

## METATHESIS OF PHENYLALKYNES AND ALDEHYDE BY NANODIMENSIONAL FERRITE CATALYST

S. Dimova<sup>1</sup>, K. Zaharieva<sup>2</sup>, Ch. Jossifov<sup>1</sup>, Z. Cherkezova-Zheleva<sup>2</sup>, I. Mitov<sup>2</sup>

<sup>1</sup>Institute of Polymers, Bulgarian Academy of Sciences,  
“Acad. G. Bonchev” St., bl. 103A, 1113 Sofia, Bulgaria,  
Telephone number: (+ 359 2) 9796319, fax number:  
(+ 359 2) 8700309, E-mail: silvy\_dimova@abv.bg

<sup>2</sup>Institute of Catalysis, Bulgarian Academy of Sciences,  
“Acad. G. Bonchev” St., bl. 11, 1113 Sofia, Bulgaria,  
E-mail: zaharieva@ic.bas.bg

Received 09 January 2012

Accepted 11 December 2012

---

### ABSTRACT

We performed polymerization by alkyne-carbonyl metathesis with varying of the monomer – 1-phenylacetylene or 1-phenyl-1-propyne and comonomer - isobutyraldehyde at 80°C, at different reaction time 4 and 24 hours in nitrogen media, respectively. In the metathesis experiments nanosized nickel containing ferrite catalysts  $Ni_xFe_{3-x}O_4$  ( $x=0.25, 0.5, 1$ ) with different amount of Ni ions, synthesized by chemical co-precipitation method in our earlier studies were used. The present study finds that, depending on the starting monomer- 1-phenylacetylene or 1-phenyl-1-propyne, the obtained products are two types of substituted polyacetylenes - with a carbonyl end group and with an olefin end group. Various physicochemical analyses - FTIR, Moessbauer, and <sup>1</sup>H-NMR spectroscopy provided us with information about the chemical structure and properties of the prepared products by metathesis and the catalytic behavior of the used nanometer nickel containing ferrite materials.

**Keywords:** alkyne-carbonyl metathesis, substituted polyacetylenes, nanosized ferrite, catalyst

---

### INTRODUCTION

The reactions between alkynes and aldehydes are important transformations in the organic synthesis as they generate new carbon – carbon bonds [1]. This transformation at an atom level is economical an alternative for the use of stabilized Wittig reagents in carbonyl olefination and may be viewed as a formal alkyne-carbonyl metathesis and simultaneous installation of a carbonyl group [2].

A wide variety of  $\pi$ -conjugated polymers have been synthesized, and their physical and chemical properties

have been investigated by many researchers [3]. The current interest in conjugated polymers is due to the substantial  $\pi$ -electron delocalization along their back-bones which leads to interesting optical and nonlinear optical properties and allows them to become good electrical conductors, typically when oxidized or reduced. These properties may develop in a variety of practical applications such as information storage and optical signal processing, substitutes for batteries and materials for solar energy conversion, etc. [4, 5]. Conjugated polymers are a novel class of semiconductors that combine the optical and electronic properties of semiconduc-

tors with the processing advantages and mechanical properties of polymers [6]. They show great promise as the semiconducting layer in devices like polymer light emitting diodes (PLEDs), organic field effect transistors (OFETs) and organic photovoltaic (OPV) cells [7, 8]. Conjugated polymers have also attracted great attention as optical limiting materials due to their large third order nonlinearity, fast nonlinear response time, high damage threshold, ease of processing, versatile structural modification, and their applicability over a wide wavelength range [9]. The opto-electronic properties vary considerably, depending on the extent of conjugation length between the consecutive repeating units [10].

