

Polymerization of nitrophenyl propargyl ethers with transition metal catalysts and characterization of polymers

H. Balcar^{a,*}, T. Kalisz^a, J. Sedláček^b, V. Blechta^c and P. Matějka^d

^aJ. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, CZ-182 23 Prague 8, Czech Republic

^bDepartment of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Albertov 2030, CZ-128 40 Prague 2, Czech Republic

^cInstitute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, CZ-165 02 Prague 6-Suchbát, Czech Republic

^dDepartment of Analytical Chemistry, ICT Prague, Technická 5, CZ-166 28 Prague 6, Czech Republic

(Revised 22 December 1997; accepted 5 January 1998)

o-, *m*- and *p*-Nitrophenyl propargyl ethers were prepared, characterized (n.m.r., i.r.) and polymerized with tungsten and molybdenum based metathesis catalyst systems. Soluble high-molecular-weight (weight-average molecular weight about 4×10^5) poly(*p*-nitrophenyl propargyl ether)s were prepared in good yields using catalyst systems MoOCl₄/Me₄Sn and MoCl₅/EtAlCl₂. Insoluble poly(*m*-nitrophenyl propargyl ether)s and poly(*o*-nitrophenyl propargyl ether)s were prepared in moderate yields with the same catalyst systems. I.r. and n.m.r. spectra of all polymers confirmed polyacetylene type polymer structure with nitrophenoxymethyl pendant groups. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: nitrophenyl propargyl ether; metathesis polymerization; polyacetylenes)

Introduction

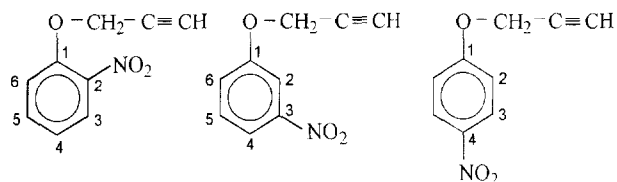
Substituted polyacetylenes are intensively studied as polymers offering promising applications in electronics and optoelectronics. Interesting properties of many of these polymers, such as photoconductivity^{1,2} and non-linear optical behaviour³, come from the combination of conjugated character of the polyacetylenic main chain with the effects of the pendant groups. For the synthesis of these polymers usually the coordination (mostly metathesis) polymerization of respective substituted acetylenes is used. Various polyacetylenes with hydrocarbon, silicon-containing and halogen-containing pendant groups have been successfully prepared in good yields^{4,5}. Synthesis of polymers containing more reactive heteroatom groups is often less effective and usually requires a proper selection of catalyst. Despite that, many oxygen-containing^{4,6} and also several nitrogen-containing monomers (nitrogen in secondary or tertiary amino groups or in heterocycles)^{7–10} have been polymerized. Little attention has been paid to the polymerizations of monomers containing NO₂-group, although this group with its great dipole moment may influence the photoelectrical properties of polymers. Only recently, we described successful polymerization of *p*-nitrophenylacetylene with WOCl₄/Me₄Sn and reported on photoelectrical properties of polymer¹¹. In this contribution, polymerization of other nitro-group containing acetylenes-nitrophenyl propargyl ethers is reported and characterization of respective polymers is given.

Experimental

Materials. Nitrophenols (*o*-, *m*- and *p*-isomers, all p.a., Lachema, CZ), propargyl benzenesulfonate (97%, Aldrich),

propargyl bromide (80 wt% in toluene, Aldrich) were used as obtained. WOCl₄ (98%, Aldrich), MoCl₅ (99.9%, Aldrich), MoOCl₄ (Aldrich) and tetramethyltin, Me₄Sn (>99%, Fluka) were used without any purification. Preparation and purification of ethylaluminium dichloride, EtAlCl₂ is described elsewhere¹². Solvents for synthesis of monomers were of analytical grade and they were purified and dried by standard methods. Benzene and 1,4-dioxane, used as solvents for polymerizations, were purified as described earlier^{13,14}.

