Journal of International Scientific Publications: Materials, Methods and Technologies

Volume 8, ISSN 1314-7269 (Online), Published at: http://www.scientific-publications.net

SYNTHESIS AND CHARACTERIZATION OF OLIGOMERIC CONJUGATED STRUCTURES VIA COUPLING REACTION USING MAGNESIUM FERRITE TYPE CATALYST

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Abstract

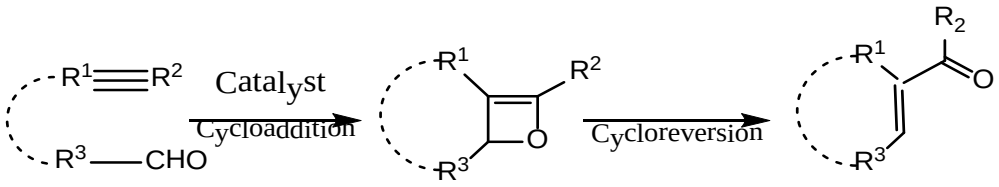
During the last few years the interest in synthesis and characteristics of well-defined oligomeric conjugated structures is constantly growing. In this study new catalysts - nanostructured magnesium ferrite type materials ($MgFe_2O_4$, $Mg_{0.5}Fe_{2.5}O_4$, $Mg_{0.25}Fe_{2.75}O_4$) - have been used for metathesis type coupling of alkynes and aldehyde. Substituted polyphenylacetylene from 1-phenylacetylene or 1-phenyl-1-propyne and isobutyraldehyde have been synthesized. Structure and molecular mass of the obtained substituted polyphenylacetylenes have been characterized by ^1H NMR, Fourier transformation infrared spectroscopy, Size exclusion chromatography (SEC). The results obtained show the presence of a conjugated double bond and a carbonyl group (confirmed by ^1H NMR and FTIR spectra) in the synthesized products. The substituted polyphenylacetylenes (PPA-1 and PPA-4) exhibit good electroconductivity. The catalytic behavior of magnesium ferrite type materials after the reaction was tested by Moessbauer spectroscopy. The prepared products could find a potential application in electronic devices.

Key words: *substituted polyphenylacetylene, coupling reaction, nanodimensional magnesium ferrite type catalysts, ^1H NMR, FTIR*