The aim of the present research was to study alkyne-carbonyl metathesis and form polyphenylacetylenes with a carbonyl end group and with an olefin end group by using of nanosized nickel containing ferrites  $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$  ( $x=0.25, 0.5, 1$ ) as catalysts. Our idea was to use the initial monomers – 1-phenylacetylene or 1-phenyl-1-propyne in excess, compared to isobutyraldehyde and the obtained product to be a substituted polyacetylene with end groups. The carbonyl compound acts as an initiator. The catalytic behavior of the nanodimensional ferrite catalysts and the physicochemical properties of prepared products at different synthesis conditions were investigated by instrumental methods - Moessbauer, FTIR and  $^1\text{H-NMR}$  spectroscopy.

## EXPERIMENTAL

### Materials and methods

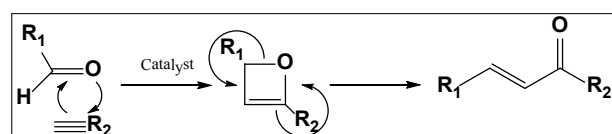
The polymerization was carried out under nitrogen atmosphere in a Schlenk flask equipped with a three-way stopcock placed in an oil bath. In the metathesis reactions as reagents were used 0.080 mmol 1-phenylacetylene ( $\text{C}_8\text{H}_6$ ) (Fluka AG) or 1-phenyl-1-propyne ( $\text{C}_9\text{H}_8$ ) (Alfa Aesar), 0.011 mmol isobutyraldehyde ( $\text{C}_4\text{H}_8\text{O}$ ) (Alfa Aesar), 4 ml solvent 1,2-dichloroethane ( $\text{C}_2\text{H}_4\text{Cl}_2$ ) and 0.011  $\mu\text{mol}$  nanosized ferrite catalysts. The 1,2-dichloroethane was dried over  $\text{CaH}_2$  then distilled, left at room temperature and blown with nitrogen. All starting organic materials were characterized by TLC analysis. The nanodimensional ferrite catalysts  $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$  ( $x=0.25, 0.5, 1$ ) were obtained by the co-precipitation procedure, conducted with aqueous solutions of

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and precipitant  $\text{NaOH}$ , described [11,12]. The mixture was stirred with a rate of 400-600 rpm and heated at  $80^\circ\text{C}$  for 4 and 24 hours. Then it was cooled. After that the solvent was removed on a rotary vacuum evaporator RVO-64. The crude mixture was purified by column chromatography with a mixture hexane: ethyl acetate = 1:10. The product was isolated as an yellow viscous liquid.

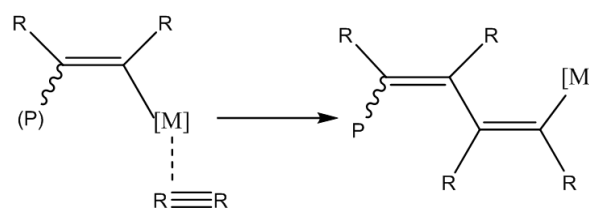
### Characterizations

The products prepared by metathesis in the catalytic experiments were studied by the following techniques:

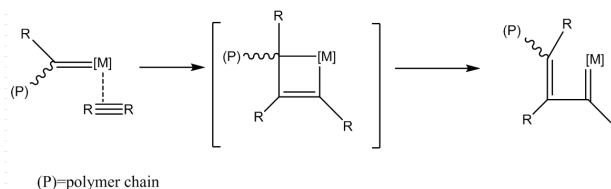
$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) spectroscopy was performed using Bruker Avance DRX 250 spectrometer at 250 MHz. The chemical shifts in the  $^1\text{H-NMR}$  measurements are presented in ppm units. FTIR spectra were recorded on a Fourier infrared spectrometer Bruker-Vector 22 using KBr plate on which the film was studied in the  $400\text{-}4000\text{ cm}^{-1}$  range. Moessbauer studies were obtained with the apparatus of Wissenschaftliche Elektronik GmbH, working with a constant acceleration mode,  $^{57}\text{Co}/\text{Cr}$  source,  $\alpha\text{-Fe}$  standard. A computer fitting was made to establish the parameters of hyperfine interactions of Moessbauer spectral components: isomer shift (IS), quadrupole splitting (QS), hyperfine effective magnetic



Scheme 1



Scheme 2



(P)=polymer chain

Scheme 3

field in the site of iron nuclei ( $H_{\text{eff}}$ ), line widths (FW) and component relative weights (G).

