

POLYMERIZATION OF NITROPHENYL AND 3-DIETHYLAMINOPHENYL PROP-2-YN-1-YL ETHERS WITH PdCl₂. POLYMERS AND COPOLYMERS CHARACTERIZATIONHynek BALCAR^a, Petr HOLLER^b, Jan SEDLACEK^c and Vratislav BLECHTA^d^a *J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, 182 23 Prague 8, Czech Republic; e-mail: balcar@jh-inst.cas.cz*^b *Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic; e-mail: holler@imc.cas.cz*^c *Department of Physical and Macromolecular Chemistry, Faculty of Sciences, Charles University, 128 40 Prague 2, Czech Republic; e-mail: jansedl@prfdec.natur.cuni.cz*^d *Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, 165 02 Prague 6-Suchbát, Czech Republic; e-mail: blechta@icpf.cas.cz*

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2-, 3- and 4-Nitrophenyl prop-2-yn-1-yl ethers were polymerized with PdCl₂ in *N,N*-dimethylformamide (DMF) giving brown polymers soluble in DMF, dimethyl sulfoxide and *N*-methylpyrrolidone. Broad (mostly bimodal) molecular weight distributions were observed by size-exclusion chromatography (SEC) with maxima at molecular weight of about $4 \cdot 10^3$ and $1 \cdot 10^5$. With the same catalyst, 3-diethylaminophenyl prop-2-yn-1-yl ether gave predominantly low molecular weight homopolymer ($M_n = 4\ 200$) soluble in DMF, *N*-methylpyrrolidone, CHCl₃ and tetrahydrofuran-soluble copolymers with 4-nitrophenyl prop-2-yn-1-yl ether (M_n about 3 000). IR, NMR and UV-VIS spectra of prepared polymers and copolymers proved the structure to consist of the polyene-type main chain with phenoxyethyl pendant groups bearing nitro or diethylamino substituents.

Key words: Propargyl ethers; Palladium dichloride; Polymerization; Copolymerization; Polyacetylenes; Homogeneous catalysis.

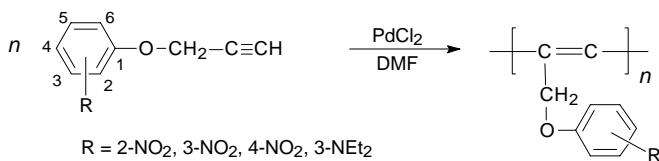
Synthesis of substituted polyacetylenes has attracted great interest because polyacetylenes with suitable substituents offer promising applications in electronics and optoelectronics^{1,2}. Introduction of proper pendant groups into polyacetylene molecules not only improves polymer solubility, processibility and stability but can also endow polymers with properties such as photoconductivity, electroluminescence, liquid crystallinity and non-linear optical effects. The importance of the influence of the polarity of pendant groups on the above listed polymer properties is known². In spite of that, polyacetylenes substituted with non-polar substituents have been mostly reported³. Mainly, this is a consequence of the fact that polymerizations of monomers with polar groups are complicated by inhibitive interactions of these groups with polymerization-inducing transition metal catalysts. Therefore, search for catalysts tolerating the

presence of polar groups in acetylenic monomers is of great importance in polyacetylene chemistry and may open ways for new polyacetylene-based materials.

Series of polyacetylenes with halogen- or oxygen-containing pendant groups have been prepared^{3,4}. However, polymerizations of acetylenes with nitrogen-containing groups still remain rather rare. As to nitro-group containing monomers, only recently the polymerization of 4-nitrophenylacetylene has been described^{5,6}. From previous reports, a mention on copolymerization of 4-nitrophenylacetylene with 4-dimethylamino-phenylacetylene is known⁷. In our preceding paper⁸, we reported a successful polymerization of nitrophenyl prop-2-yn-1-yl ethers (2-NPPE, 3-NPPE and 4-NPPE) with MoCl₅- and MoOCl₄-based metathesis catalysts. With these catalysts, high-molecular-weight polymers were prepared, of which only poly(4-nitrophenyl prop-2-yn-1-yl ether), [poly(4-NPPE)] was soluble in solvents such as dimethyl sulfoxide (DMSO) or *N*-methylpyrrolidone (NMP). Poly(3-nitrophenyl prop-2-yn-1-yl ether), [poly(3-NPPE)] and poly(2-nitrophenyl prop-2-yn-1-yl ether), [poly(2-NPPE)] were insoluble and could not be completely characterized.