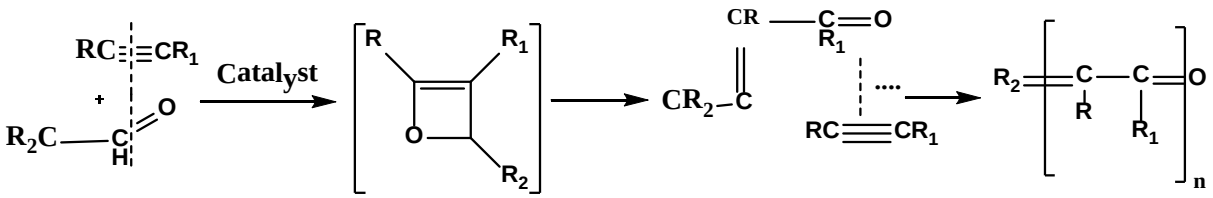
1. INTRODUCTION

It has been established that the electrical, magnetic and optical properties of polyacetylenes are based on the arrangement of alternating double and single bonds along the polymer backbone. Introduction of appropriate substituents in the chain results in improved stability, processability and solubility (Karim et. 1999)). Polyacetylene has been commonly used as a component in electronic circuits like the cell dual emission light (LED) light emitting diodes and has found pharmaceutical application as well, (Mandeel et al. 2012). Substituted polyacetylene and liquid crystals are widely used in contemporary optical display systems (Tang et al. 1998). The main chains of substituted polyacetylenes consist of alternating single and double C-C bonds. Based on main-chain configuration and type of substituents, the main-chain double bonds are more or less conjugated. Such covalent structure depending on the substituents determines the unique properties of substituted polyacetylenes (Trhlíková et al. 2011). Attachment of aromatic substituents to the polyacetylene backbone is a possible way to overcome problems associated with intractability and thermal degradation (Mandeel et al. 2012). Masuda et al. obtained poly(phenylacety1ene)s using polymerization at 30^o C catalyzed by WCl_6 or $MoCI_5$ in several solvents (C_6H_6, CCl_4, $CHCI_3$ and CH_2Cl_2) (Masuda et al. 1975). The polyphenylacetylene possesses four possible geometries as trans-transoidal, cis-transoidal, trans-cisoidal and cis-cisoidal, easily distinguished by IR and ^{1}H-NMR spectroscopy (Rivera, 2004). Cis-transoidal (orange, soluble, and of low crystallinity) and cis-cisoidal (red, insoluble, and highly crystalline) polyphenylacetylenes (PPA) were synthesized by Ziegler-Natta catalysts and trans-cisoidal (yellow, soluble, and amorphous) polyphenylacetylenes were produced by using phosphine complexes, $TiCl_4$ and by thermal initiation (Simionescu et al. 1977). The aldolic polycondensation of phenylacetaldehyde renders polyphenylacetylene (Cataldo, 1996). New substituted polyacetylenes with very high molecular mass ($M_w = 10^4–10^6$) using different catalysts based on group 5, 6, and 9 transition metals (Nb, Ta, Mo, W, and Rh) have been reported (Masuda, 2007). Nano-beads of a polyphenylacetylene were prepared successfully by catalytic emulsion polymerisation technique (D'Amato et al. 2003).

The objective of our study was to obtain substituted polyphenylacetylenes using new nanodimensional magnesium ferrite type catalysts $Mg_xFe_{3-x}O_4$ (x=0.25, 0.5, 1) in alkyne-carbonyl coupling reactions between 1-phenylacetylene or 1-phenyl-1-propyne and isobutyraldehyde (see Scheme 1 and Scheme 2). The initiator of the reaction can be a comonomer-carbonyl compound. The structure and chemical composition of the synthesized oligomeric products and ferrite catalysts were studied by FTIR, ^{1}H NMR and Moessbauer spectroscopy techniques. The electroconductivity of the prepared samples has been measured as well.



Scheme 1. Alkyne-carbonyl coupling reaction.



R=H, R_1=Ph, R_2= $(CH_3)_2CH$

Scheme 2. Design of polyphenylacetylene by alkyne-carbonyl coupling reaction.

2. EXPERIMENTAL

2.1. Materials

All chemicals were used as received: 1-phenylacetylene (C_8H_6) (Fluka AG), 1-phenyl-1-propyne (C_9H_8) (Alfa Aesar), isobutyraldehyde (C_4H_8O) (Alfa Aesar) was used as momoners. 1,2-dichloroethane ($C_2H_4Cl_2$) from Fluka AG was used as the solvent for the copolymerization. All other used chemicals were received from Fluka.

2.2. Measurements

The synthesized substituted polyphenylacetylenes and ferrite type catalysts are investigated using different methods:

FTIR spectroscopy were performed on a Fourier infrared spectrometer Bruker-Vector 22. The obtained samples as film on KBr plate were investigated in the 400-4000 cm^{-1} range.

^1H, ^{13}C NMR spectra were recorded with by Bruker Avance DRX 250 spectrometer at 250 MHz in $CDCl_3$. Chemical shifts (δ) are expressed in parts per million (ppm) and are referenced to $CDCl_3$ (δ = 7.25 ppm) as an internal standard.

The number average molecular weight (M_n), average molecular weight (M_w), and molar mass dispersity of obtained products were determined by means of a size exclusion chromatography (SEC) system Waters equipped with a double detection - differential refractometer RI M410 and a UV M490 detector. The analyses were performed on a three columns - Phenogel 50 A; + Phenogel 100 A; + Phenogel 10000 A) calibrated with PS standards, mobile phase - THF, flow rate - 1 ml/min, temperature - 40 ^oC and pressure - 500 psi.

The electroconductivity of samples PPA-1 and PPA-4 was measured by the four-probe in plane method at RT (Tesla multimeter BM518). The products were prepared as a thin film and $1x10^{-3}$ cm thickness.