## RESULTS AND DISCUSSION

The alkyne-carbonyl metathesis can be presented with Scheme 1 (where  $R_1$ ,  $R_2$  = alkyl, aryl and Catalyst =  $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$  ( $x=0.25, 0.5, 1$ )) [13].

Depending on the initiating system two different mechanisms (Scheme 2 or Scheme 3) for propagation of "live" polymerization, discussed in [14] can be accepted:

The chemical structure of the reaction products obtained by alkyne-carbonyl metathesis was proved by FTIR spectroscopy. Fig. 1 illustrates the FTIR spectra of polyphenylacetylene with a carbonyl end group, prepared using as monomer 1-phenylacetylene, comonomer - isobutyraldehyde and nanosized nickel containing ferrite catalysts - samples  $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$  ( $x=0.25, 0.5, 1$ ) at

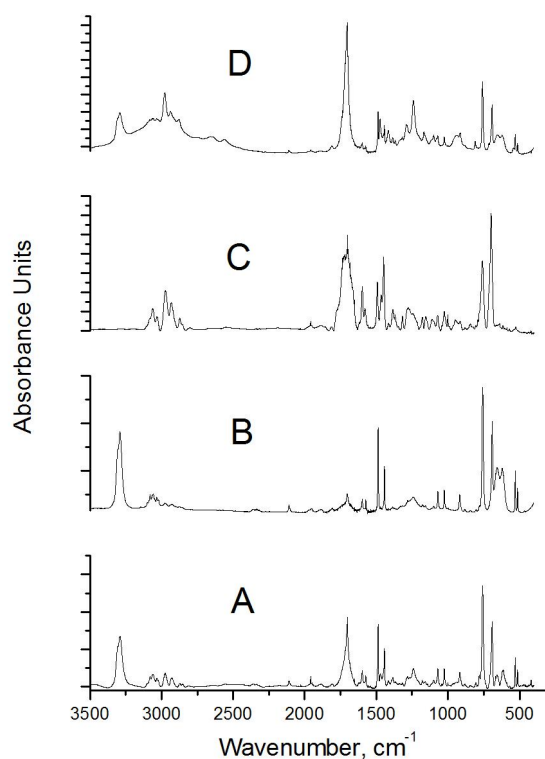


Fig. 1. FTIR spectra of polyphenylacetylenes with a carbonyl end group, prepared by the metathesis reaction using 1-phenylacetylene, isobutyraldehyde and nanosized nickel containing ferrite catalysts: **A** -  $\text{Ni}_{0.25}\text{Fe}_{2.75}\text{O}_4$  for 4 hours, **B** -  $\text{Ni}_{0.5}\text{Fe}_{2.5}\text{O}_4$  for 4 hours, **C** -  $\text{Ni}_{0.5}\text{Fe}_{2.5}\text{O}_4$  for 24 hours and **D** -  $\text{NiFe}_2\text{O}_4$  for 4 hours.

different reaction time - 4 and 24 hours. The absorption peaks around  $1700\text{ cm}^{-1}$  are attributed to the stretching vibrations of the carbonyl groups. In the FTIR spectra of polyphenylacetylene with an olefin end group, obtained with 1-phenyl-1-propyne, isobutyraldehyde and nanodimensional nickel containing ferrite catalysts  $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$  ( $x=0.25, 0.5$ ) for 4 hours (see Fig. 2) the presence of conjugated  $\text{C}=\text{C}$  bonds corresponding to the bands at around  $1600\text{ cm}^{-1}$  is observed [15].