Preparation and characterization of monomers. *o*-, *m*- and *p*-Nitrophenyl propargyl ethers (*o*-NPE, *m*-NPE and *p*-NPE, respectively) (Scheme 1) were synthesized by alky-



Scheme 1

lation of corresponding nitrophenols with propargyl benzenesulfonate or propargyl bromide. Procedure according to Reppe¹⁵ and modification of a method designed by Bell¹⁶ were used. Product purity was checked by GC (27 m capillary column, 200°C).

o-Nitrophenyl propargyl ether (*o*-NPE) was synthesized via alkylation of *o*-nitrophenol by propargyl benzenesulfonate using aqueous NaOH solution (35 wt%) according to Reppe¹⁵. Crude product was purified by vacuum sublimation. Pale crystals (m.p. 73–75°C) were obtained. Yield: 32%. I.r. (KBr) cm⁻¹: 3245 ν (≡C–H), 2127 ν (C≡C), 1520 ν_{as} (NO₂), 1350 ν_s (NO₂). ¹H n.m.r. (dimethyl sulfide)-d₆ (DMSO)-d₆, ppm: δ = 3.68 (*t*, ≡C–H), 5.02 (*d*,

* To whom correspondence should be addressed

–CH₂–), 7.17 (*t*, H⁴), 7.42 (*d*, H⁶), 7.68 (*t*, H⁵), 7.88 (*d*, H³). ¹³C n.m.r. (DMSO)-*d*₆, ppm: δ = 57.06 (CH₂), 78.29 (–C ≡), 79.55 (≡ C–H), 115.75 (C⁶), 121.55 (C⁴), 125.13 (C³), 134.32 (C⁵), 140.11 (C²), 149.83 (C¹).

m-Nitrophenyl propargyl ether (*m*-NPE) was synthesized from *m*-nitrophenol and propargyl benzenesulfonate in *N,N*-dimethylformamide (DMF) using CuCl as catalyst¹⁶. *m*-Nitrophenol (2.8 g, 20 mmol) was mixed with KI (3.3 g), CuCl (25 mg) and Na₂CO₃ (10.5 g) in 30 mL of dry DMF under argon. Then propargyl benzenesulfonate (4.2 g, 21 mmol) was added and the mixture was stirred for 2.5 h at 65–70°C. After cooling, 300 mL of diluted HCl (5 wt%) was added and the mixture was extracted with toluene. The toluene phase was washed (aqueous NaOH and water), dried (Na₂SO₄) and crude product was obtained after evaporating toluene off. From it, pale yellow crystals (m.p. 60–65°C) were isolated by sublimation *in vacuo*. Yield: 48%. I.r. (KBr), cm⁻¹: 3268 ν(≡ C–H), 2127 ν(C≡C), 1520 ν_{as}(NO₂), 1350 ν_s(NO₂). ¹H n.m.r. (DMSO)-*d*₆, ppm: δ = 3.36 (*t*, ≡ C–H), 4.68 (*d*, CH₂), 7.17 (*m*, H⁶), 7.31 (*t*, H⁵), 7.50 (*t*, H²), 7.56 (*m*, H⁴). ¹³C n.m.r. (DMSO)-*d*₆, ppm: δ = 56.35 (–CH₂), 78.57 (–C≡), 79.26 (≡ C–H), 109.37 (C²), 116.37 (C⁴), 122.56 (C⁶), 130.87 (C⁵), 148.81 (C³), 157.82 (C¹).

p-Nitrophenyl propargyl ether (*p*-NPE) was prepared in the similar way as *meta*-isomer, but propargyl bromide was used instead of propargyl benzenesulfonate. To the mixture of *p*-nitrophenol (7 g, 50 mmol), KI (8.8 g), CuCl (50 mg), Na₂CO₃ (30 g) in 50 mL of dry DMF propargyl bromide (6 g, 50 mmol, in toluene) was added. The mixture was stirred under argon for 5 h at 65°C. After cooling, it was poured into 800 mL of water and the yellow–green precipitate was isolated, washed (aqueous NaOH, water, diluted HCl). By sublimation *in vacuo* white crystals (m.p. 113–114°C) were obtained. Yield: 77%. I.r. (KBr), cm⁻¹: 3255 ν(≡ C–H), 2125 ν(C≡C), 1500 ν_{as}(NO₂), 1350 ν_s(NO₂). ¹H n.m.r. (DMSO)-*d*₆, ppm: δ = 3.66 (*t*, ≡ C–H), 4.98 (*d*, CH₂), 7.18 (*d*, H²), 8.22 (*d*, H³). ¹³C n.m.r. (DMSO)-*d*₆, ppm: δ = 56.49 (CH₂), 78.31 (≡ C–), 79.25 (H–C≡), 115.54 (C²), 125.90 (C³), 141.50 (C⁴), 162.49 (C¹).