Moessbauer investigations of nanosized magnesium ferrite type catalysts were recorded with the apparatus of Wissenschaftliche Elektronik GmbH, working with a constant acceleration mode, $^{57}Co/Cr$ source, α-Fe standard. The parameters of hyperfine interactions of Moessbauer spectral components as isomer shift (IS), quadrupole splitting (QS), hyperfine effective magnetic field in the site of iron nuclei (H_{eff}), line widths (FW) and component relative weights (G) were determined by a computer fitting.

2.3. Synthetic procedure

Polymerization was conducted in a Schlenk flask equipped with a three-way stopcock under an argon atmosphere at room temperature and heated at 80^oC - 120^oC. The appropriate amounts of monomers 0.07 mmol

1-phenylacetylene or 0.07 mmol 1-phenyl-1-propyne, 0.011 mmol, comonomer - isobutyraldehyde, 4 ml 1,2-dichloroethane ($C_2H_4Cl_2$) and 0.010 µmol nanostructure magnesium ferrite type catalysts $Mg_xFe_{3-x}O_4$ (x=0.25, 0.5, 1) were mixed. The synthesis conditions in summary are presented in Table 1. The solvent 1,2-dichloroethane was dried over CaH_2 then distilled, left at room temperature and blown with argon. The initial organic reagents were tested by TLC analysis. The nanosized magnesium ferrite type catalysts $Mg_xFe_{3-x}O_4$ (x=0.25, 0.5, 1) were prepared and presented in previous investigations by the co-precipitation method using starting aqueous solutions of 0.03 M $MgCl_2 \cdot 6H_2O$, 0.03 M $FeCl_2 \cdot 4H_2O$, 0.03 M $FeCl_3 \cdot 6H_2O$ and precipitant 0.3 M NaOH (Zaharieva et al. 2013). The reaction mixture was heated at 80^o - 120^o C and stirred with a rate of 400-600 rpm for 4 hours. After that it was cooled. The crude mixture was purified by column chromatography with a mixture hexane:ethyl acetate = 1:10. Then the removal of solvent was made on a rotary vacuum evaporator RVO-64. The obtained substituted polyphenylacetylenes (PPA-1, PPA-2, PPA-3 and PPA-4) were yellow to red brown compounds. The PPA-5 was isolated as a yellow product. All synthesized samples were viscous liquids.

Table 1. Preparation conditions of substituted polyphenylacetylenes.

Monomer	Comonomer	Catalyst	Temperature °C	Product
1-phenylacetylene 0.07 mmol	Isobutyraldehyde 0.011 mmol	$Mg_{0.5}Fe_{2.5}O_4$ 0.010 µmol	80	PPA-1
1-phenylacetylene 0.07 mmol	-	$Mg_{0.5}Fe_{2.5}O_4$ 0.010 µmol	80	PPA-2
1-phenylacetylene 0.07 mmol	Isobutyraldehyde 0.011 mmol	$Mg_{0.25}Fe_{2.75}O_4$ 0.010 µmol	80	PPA-3
1-phenylacetylene 0.07 mmol	Isobutyraldehyde 0.011 mmol	$MgFe_2O_4$ 0.010 µmol	120	PPA-4
1-phenyl-1-propyne 0.07 mmol	Isobutyraldehyde 0.011 mmol	$Mg_{0.5}Fe_{2.5}O_4$ 0.010 µmol	120	PPA-5

Experimental conditions: All experiments were carried out in t = 4h.

3. RESULTS AND DISCUSSION

During the last decade a new synthetic route for the preparation of oligomeric products, bases on carbonyl-olefin exchange reaction and reductive coupling of conjugated dicarbonyl compounds, has been developed. The products thus obtained are well soluble, stable in air and still possess the physical properties of conjugated polymers. This approach provides the possibility for synthesizing polyphenylacetylenes with different end-groups (Kalinova and Jossifov, 2007). Using this approach we prepared substituted polyacetylenes - the reaction conditions are given in Table 1. The best solvent found for copolymerization of 1-phenylacetylene/1-phenyl-1-propyne with isobutyraldehyde was dichloroethane. According to IR, ^{1}H-NMR and SEC analyses data the products thus obtained are oligomers, containing carbonyl or olefin end groups.

