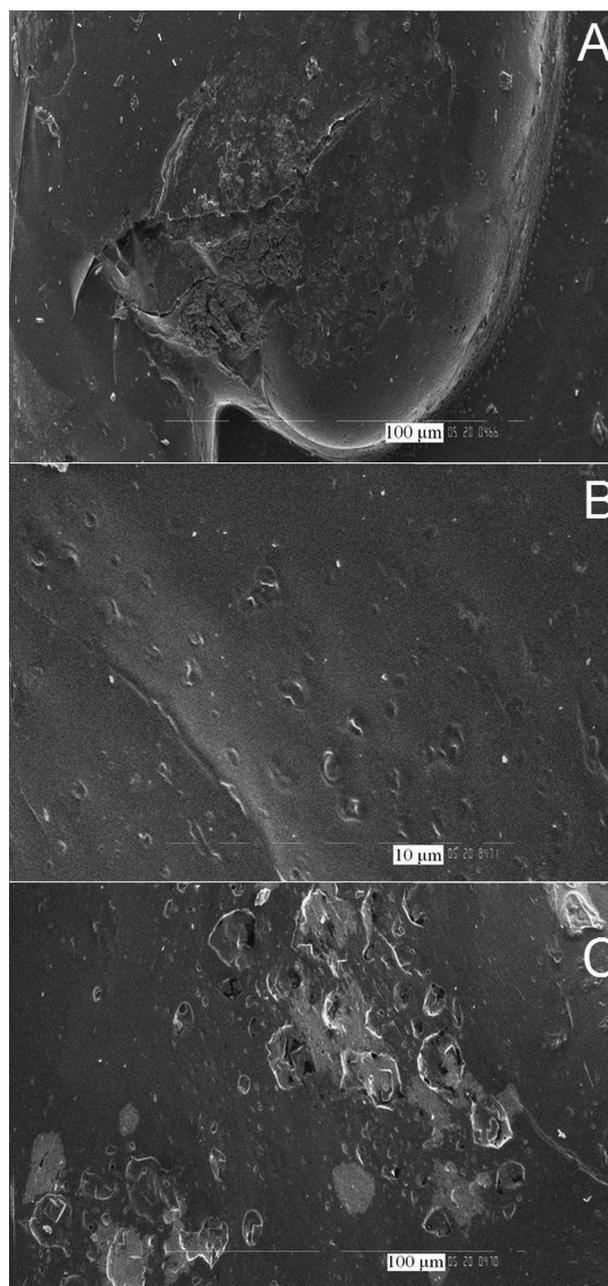


Fig. 6. SEM images of P2-CO at magnifications: 200x (A); 1000x (B); 5000x (C).

uct, irrespectively of the amount of catalyst and the polymerization time.

The SEM images of P1-CO and P2-CO are displayed on Figures 5 and 6 showing different morphological structures of obtained products at different magnifications.

The SEM analysis of the films, prepared from the polymerized samples, show essentially a glass-like matrix structure and enamel-like structure [10].

CONCLUSIONS

The present comparative study shows that by varying the metathesis reaction conditions – starting monomers, reaction time, temperature and ferrite-type catalysts – a series of substituted polyphenylacetylenes with a carbonyl or olefin end groups have been obtained. The structure and chemical composition of these products were investigated in detail

by FTIR, ¹H-NMR spectroscopy and Scanning electron microscopy. The results obtained confirm that the materials prepared are oligomers with an alternating C=C double bond system which limits the conjugation in the backbone, having mainly trans-configuration.

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ПРЕДСТАВЯНЕ НА МЕТАТЕЗНИ РЕАКЦИИ, ИЗПОЛЗВАЙКИ РАЗЛИЧНИ НАНОРАЗМЕРНИ ФЕРИТЕН ТИП КАТАЛИЗАТОРИ

С. С. Димова^{1*}, К. Л. Захариева², Ф. С. Ублеков¹, Хр. П. Пенчев¹

¹ *Институт по полимери, Българска академия на науките, „Акад. Г. Бончев“, бл.103А, 1113 София, България*

² *Институт по катализ, Българска академия на науките, „Акад. Г. Бончев“, бл. 11, 1113 София, България*

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(Резюме)

Тази статия представя сравнително изследване върху метатезна реакция в присъствието на различни наноразмерни феритен тип катализатори. Получените продукти – заместени полифенилацетилени, са охарактеризирани чрез FTIR спектроскопия, ¹H-ЯМР спектроскопия, хроматография с изключване по размера и сканираща електронна микроскопия. Като мономери са използвани – 1-фенилацетилен или 1-фенил-1-пропин, съмономер – изобутиралдехид и различни наноструктурирани феритен тип катализатори – Ni_xFe_{3-x}O₄, Mg_xFe_{3-x}O₄, Co_xFe_{3-x}O₄ (x=0.25, 0.5, 1). Получените резултати показват, че промяната на реакционните условия на алкин-карбониловата метатеза – начални мономери, реакционно време, температура и феритен тип катализатори, води до образуване на полифенилацетилени с крайни карбонилни или олефинови групи. Алкин-карбонилната метатезна реакция е обещаващ метод за получаване на органични съединения и полимери със специфични свойства.