Fig. 3 and Fig. 4 show  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) spectra of the polyphenylacetylenes with carbonyl end group. The chemical shift about 10 ppm corresponds to the carbonyl group. The peaks observed in the range 7.2 - 7.5 ppm are assigned to the  $\text{C}_6\text{H}_5$  group. The signals at 1.3 ppm and 2 - 2.3 ppm are characteristics for the presence of  $\text{R-CH}_2$  and  $\text{R}_2\text{-CH}_2$ , respectively. The  $^1\text{H-NMR}$  results are in agreement with investigations concerning FTIR analyses of the obtained products presented in this paper.

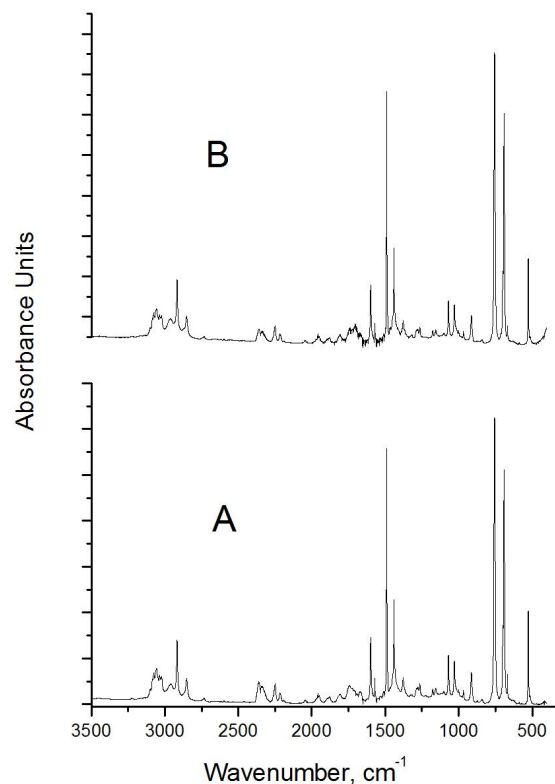


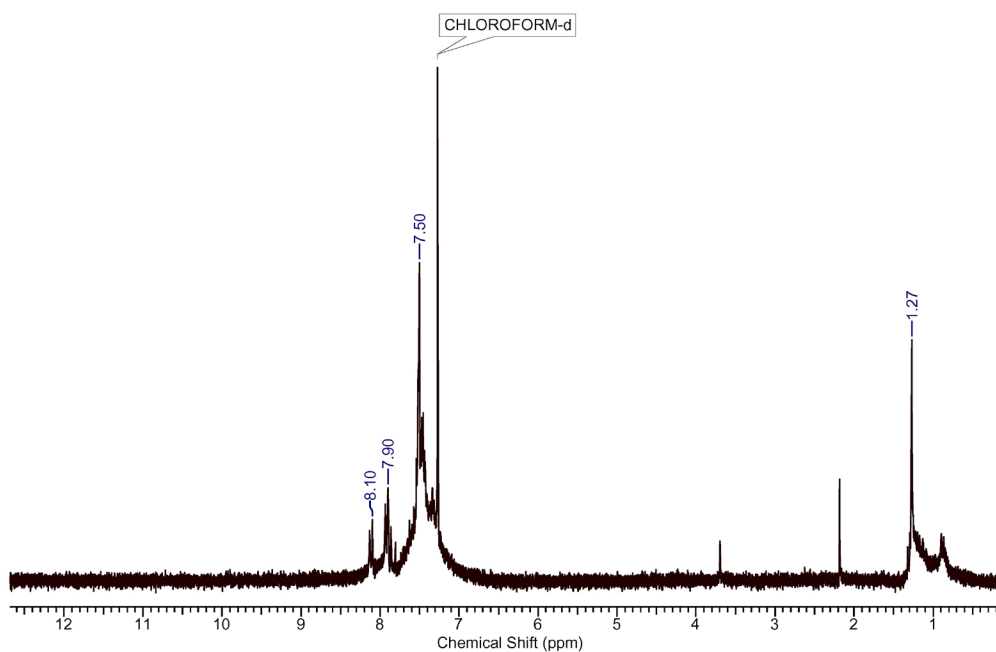
Fig. 2. FTIR spectra of polyphenylacetylenes with an olefin end group, prepared by the metathesis reaction using 1-phenyl-1-propyne, isobutyraldehyde and nanosized nickel containing ferrite catalysts  $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$  ( $x=0.25, 0.5$ ) for 4 hours.