The substituted polyphenylacetylenes synthesized are bright yellow to red brown in color, depending on the structure of the side chain. The color of the polymers from meta-substituted monomer is yellow and para substituted polymers are red brown. The cis-cisoidal and cis-transoidal structures of substituted polyphenylacetylene cannot be separated due to their good solubility (Fujita et al. 1998).

The FT-IR spectra of obtained products are presented in Fig.1 and Fig.2. Characteristic peaks observed: about 3058 cm^{-1} (=C-H), 2925 cm^{-1}, 2860 cm^{-1} (CH_2 and CH_3), 1597 cm^{-1} (C=C Ar ring), 1448 cm^{-1} (CH), 1321 cm^{-1} (C-H), 1180-1029 cm^{-1} (=C-H).

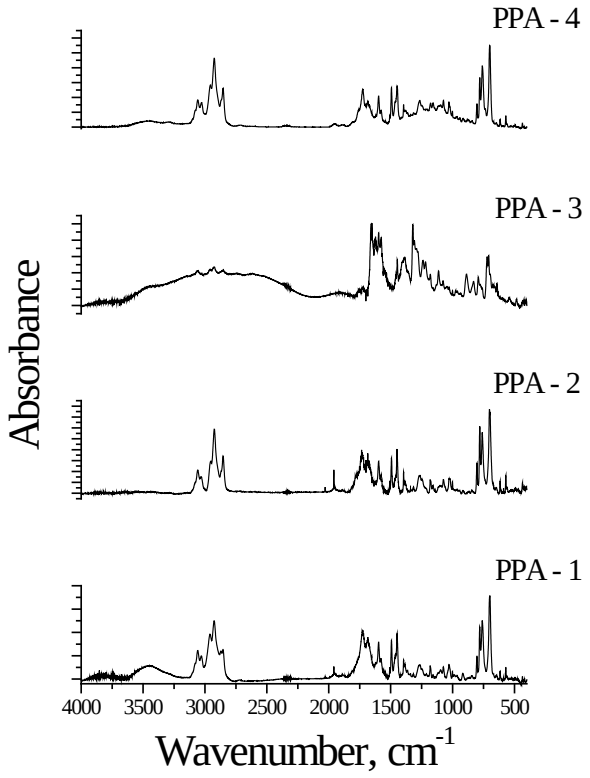


Fig. 1. FT-IR spectra of the obtained substituted polyphenylacetylenes.

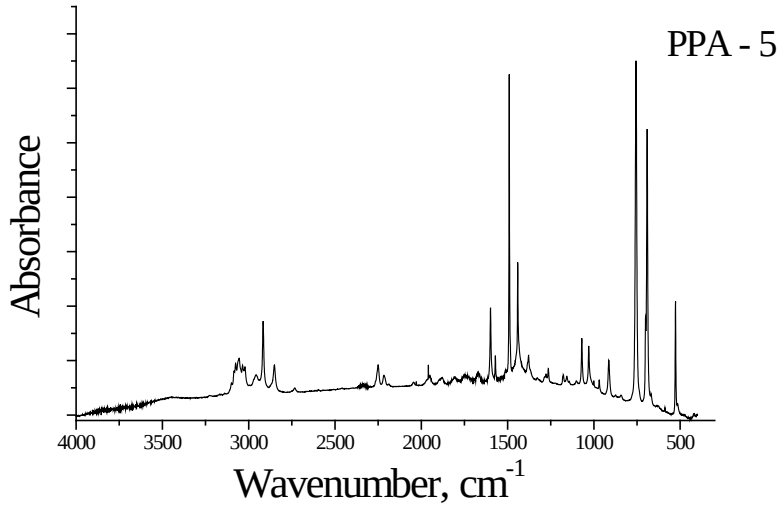


Fig. 2. FT-IR spectra of synthesized substituted polyphenylacetylene PPA-5.

Fig.1 illustrated the FT-IR spectra of polyphenylacetylenes with end carbonyl (PPA-1) and end olefin (PPA-2, PPA-3 and PPA-5) groups, prepared from copolymerization of 1-phenylacetylene, isobutyraldehyde and nanodimensional magnesium ferrite type catalysts $Mg_xFe_{3-x}O_4$(x=0.25, 0.5, 1). The spectra exhibit no

absorption characteristics for the acetylene part in the monomer, i.e. ν (≡C-H) and δ (C≡C) vibrations at 3300 cm^{-1} and 2100 cm^{-1} are missing. This indicates the opening of the acetylenic triple bond in the monomer.