Polymerization. Polymerizations were performed using the standard vacuum break–seal technique¹³. Unless otherwise stated, polymerization conditions were as follows: initial monomer concentration = 0.16 mol L⁻¹; initial mole ratio monomer:catalyst = 50; benzene or benzene/50 vol% 1,4-dioxane as solvent; reaction time 8 h at 60°C. Initial mole ratios catalyst:cocatalyst were: WOCl₄:Me₄Sn = 1:3; MoOCl₄:Me₄Sn = 1:3; MoCl₅:EtAlCl₂ = 1:1. WOCl₄ was dosed as stock solution in benzene, MoOCl₄ and MoCl₅ were charged as solids and dissolved in benzene just before the polymerization experiment. For polymerization in benzene, solutions of catalyst (0.02 mmol) and cocatalyst were mixed, the mixture was allowed to ripen for 15 min at room temperature and then mixed with monomer in benzene. For polymerization performed in benzene/1,4-dioxane, 1,4-dioxane was added to the benzene solution of ripe catalyst/cocatalyst system (after 15 min reaction in benzene). The resulting mixture was allowed to react for 15 min again (room temperature) and then mixed with monomer in benzene/1,4-dioxane. In most cases the polymer was precipitated during the polymerization. Polymerization was always quenched by pouring the reaction suspension (6.2 mL) into methanol (25 mL). The methanol-insoluble polymer was isolated, washed by methanol and dried *in*

vacuo at 40°C to the constant weight. The polymer yield was determined gravimetrically. The supernatant from the polymer isolation was (after evaporating solvents) analyzed by size exclusion chromatography to determine the yield of methanol-soluble products.

Techniques. I.r. spectra of monomers were recorded on a Specord 75 i.r. spectrometers in KBr pellets. For i.r. spectra of polymers a Nicolet 210 FT.i.r. spectrometer and the diffuse reflectance technique with non-diluted powdered sample was used.

¹³C and ¹H n.m.r. spectra of all monomers and poly(*p*-nitrophenyl propargyl ether)s, [P(*p*-NPE)], were recorded in (DMSO)-*d*₆ solution on Varian UNITY-200 n.m.r. spectrometer. The spectra were referenced to the solvent multiplet central line (2.5 ppm for ¹H and 39.7 ppm for ¹³C n.m.r. spectra). Necessary assignments were made exploiting chemical shifts, proton selective homonuclear decoupling, heteronuclear 2D correlation experiment¹⁷, ¹³C multiplicity search by DEPT¹⁸, editation and published data^{19,20}. Solid state ¹³C CP MAS n.m.r. spectra of poly(*m*-nitrophenyl propargyl ether)s, [P(*m*-NPE)], and poly(*o*-nitrophenyl propargyl ether)s, [P(*o*-NPE)], were measured on BRUKER DSX-200 spectrometer (using 4 mm spinner) and were referenced externally to carbonyl line of glycine at 176.03 ppm. The following parameters were used: cross polarization delay 2 ms, relaxation period 6 s, spinning speed about 6400 Hz, acquisition time 50 ms, 10 000 scans and 20 000 scans for [P(*o*-NPE)] and [P(*m*-NPE)], respectively.