Table 1. Synthesis conditions and yield of products by the alkyne-carbonyl metathesis reaction.

Number	Monomer, ml	Comonomer, ml	Catalyst	Temperature, °C	Time, h	Yield, %
1	1-phenylacetylene 0.8 ml	isobutyraldehyde 0.5 ml	Ni <sub>0.25</sub> Fe <sub>2.75</sub> O <sub>4</sub>	80	4	70
2	1-phenylacetylene 0.8ml	isobutyraldehyde 0.5ml	Ni <sub>0.5</sub> Fe <sub>2.5</sub> O <sub>4</sub>	80	4	76
3	1-phenylacetylene 1ml	isobutyraldehyde 0.1ml	Ni <sub>0.5</sub> Fe <sub>2.5</sub> O <sub>4</sub>	80	24	80
3a	1-phenylacetylene 1 ml	isobutyraldehyde 0.1ml	NiFe <sub>2</sub> O <sub>4</sub>	80	4	65
4	1-phenyl-1-propyne 1 ml	isobutyraldehyde 0.1ml	Ni <sub>0.25</sub> Fe <sub>2.75</sub> O <sub>4</sub>	80	4	Only for analyses
5	1-phenyl-1-propyne 1ml	isobutyraldehyde 0.1 ml	Ni <sub>0.5</sub> Fe <sub>2.5</sub> O <sub>4</sub>	80	4	72

Table 2. Moessbauer parameters of the nanosized nickel containing ferrite catalysts, after catalytic tests.

Sample	Components	IS, mm/s	QS, mm/s	FMHW, mm/s	G, %
Ni <sub>0.25</sub> Fe <sub>2.75</sub> O <sub>4</sub>	Dbl 1	0.37	0.56	0.32	59
	Dbl 2	0.37	0.94	0.35	41
Ni <sub>0.5</sub> Fe <sub>2.5</sub> O <sub>4</sub>	Dbl 1	0.36	0.55	0.34	52
	Dbl 2	0.37	0.93	0.38	48
NiFe <sub>2</sub> O <sub>4</sub>	Dbl 1	0.36	0.54	0.33	63
	Dbl 2	0.36	0.90	0.35	37

Fig. 3. <sup>1</sup>H-NMR spectrum of polyphenylacetylene with a carbonyl end group, prepared by the metathesis reaction using 1-phenylacetylene, isobutyraldehyde and nanosized nickel containing ferrite catalyst Ni<sub>0.5</sub>Fe<sub>2.5</sub>O<sub>4</sub> for 4 hours.