The presence of conjugated bonds corresponding to the bands around 1600 cm^{-1} are registered in the spectrum of polyphenylacetylene with an olefin end group shown in Fig.2 The absorption peak around 1700 cm^{-1} (stretching vibrations of the carbonyl group) is registered in the spectrum of PPA-1. The spectra are rather similar to the ones reported for polyphenylacetylenes, prepared by other method, especially to the trans-structure of samples PPA-4 and PPA-5 (see Fig. 1 and Fig. 2) (Shopov and Jossifov, 1983). Shopov and Jossifov 1983 report that polymerization of phenylacetylene using WCl_6 catalyst leads to formation of polyphenylacetylene possessing predominantly a trans-structure. The similarity with structures of our new olygomers shows that the nanosized magnesium ferrites are efficient catalysts for the synthesis of substituted polyphenylacetylenes.

The ^1H NMR and ^{13}C NMR spectra of the synthesized substituted polyphenylacetylenes are shown in Figs. 3-5. In the spectrum of trans- PPA-4 the signals around δ = 7 ppm are typical for the aromatic substituted protons and trans-polyenic protons.

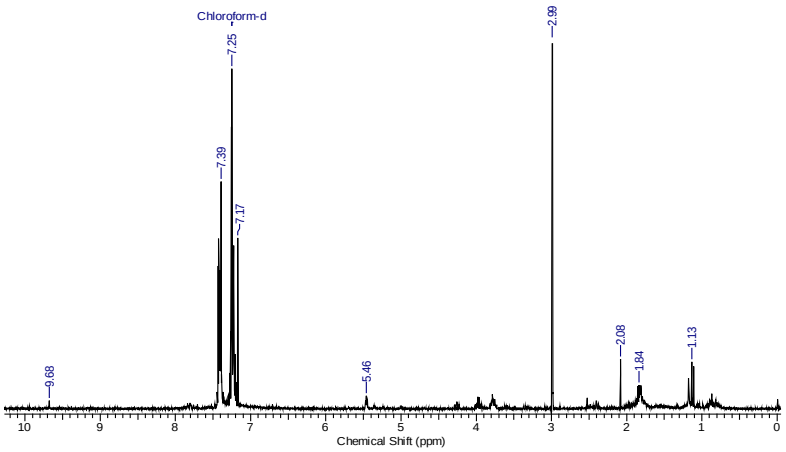


Fig. 3 ^1H-NMR spectrum of substituted polyphenylacetylene PPA-1.

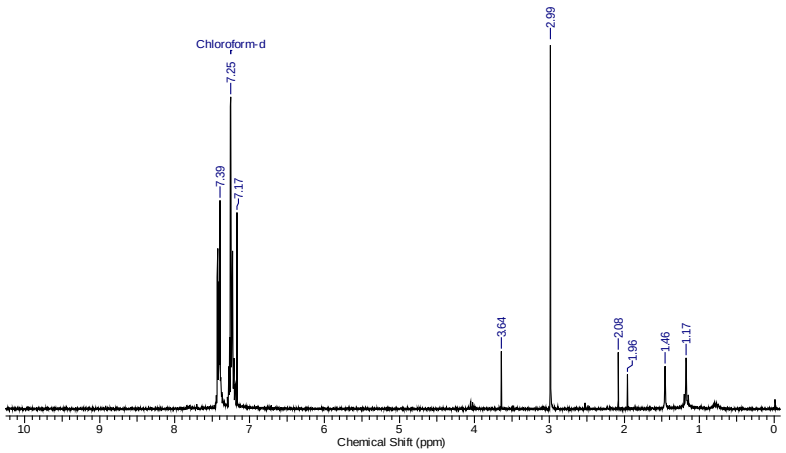


Fig. 4.^1H-NMR spectrum of substituted polyphenylacetylene PPA-4.