Size exclusion chromatography (SEC) analyses of P(*p*-NPE)s were performed on following apparatus train: high pressure pump HPP 5001 (Laboratorní přístroje, CZ), Rheodyne sampling valve 7125 (Rheodyne, USA), 8 × 500 mm GM 1000 column (Labio, CZ), u.v. detector HP1030B (Hewlett Packard). *N*-methyl pyrrolidone (NMP) was used as mobile phase (1 mL min⁻¹). SEC analyses of methanol-soluble products were performed using TSP (Thermo Separation Products, Florida, USA) chromatograph, series of two PL columns (Mixed B and C) and tetrahydrofuran (THF) as mobile phase (0.7 mL min⁻¹). In both cases u.v. detector operating at 254 nm was used and all analyses were performed at room temperature. Molecular weight averages relative to polystyrene standards are reported.

Results and discussion

The results of polymerization experiments are given in Table 1. The data on methanol-soluble products given in Table 1 come from SEC analyses of methanol-soluble fractions of terminated reaction mixtures (see Experimental). In all cases good SEC separation of unreacted monomer and higher-molecular-weight products was achieved. In experiments No. 3, 4 and 6 SEC records showed presence of small amounts of low oligomers (probably cyclotrimers), but in experiments No. 1 and 5 very broad traces were detected corresponding to molecular weight in the region from 500 to 50 000. Attempts to separate methanol-soluble polymers from oligomers and unreacted monomer were unsuccessful.

Catalyst system WOCl₄/Me₄Sn in benzene/1,4-dioxane, which was found recently to polymerize *p*-nitrophenylacetylene (NPA) with a high polymer yield at room temperature¹¹, showed low efficiency in the case of polymerization of *p*-NPE. Only methanol-soluble polydisperse

Table 1 Yield, weight-average molecular weight \bar{M}_w and polydispersity index \bar{M}_w/\bar{M}_n of products formed in polymerization of *o*-, *m*- and *p*-nitrophenyl propargyl ethers (*o*-NPE, *m*-NPE and *p*-NPE, respectively) with various catalyst systems in benzene (B) and benzene/50 vol% 1,4-dioxane (B/D). Polymerization conditions: initial monomer concentration = 0.16 mol L⁻¹; initial mole ratio monomer:catalyst = 50:1; reaction time 8 h; temperature 60°C

No.	Monomer	Catalyst system	Solvent	Products					
				Methanol-insoluble			Methanol-soluble		
				Yield (%)	10 ⁻³ \bar{M}_w	\bar{M}_w/\bar{M}_n	Yield (%)	10 ⁻³ \bar{M}_w	\bar{M}_w/\bar{M}_n
1	<i>p</i> -NPE	WOCl ₄ /Me ₄ Sn ^a	B/D	0	–	–	15	29	5.2
2	<i>p</i> -NPE	WOCl ₄ /Me ₄ Sn	B/D	0	–	–	0	–	–
3	<i>p</i> -NPE	MoOCl ₄ /Me ₄ Sn	B/D	16	–	–	2	0.7	1.1
4	<i>p</i> -NPE	MoOCl ₄ /Me ₄ Sn	B	45	350 ^b	1.5 ^b	3	0.8	1.1
					25 ^c	1.3 ^c			
5	<i>p</i> -NPE	MoCl ₅ /EtAlCl ₂	B	66	480 ^b	1.3 ^b	7	35	9.5
					60 ^c	1.1 ^c			
6	<i>m</i> -NPE	MoOCl ₄ /Me ₄ Sn	B	48	insoluble	–	3	0.9	1.1
7	<i>m</i> -NPE	MoCl ₅ /EtAlCl ₂	B	18	insoluble	–	15	9	1.7
8	<i>o</i> -NPE	MoOCl ₄ /Me ₄ Sn	B	24	insoluble	–	0	–	–
9	<i>o</i> -NPE	MoCl ₅ /EtAlCl ₂	B	15	insoluble	–	0	–	–

^aRoom temperature, reaction time = 24 h.

^bMain polymer fraction (ca. 80%).