In the literature, there are several reports on polymerizations of tertiary and secondary prop-2-yn-1-ylamines⁹⁻¹³ with transition metal catalysts. In addition to molybdenum-based catalysts, PdCl₂ showed remarkable activity in these reactions. However, no attempt to polymerize or copolymerize dialkylaminophenyl prop-2-yn-1-yl ethers has been made, to our best knowledge.

We have found that PdCl₂ in *N,N*-dimethylformamide (DMF) initiates the polymerization of 2-NPPE, 3-NPPE and 4-NPPE (Scheme 1) providing soluble polymers suitable for further characterization. PdCl₂ has been found to be also active in polymerization of 3-diethylamino phenyl prop-2-yn-1-yl ether (3-DEAPPE) (Scheme 1) and in copolymerization of 3-DEAPPE with 4-NPPE. The results are presented in this paper.



SCHEME 1

EXPERIMENTAL

Materials

PdCl₂ (Aldrich, 99%) was used as obtained. *N,N*-Dimethylformamide (DMF) (Lachema, Czech Republic, purum) was dried with P₂O₅ and distilled under argon. Preparation and characterization of 2-, 3- and 4-nitrophenyl prop-2-yn-1-yl ethers are described elsewhere⁸.

3-Diethylaminophenyl prop-2-yn-1-yl ether (3-DEAPPE) was prepared by alkylation of the corresponding phenol with prop-2-yn-1-yl bromide in the presence of excess of NaOH. The amount of 3.3 g

(20 mmol) of 3-diethylaminophenol (Aldrich, 97%) was mixed with 1.6 g (40 mmol) of NaOH (pulverized), 3.3 g of KI and 17 g of anhydrous Na_2CO_3 (pulverized) in 40 ml of dry DMF. Then 3 g (20 mmol) of prop-2-yn-1-yl bromide in toluene (Aldrich, 80 wt.%) was added and the reaction mixture was stirred at 50 °C for 8 h. After cooling, it was poured into 500 ml of water and organic products were extracted with diethyl ether. The ether layer was separated, and after washing with 1 M NaOH and water, dried with anhydrous Na_2SO_4 . After evaporating ether, the dark oil was purified by distillation *in vacuo*. Pure product (99%, GC-MS) was obtained as orange liquid (density 1.03 g/ml) soluble in common organic solvents (aromatics, CHCl_3 , DMF, methanol). Yield: 14%. IR spectrum (KBr), cm^{-1} : 3 270 ($\equiv\text{C-H}$), 2 110 ($\text{C}\equiv\text{C}$). ^1H NMR spectrum (CDCl_3), ppm (for atom numbering, see Scheme 1): 1.14 t, 6 H, $J(\text{CH}_3, \text{NCH}_2) = 7.0$ (CH_3); 2.48 t, 1 H, $J(\equiv\text{CH}, \text{O-CH}_2) = 2.1$ ($\equiv\text{CH}$); 3.31 q, 4 H (N-CH_2); 4.64 d, 2 H (O-CH_2); 6.22 dd, 1 H (H-4 or H-6); 6.30 dd, 1 H (H-4 or H-6); 6.26 t, 1 H (H-2); 7.11 t, 1 H, $J(\text{H-5}, \text{H-4}) = 7.9$, $J(\text{H-5}, \text{H-6}) = 7.9$ (H-5). ^{13}C NMR spectrum (CDCl_3), ppm (for atom numbering, see Scheme 1): 12.50 (CH_3), 44.31 (N-CH_2), 55.54 (O-CH_2), 75.06 ($\text{C}\equiv\text{CH}$), 78.96 ($\text{C}\equiv\text{CH}$), 99.02 (C-2), 100.63 (C-4 or C-6), 105.63 (C-4 or C-6), 129.75 (C-5), 149.02 (C-3), 158.90 (C-1). Attempts to resolve positions 4 and 6 were not successful.

Polymerization

Polymerizations were performed using the standard vacuum break-seal technique¹⁴ and DMF as solvent. The reaction conditions were (unless otherwise stated): initial monomer concentration 0.5 mol/l, initial molar ratio monomer : catalyst 50, reaction temperature 85 °C, reaction time 24 h. Polymerizations were started by mixing PdCl_2 in DMF with DMF solution of monomer (2-NPPE, 3-NPPE, 4-NPPE, 3-DEAPPE) or mixture of comonomers (4-NPPE + 3-DEAPPE). In the time depending experiment, PdCl_2 in DMF was mixed with 4-NPPE solution in DMF. After 10 min of stirring at 85 °C, the reactor was removed from a bath and the orange solution was divided into individual ampoules, which were, after sealing off, treated separately. The reactions were always quenched by pouring the reaction mixture into an excess of methanol or water (in the case of homopolymerization of 3-DEAPPE). The methanol- or water-insoluble product was isolated, washed with methanol and dried *in vacuo* at 40 °C to constant weight. The yield of polymer was determined gravimetrically. The supernatant from the polymer isolation was (after evaporating solvents) analyzed by SEC, IR and GC.