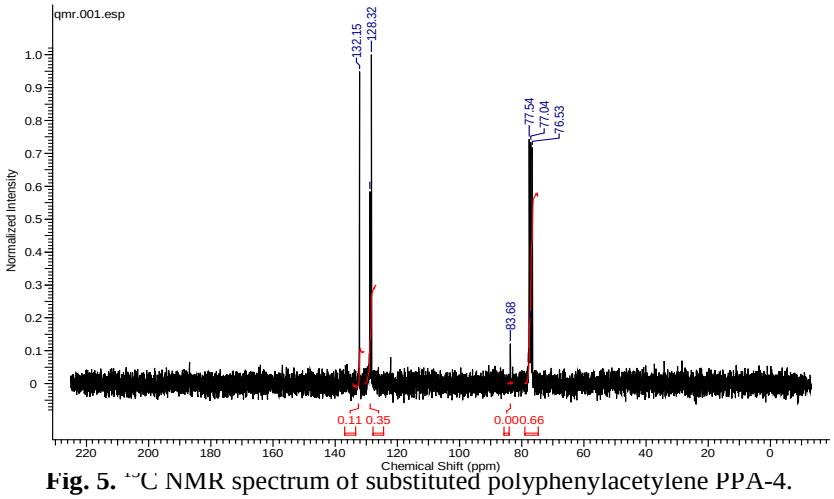


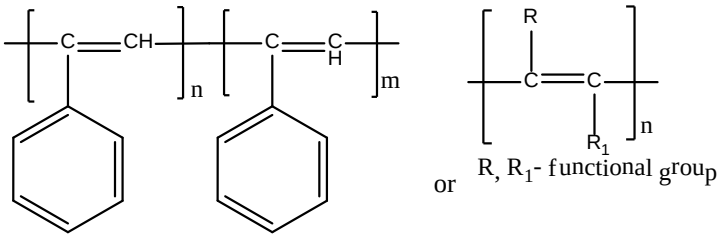
Fig. 5. ^{13}C NMR spectrum of substituted polyphenylacetylene PPA-4.

According to the literature in the ^{13}C NMR spectrum signals due to carbon atoms from the polymer polyphenylacetylene have to be obsereved at 132 and 139 ppm. The spectrum of PPA-4 containing - -C(C_6H_5)=CH- segments exhibits two signals around 128 and 132 ppm. This indicates that opening of the acetylenic -C≡C- bond in the monomer has taken place – obviously catalyzed by magnesium ferrites with different stoichiometry to give a linear polymer with conjugated double bonds. This fact strongly suggests the insertion polymerization mechanism rather than the metathesis pathway (Salamone, 1996).

In the ^{1}H NMR spectrum of the predominantly cis-polyphenylacetylene PPA-1, the peak, characteristic for the proton, attached to the cis-sequence of the double bond, is observed at 5.4 ppm.

It is known from the literature that if the polymerization of arylacetylenes is catalyzed by W, Mo, Rh, mainly cis-transoidal structure is obtained. Our sample PPA-1 gives a singlet signal at δ =5.4 that has to be assigned to the olefinic protons in the cis-transoidal main chain.

The possible molecular structures of our new substituted polyphenylacetylenes are presented in Scheme 3.



Scheme 3

Materials PPA-1 and PPA-4 showed the best electroconductivity - $0.9x10^{-3}$ -$1.2x10^{-3}$ S/cm.

The SEC measurements of the products PPA-3 and PPA-4 show the presence of various fractions with different molecular masses - 10^2 – 10^4 g/mol. The highest molecular masses of PPA-3 and PPA-4 are 548 and about 17000 g/mol respectively. The low molecular mass of PPA-3 has to be attributed to the presence of unreacted monomer and dimer. The removal of these products has been extremely difficult, despite of the efforts involved.