^cminor polymer fraction (ca. 20%).

polymeric product containing most probably also cyclotrimers was formed at the room temperature. At 60°C the WOCl₄/Me₄Sn system was completely inactive. On the other hand, analogous systems MoOCl₄/Me₄Sn, which was inefficient for NPA polymerization¹¹, gave with *p*-NPE a moderate yield of methanol-insoluble polymer. The polymerization was more efficient in benzene than in benzene/1,4-dioxane solvent. The difference in activity of MoOCl₄/Me₄Sn and WOCl₄/Me₄Sn catalyst systems corresponds with data of Lee *et al.*^{6,21}, showing that for polymerization of propargyl and dipropargyl ethers, the molybdenum containing catalysts are more efficient in comparison with their tungsten analogues. MoOCl₄/Me₄Sn was found to be active also in polymerization of *o*-NPE and *m*-NPE. Polymerizations with this catalyst system always resulted predominantly in methanol-insoluble polymers. All three monomers were successfully polymerized also with MoCl₅/EtAlCl₂. This system was most active in polymerization of *p*-NPE, but in polymerization of *o*-NPE and *m*-NPE its activity was lower than that of MoOCl₄/Me₄Sn. Moreover, compared to MoOCl₄/Me₄Sn, polymerizations of *m*-NPE and *p*-NPE with MoCl₅/EtAlCl₂ was accompanied by an enhanced formation of methanol-soluble products. If the efficiency of Mo-based catalyst systems for individual monomers is compared, the decrease in the following series is evident: *p*-NPE > *m*-NPE ≅ *o*-NPE (for MoCl₅/EtAlCl₂) and *p*-NPE ≅ *m*-NPE > *o*-NPE (for MoOCl₄/Me₄Sn).

All methanol-insoluble polymers prepared were yellow-brown solids, completely amorphous (according to X-ray diffraction spectra) and insoluble in aromatics, THF, CHCl₃. P(*p*-NPE)s were soluble in DMSO, DMF and NMP into dark yellow solutions. SEC analyses of P(*p*-NPE)s (Table 1, No. 4 and 5) done in NMP showed a bimodal molecular-weight distribution. Beside the predominating high-molecular-weight fraction both samples contained ca. 20% (according to areas of SEC records) of lower-molecular-weight fraction (for molecular-weight characteristics of both fraction see Table 1). P(*m*-NPE)s and P(*o*-NPE)s were completely insoluble in all solvents mentioned above.

Polymers prepared were characterized using i.r. and n.m.r. spectroscopies. No significant differences in either i.r. or n.m.r. spectra of individual polymers prepared with different catalyst systems were observed. In Figure 1 i.r. spectra of P(*p*-NPE), P(*m*-NPE) and P(*o*-NPE) are given. The spectra were interpreted on the basis of characteristic

group frequencies^{22–24}. The absence of bands 3270–3245 cm⁻¹ ν (≡C–H) and about 2125 cm⁻¹ ν (C≡C) shows that polymerization occurred by transformation of carbon-carbon triple bond. The presence of characteristic bands of CH₂-group (2932, and 2872 cm⁻¹), NO₂-group (1540–1522 cm⁻¹ and about 1355 cm⁻¹) and phenyl ring affected by NO₂-substitution (in the regions 3120–3030 cm⁻¹ and 2000–1750 cm⁻¹, at about 1610, 1585 and 1490 cm⁻¹ and between 875 and 700 cm⁻¹) confirms the presence of nitrophenoxymethyl pendant groups. The bands characteristic of polyacetylenic main chain, however, cannot be distinguished well because of their overlapping by other more intensive bands in the region 3060–3000 cm⁻¹ ν (=C–H), at about 1600 cm⁻¹ ν (C=C) and between 850 and 730 cm⁻¹ δ (C=C–H). The difference in spectra of individual poly(nitrophenyl propargyl ether)s can be attributed to different position of NO₂-group on phenyl ring. Especially, overtone bands in the range 2000–1750 cm⁻¹, which are characteristics of various types of substitution on aromatic ring, as well as the bands of δ (ring) and γ (C–H) deformation vibrations between 875 and 700 cm⁻¹ are in agreement with the literature data given for the particular types of phenyl ring substitution with strong electron-withdrawing groups²³.