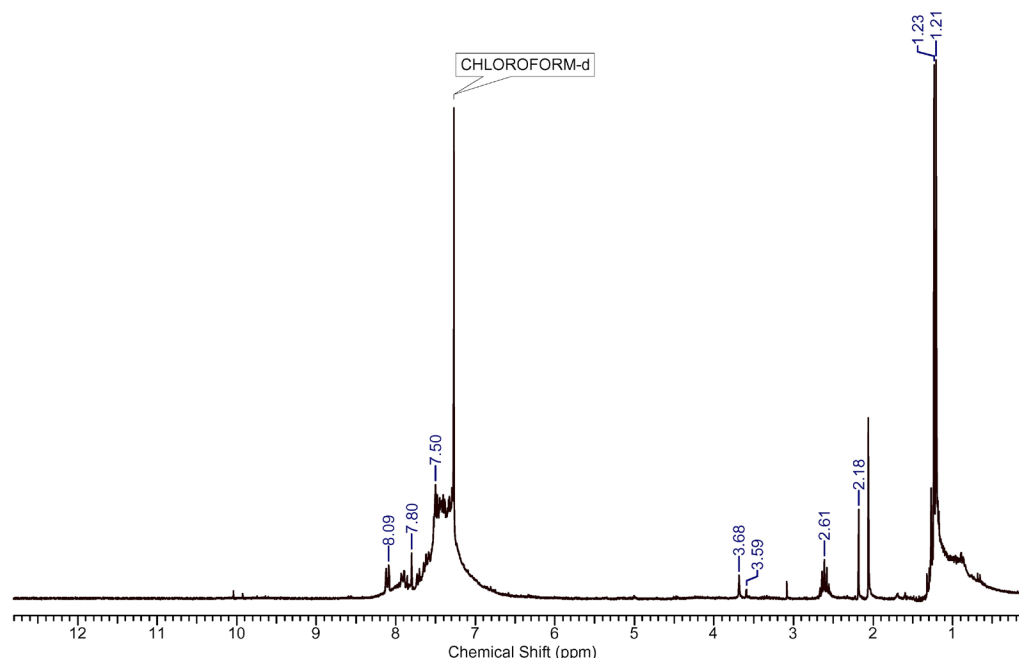


Fig. 4.  $^1\text{H}$ -NMR spectrum of polyphenylacetylene with a carbonyl end group, prepared by the metathesis reaction using 1-phenylacetylene, isobutyraldehyde and nanosized nickel containing ferrite catalyst  $\text{Ni}_{0.5}\text{Fe}_{2.5}\text{O}_4$  for 24 hours.

From the data given in Table 1 we may conclude that the isolated yield of obtained polyphenylacetylenes with an end groups is 70 - 80%.

In our previous research [11, 12] nickel containing ferrite samples  $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$  ( $x=0.25, 0.5, 1$ ) have been prepared by the wet chemical method and investigated by X-ray diffraction analysis, thermal analysis (TG, DTG and DTA), Moessbauer and FTIR spectroscopy. The results confirmed a spinel structure of the ferrite materials, average crystallite size about 10 nm and also the existence of iron ions, coordinated in an oxyhydroxide phase ( $\beta\text{-FeOOH}$ ) [11, 12]. The structural changes of nanodimensional nickel containing ferrite catalysts, after the metathesis reactions are examined with Moessbauer spectroscopy. Registered Moessbauer spectra of the samples after the catalytic tests (Fig. 5) reveal nonsignificant change of the materials when compared with the Moessbauer results of the initial nanosized nickel containing samples  $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$  ( $x=0.25, 0.5, 1$ ) discussed in [11, 12]. The doublet type spectra are preserved and the best spectra fit includes superposition of two doublet components. Calculated hyperfine parameters (presented in Table 2) could be attributed to the presence of iron ions in the ferrite phase with size below 10 nm

and superparamagnetic behaviour, i.e. ultradisperse ferrite particles [16, 17].

## CONCLUSIONS

We present a new method for the preparation of substituted polyacetylenes. The appropriate metathesis conditions for preparing of polyphenylacetylenes with a carbonyl end group and with an olefin end group have been found. The nanodimensional ferrite materials  $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$  ( $x=0.25, 0.5, 1$ ) have been used successfully as catalysts for alkyne-carbonyl metathesis in our experiments. The structure of the reaction products and the nanosized nickel containing ferrite catalysts is confirmed by FTIR, Moessbauer and  $^1\text{H}$ -NMR measurements. The Moessbauer analysis indicates that nickel containing ferrite catalysts consist of superparamagnetic nanosized particles. The investigation shows that the obtained polyphenylacetylenes with a carbonyl end group and polyphenylacetylenes with an olefin end group are oligomers. The use of catalysts for alkyne carbonyl metathesis and the mechanism of this alternative reaction are still under active development.