In our previous studies, concerning the physicochemical characterization of nanosized magnesium ferrite type catalysts $Mg_xFe_{3-x}O_4$ (x=0.25, 0.5, 1) - X-ray diffraction analysis, Moessbauer and FTIR spectroscopy - we showed the existence of non-stoichiometric ferrite phase and additional amount of iron oxihydroxide in ferrite material $Mg_xFe_{3-x}O_4$ (x=0.25). For samples $Mg_xFe_{3-x}O_4$ (x=0.5;1) the presence of ferrite phase and intermediate phases iron oxihydroxides and double layered hydroxides have been registered. The average particle size of

magnesium ferrite type catalysts was determined about 9 nm (Zaharieva et al. 2013). The catalytic behavior of $Mg_{0.5}Fe_{2.5}O_4$ after the coupling reaction for preparation of substituted polyphenylacetylene PPA-1 was investigated by Moessbauer spectroscopy. The recorded spectrum of the catalyst, presented in Fig. 6, is a superposition of three sextet components. The calculated Moessbauer parameters are given in Table 2. The presence of spinel ferrite phase is registered by two sextet components – Sxt 2 attributed to the tetrahedrally coordinated Fe^{3+} ions and Sxt 3 due to octahedrally coordinated Fe^{3+} ions. The sextet component Sxt 1 can be related to the existence of hematite phase (α-Fe_2O_3). The comparison of Moessbauer results before and after catalytic test established the partial oxidation of iron containing phases.

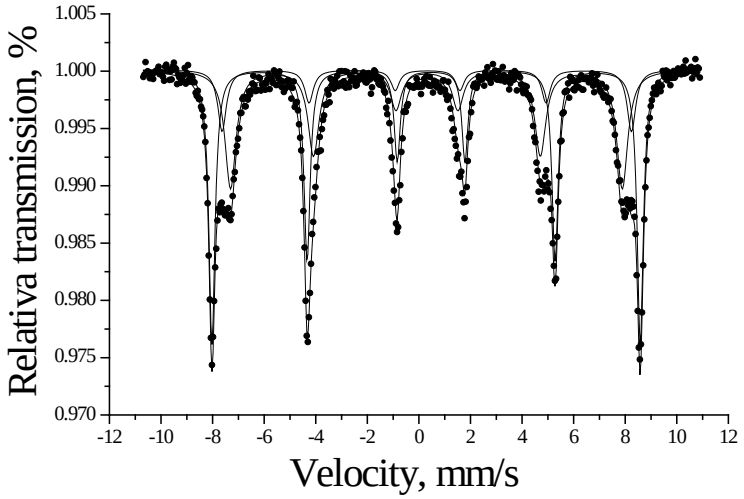


Fig. 6. Moessbauer spectrum of nanostructured magnesium ferrite type catalyst $Mg_{0.5}Fe_{2.5}O_4$ after catalytic test using for preparation of substituted polyphenylacetylene PPA-1.

Table 2. Moessbauer parameters of the nanodimensional magnesium ferrite type catalyst $Mg_{0.5}Fe_{2.5}O_4$ after catalytic test using for preparation of substituted polyphenylacetylene PPA-1.

Sample	Components	IS, mm/s	QS, mm/s	H_{eff}, T	FMHW, mm/s	G, %
$Mg_{0.5}Fe_{2.5}O_4$	Sxt 1 - α-Fe_2O_3	0.37	-0.19	51.59	0.30	48.3
	Sxt 2 - Fe^{3+}-tetra, spinel	0.32	-0.03	49.30	0.40	13.9
	Sxt 3 - Fe^{3+}-octa, spinel	0.30	-0.02	47.18	0.52	37.8

4. CONCLUSIONS

Substituted polyphenylacetylenes with end carbonyl or end olefin groups, prepared by alkyne carbonyl coupling polymerization in dichloroethane at 80°C - 120°C, using magnesium ferrite type catalysts, has been synthesized. The obtained polymers were studied by FTIR, ^1H and ^{13}C NMR spectroscopy. At the reaction conditions used polyphenylacetylenes with mixed cis- and trans- configuration of the alternating C-C double bond system and limited conjugation have been prepared. The best electroconductivity was measured for products PPA-1 and PPA-4 - $0.9x10^{-3}$ -$1.2x10^{-3}$ S/cm. The SEC study showed that PPA-4 is a polymer product - molecular mass about 17000. The synthetic procedure applied has to be further optimized in order to obtain products with higher molecular masses. This will make such conjugated polymers promising candidates for possible applications in electronic devices.

ACKNOWLEDGEMENTS

The authors from IP-BAS thank to the Bulgarian Academy of Sciences for the financial support.

The authors from IC-BAS thank to the Bulgarian National Fund by Project DFNI-E01/7/2012 for sponsorship.

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