¹H and ¹³C n.m.r. spectra of P(*p*-NPE) in (DMSO)-*d*₆ are given in Figure 2. Sharp high lines at 2.5 and 3.4 ppm in ¹H spectrum [Figure 2(a)] are solvent and solvent water line, respectively. Broad peak at about 4.5 ppm is due to OCH₂-group and other two broad peaks at 6.8 ppm and 7.8 ppm were assigned, according to spectrum of monomer, to H² and H³ proton of phenyl ring, respectively. Peaks in ¹³C n.m.r. spectrum [Figure 2(b)] were assigned according to monomer lines, as follows: 163.0 ppm (C¹), 140.9 ppm (C⁴), 125.6 ppm (C³), 115.0 ppm (C²). Peak at 70.0 ppm was assigned to carbon of OCH₂-group on the bases of chemical shift of corresponding carbon in allyl ethers²⁰ and broad low signal between 120 and 140 ppm were ascribed to carbons of polymer main chain. ¹³C CP MAS solid state n.m.r. spectra of P(*o*-NPE) and P(*m*-NPE) are also given in Figure 2. Tentative peak assignment were made using chemical shifts of monomers in (DMSO)-*d*₆ as follows: for P(*m*-NPE) [Figure 2(c)] 158.7 ppm (C¹), 148.8 ppm (C³), 130.0 ppm (C⁵, C⁶), 116.0 ppm (C⁴), 106.1 ppm (C²) and for P(*o*-NPE) [Figure 2(d)] 159.1 ppm (C¹), 134.9 ppm (C², C⁵), 125.8 ppm (C³, C⁴), shoulder at 116 ppm (C⁶). For