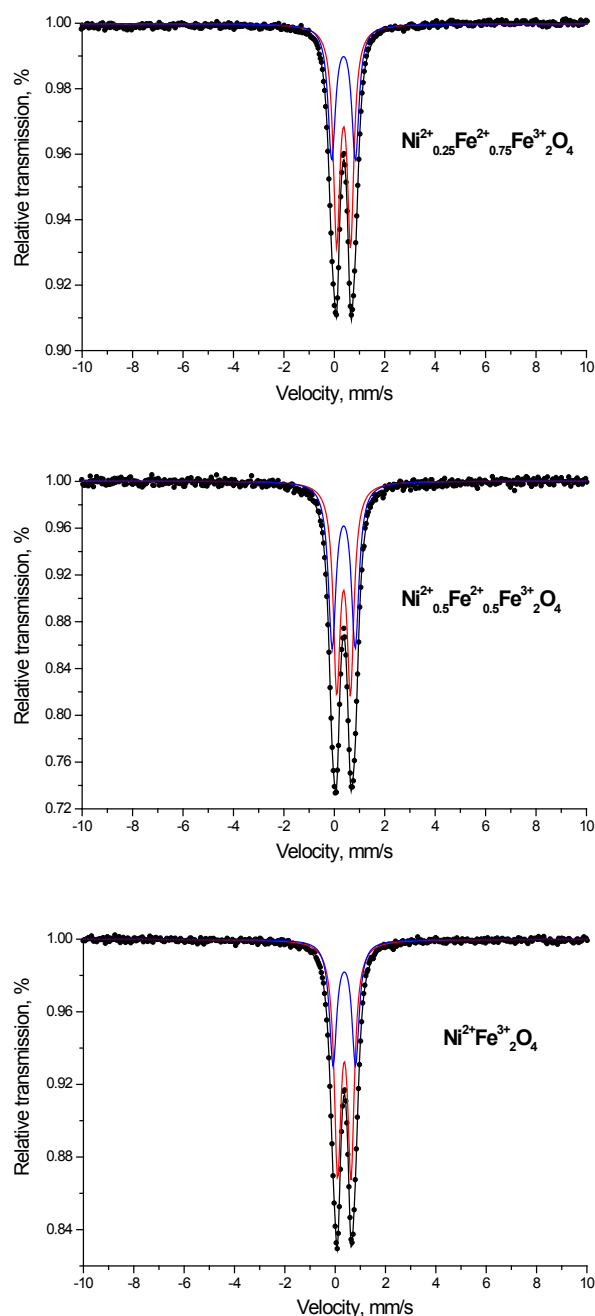


Fig. 5. Moessbauer spectra of the used nanosized nickel containing ferrite catalysts  $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$  ( $x=0.25, 0.5, 1$ ), after catalytic tests.

#### Acknowledgements

The present study is financially supported by the Bulgarian Science Fund at the Ministry of Education, Youth and Science through projects DFNI-E01/7/2012; DID 02-38/2009 and by the Institute of polymers - BAS.

#### REFERENCES

1. Ganapathy S. Viswanathan, Chao-Jun Li, A highly stereoselective, novel coupling reaction between alkynes and aldehydes, *Tetrahedron Letters*, **43**, 2002, 1613–1615.
2. J.U. Rhee, M.J. Krische, Alkynes as synthetic equivalents to stabilized Wittig reagents: Intra- and intermolecular carbonyl olefinations catalyzed by Ag(I),  $\text{BF}_3$ , and  $\text{HBF}_4$ , *Organic Letters*, **7**, 12, 2005, 2493 - 2495.
3. Takakazu Yamamoto, Take-aki Koizumi, Synthesis of  $\pi$ -conjugated polymers bearing electronic and optical functionalities by organometallic polycondensations and their chemical properties, *Polymer*, **48**, 19, 2007, 5449-5472.
4. W.J. Feast, J. Tsibouklis, K.L. Pouwer, L. Groenendaal, E. W. Meijer, Synthesis, processing and material properties of conjugated polymers, *Polymer*, **37**, 22, 1996, 5017-5047.
5. F. Babudri, G. M. Farinola, F. Naso, Synthesis of conjugated oligomers and polymers: the organometallic way, *J. Mater. Chem.*, **14**, 2004, 11 – 34.
6. Fumitomo Hide, María A. Díaz-García, Benjamin J. Schwartz, Alan J. Heeger, New developments in the photonic applications of conjugated polymers, *Acc. Chem. Res.*, **30**, 10, 1997, 430-436.
7. Masaki Horie, I-Wen Shen, Sachetan M. Tuladhar, Henry Leventis, Saif A. Haque, Jenny Nelson, Brian R. Saunders, Michael L. Turner, Poly(thienylenevinylene) prepared by ring-opening metathesis polymerization: Performance as a donor in bulk heterojunction organic photovoltaic devices, *Polymer*, **51**, 7, 2010, 1541–1547.
8. Jian Chen, Min-Min Shi, Xiao-Lian Hu, Mang Wang, Hong-Zheng Chen, Conjugated polymers based on benzodithiophene and arylene imides: Extended absorptions and tunable electrochemical properties, *Polymer*, **51**, 13, 2010, 2897-2902.
9. Shouchun Yin, Hongyao Xu, Wenfang Shi, Yachen Gao, Yinlin Song, Jacky Wing Yip Lam, Ben Zhong Tang, Synthesis and optical properties of polyacetylenes containing nonlinear optical chromophores, *Polymer*, **46**, 18, 2005, 7670–7677.



10. Juan Manuel Reyna-González, Martha Aguilar-Martínez, Alberto García-Concha, Celso Palomar, Ernesto Rivera, A comparative investigation between poly(1-ethynylpyrene) and poly(1,6-(3-ethynylpyrenylene)): Influence of the structure on the thermal, optical, electrochemical properties and conductivity, *Synthetic Metals*, **159**, 7-8, 2009, 659–665.
11. Z. Cherkezova-Zheleva, K. Zaharieva, B. Kunev, M. Shopska, I. Mitov, Synthesis and characterization of ferrite nanosized materials, *Nanoscience & Nanotechnology*, **12**, edited by E. Balabanova and E. Mileva, 2012, 123-126.
12. Z. Cherkezova-Zheleva, K. Zaharieva, V. Petkova, B. Kunev, I. Mitov, Preparation and investigation of nanodimensional nickel ferrite, *Bulgarian Chemical Communications*, **44**, Proceedings of the III<sup>rd</sup> National Crystallographic Symposium, 2012, 24-29.
13. A. Saito, M. Umakoshi, N. Yagyu, Y. Hanzawa, Novel one-pot approach to synthesis of indanones through Sb(V)-catalyzed reaction of phenylalkynes with aldehydes, *Organic Letters*, **10**, 9, 2008, 1783 - 1785.
14. M.G. Mayershofer, O. Nuyken, Living polymerization of substituted acetylenes, *J. Polym. Sci. Part A : Polym. Chem.*, **43**, 2005, 5723 -5747.
15. J.M. Sibanyoni, G.B. Bagihalli, S.F. Mapolie, Binuclear Pd-methyl complexes of N,N'-{1, n}-alkanediyl-bis(pyridinyl-2-methanimine) ligands (n = 5, 8, 9, 10 and 12): Evaluation as catalysts precursors for phenylacetylene polymerization, *J. Organometallic Chem.*, **700**, 2012, 93-102.
16. V. Šepelak, Nanocrystalline materials prepared by homogeneous and heterogeneous mechanochemical reactions, *Ann. Chim. Sci. Mat.*, **27**, 6, 2002, 61 - 76.
17. U. Schwertmann, R. Cornell, *Iron Oxides in the Laboratory*, Weinheim, New York-Basel-Cambridge, 1991.