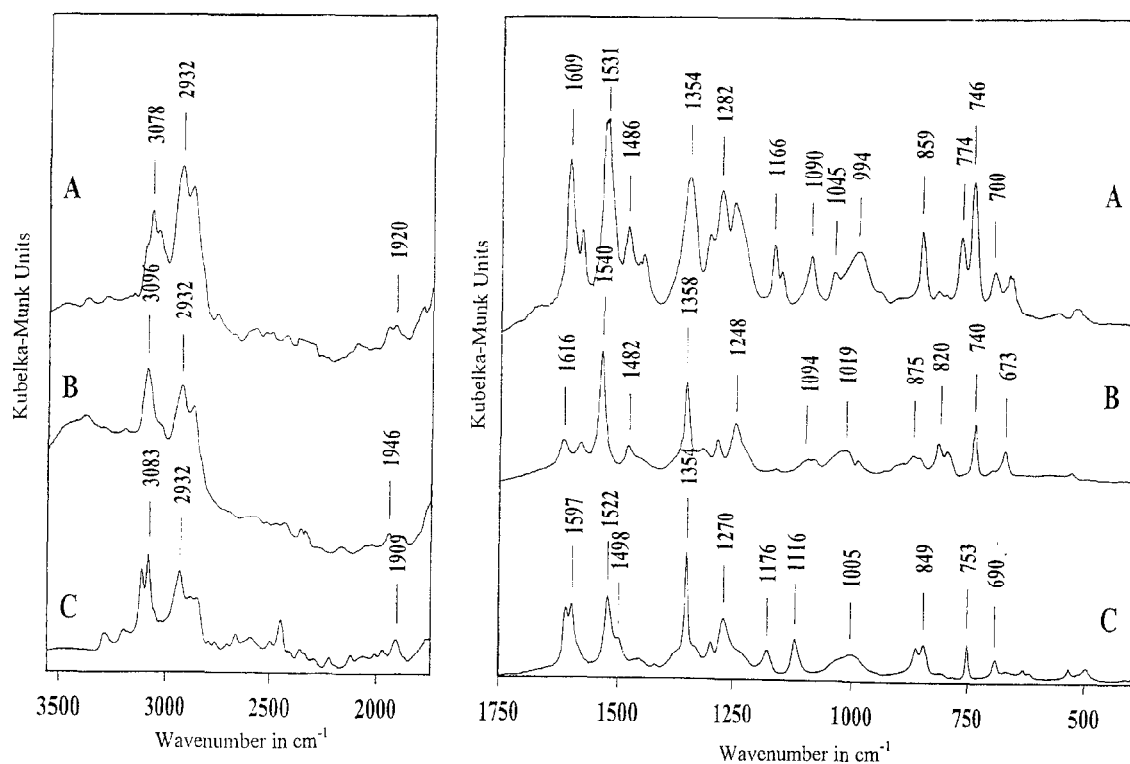


Figure 1 Diffuse reflectance i.r. spectra of P(*o*-NPE) sample No. 8 in Table 1 (spectrum A), P(*m*-NPE) sample No. 7 in Table 1 (spectrum B), P(*p*-NPE) sample No. 4 in Table 1 (spectrum C)

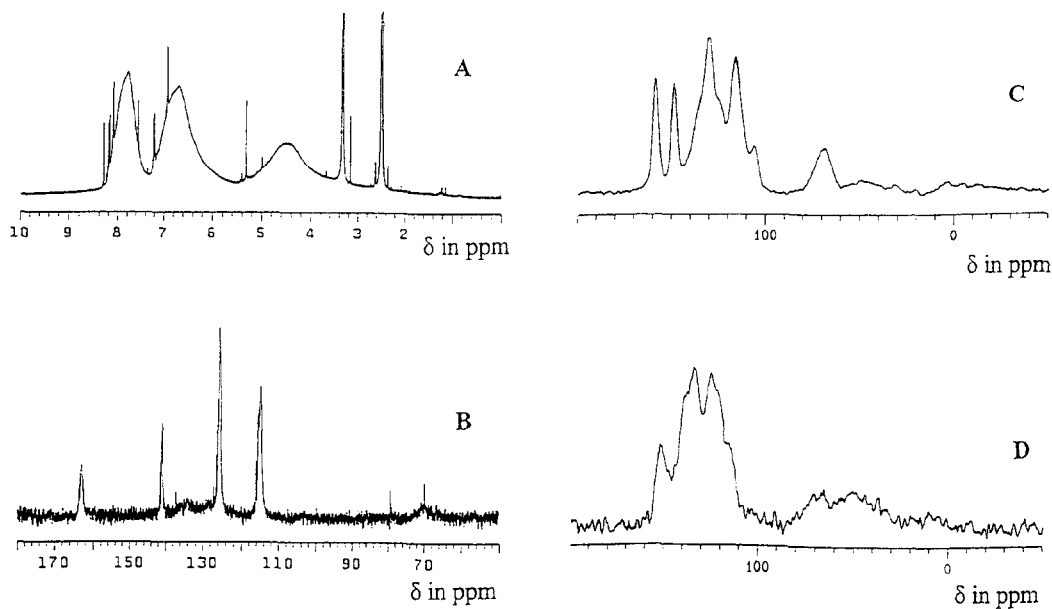


Figure 2 ¹H-n.m.r. (a) and ¹³C n.m.r. (b) spectra of P(*p*-NPE) sample No. 4 in Table 1 and ¹³C CP MAS n.m.r. spectra of P(*m*-NPE) sample No. 6 in Table 1 (c), and P(*o*-NPE) sample in No. 8 Table 1 (d)

both polymers, signals of main chain carbons are supposed to be broad and overlapped by signals of phenyl carbons. Broad peaks at about 68 and 50 ppm in spectra of both polymers may be ascribed to carbon in CH₂O-group. The splitting of CH₂O-group signal may be connected with some kind of polymer pendant groups ordering in solid state.

Summary

It has been shown that nitrophenyl propargyl ethers can

be polymerized with a good yield using molybdenum based catalyst systems under formation of polyacetylene type polymers. Their limited solubility (or total insolubility), however, represents unpleasant restriction for many applications, e.g. attempts to prepare thin layers for photoconductivity measurements were unsuccessful. Copolymerization of nitrophenyl propargyl ethers with proper comonomers may provide materials of solubility suitable for these purposes. Research in this direction is in progress.

Acknowledgements

The authors are indebted to Dr. P. Holler and Dr. Drahomíra Hlavatá (Institute of Macromolecular Chemistry, Academy of Science, CZ) for SEC measurements in NMP and X-ray diffraction spectra. Financial support from EU Commission (PECO, supplementary contract ERBCIPDCT 940617) and from grant No. VS 97103 (CZ) is gratefully acknowledged.

References

1. Brédas, J. L. and Silbey, R. (Eds.), *Conjugated Polymers*. Kluwer Academic Publishers, Dordrecht, 1991.
2. Pfeleger, J., Nešpůrek, S. and Vohlídal, J., *Adv. Mater. Opt. Electr.*, 1996, **6**, 325.
3. Long, N. J., *Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 1.
4. Ivin, K. J. and Mol, J. C., *Olefin Metathesis and Metathesis Polymerization*. Academic Press, London, 1997, p. 204.
5. Vohlídal, J., Sedláček, J., Pacovská, M., Lavastre, O., Dixneuf, P. H., Balcar, H. and Pfeleger, J., *Polymer*, 1997, **38**, 3359.
6. Lee, W. C., Gal, Y. S., Jin, S. H., Choi, S. J., Lee, H. J. and Choi, S. K., *J. Macromol. Sci., Pure Appl. Chem. A*, 1994, **31**, 737.
7. Choi, S. J., Jin, S. H., Park, J. W., Cho, H. N. and Choi, S. K., *Macromolecules*, 1994, **27**, 309.
8. Lee, W. C., Gal, Y. S. and Choi, S. K., *J. Macromol. Sci., Pure Appl. Chem. A*, 1997, **34**, 99.
9. Kalvoda, L., Kmínek, I., Cimrová, V., Nešpůrek, S., Schnabel, W. and Sedláček, J., *Colloid. Polym. Sci.*, 1990, **268**, 1024.
10. Kmínek, I., Cimrová, V., Nešpůrek, S. and Vohlídal, J., *Makromol. Chem.*, 1989, **190**, 1025.
11. Sedláček, J., Vohlídal, J., Štícha, M., Balcar, H., Lavastre, O., Cabioch, S., Dixneuf, P.H., Pfeleger, J. and Blechta, V., *Macromol. Chem. Phys.*, 1998, **199**, 155.
12. Mach, K., *Collect. Czech. Chem. Commun.*, 1965, **30**, 277.
13. Balcar, H., Dosedlová, A., Hanuš, V., Petrusová, L. and Matyska, B., *Collect. Czech. Chem. Commun.*, 1984, **49**, 1737.
14. Sedláček, J., Pacovská, M., Vohlídal, J., Grubišič-Gallot, Z. and Žigon, M., *Macromol. Chem. Phys.*, 1995, **196**, 1705.
15. Reppe, W., *Justus Liebigs Ann. Chem.*, 1955, **596**, 1.
16. Bell, D., Davies, M. R., Geen, G. R. and Mann, I. S., *Synthesis*, 1995, 707.
17. Bodenhausen, G. and Freeman, R., *J. Am. Chem. Soc.*, 1978, **100**, 320.
18. Doddrell, D. M., Pegg, D. T. and Bendall, M. R., *J. Magn. Reson.*, 1982, **48**, 323.
19. Kalyanaraman, P. S., Garito, A. G., McGhie, A. R. and Desai, K. N., *Makromol. Chem.*, 1979, **180**, 1393.
20. Kalinowski, H. O., Berger, S. and Braun, S., *¹³C n.m.r. Spectroscopy*. G. Thieme Verlag, Stuttgart, 1984, p. 165.
21. Lee, H. J., Choi, S. K. and Gal, Y. S., *J. Macromol. Sci., Pure Appl. Chem. A*, 1995, **32**, 1863.
22. Socrates, G., *Infrared Characteristic Group Frequencies*. J. Wiley, Chichester, 1980.
23. Roeges, N. P. G., *A Guide to the Complete Interpretation of Infrared Spectra of Organic Structures*. J. Wiley, Chichester, 1993.
24. Gloor, A. et al., *SpecTool for Windows v.2.1* (A hypermedia book for structure elucidation of organic compounds with spectroscopic methods). Chemical Concepts GmbH, Weinheim, 1996.