Techniques

IR spectra were recorded on a Specord 75 IR spectrometer in KBr pellets, UV-VIS spectra on a Hewlett-Packard HP 89500 spectrometer.

^1H and ^{13}C NMR spectra of polymers were measured in CDCl_3 or in $\text{DMSO}-d_6$ solution on a Varian UNITY-500 NMR spectrometer. A basic one-pulse sequence with broad-band ^1H decoupling for the ^{13}C nucleus were used. The relaxation delay and acquisition time were respectively 5 and 1 s for ^{13}C , 5 or 8 s and 1 or 2 s for ^1H . An exponential weighting function (linebroadening 4 Hz for ^{13}C and 1 Hz for ^1H NMR spectra) was applied. ^1H NMR spectra measured in CDCl_3 solution were referenced to hexamethyldisilane (HMDS, δ 0.04), used as an internal standard. The remaining spectra were referenced to a central line of the solvent multiplet: δ 76.99 for CDCl_3 , δ 39.7 for $\text{DMSO}-d_6$, δ 2.5 for DMSO.

^1H and ^{13}C NMR spectra of the 3-DEAPPE monomer were recorded on a Varian UNITY-200 NMR spectrometer in a CDCl_3 solution with HMDS added and referenced like in the previous cases. Homonuclear selective decoupling and chemical shifts were used for the ^1H NMR line assignment. Chemical shifts and line multiplicities found by DEPT (ref.¹⁵) editing helped in ^{13}C NMR line assignment of NEt_2 , $\text{CH}_2\text{-O}$ and $\text{C}\equiv\text{CH}$ groups. Quaternary C-1 and C-3 carbons were assigned by ^{13}C

proton selective decoupling experiments while tertiary C-2, C-4, C-5 and C-6 were assigned using HETCOR spectrum.

For SEC analyses, two devices were used: (i) Apparatus train consisting of a high-pressure pump HPP 5001 (Laboratorní přístroje, Czech Republic), Rheodyne sampling valve 7125 (Rheodyne, U.S.A.), GM 1000 column (Labio, Czech Republic; exclusion limits $6 \cdot 10^5$ and $1 \cdot 10^3$) or PL 1000 column (Polymer Laboratories, United Kingdom), and UV detector HP1030B (Hewlett-Packard) operating at 254 or 400 nm. As a mobile phase, *N*-methylpyrrolidone (NMP) (distilled *in vacuo*) was used with Labio column (flow rate 1 ml/min) and tetrahydrofuran (THF) (distilled, dried over molecular sieve) was applied for PL column with the same flow rate. (ii) TSP (Thermo Separation Products, Florida, U.S.A.) chromatograph, series of two PL column (Mixbed B and C), UV detector operating at 254 nm and THF as a mobil phase (flow rate 0.7 ml/min). In all cases, the analyses were performed at room temperature and molecular weights relative to polystyrene standards are reported.

RESULTS AND DISCUSSION

Polymerization of 2-, 3- and 4-Nitrophenyl Prop-2-yn-1-yl Ethers

The results of polymerization of 2-, 3- and 4-NPPE are given in Table I. PdCl₂ polymerizes all three monomers providing brown methanol-insoluble polymers in good yields. Analyses of supernatants collected after polymer isolation (IR, SEC) revealed only unreacted monomers accompanied by a small amount (<10%) of low oligomers

TABLE I

Results of polymerization of 2-, 3- and 4-nitrophenyl prop-2-yn-1-yl ethers with PdCl₂. Initial catalyst concentration 0.5 mol/l, monomer : catalyst molar ratio 50, DMF, 85 °C

| No. | Monomer | Reaction time | Polymer yield, % | Polymer fraction, % ^a | | |
|-----|---------------------|---------------|------------------|----------------------------------|-------------------------------|------------------|
| | | | | MW | | |
| | | | | $1 \cdot 10^3 - 1 \cdot 10^4$ | $1 \cdot 10^4 - 5 \cdot 10^4$ | $> 5 \cdot 10^4$ |
| 1 | 2-NPPE | 24 h | 41 | 22 | 16 | 62 |
| 2 | 3-NPPE | 24 h | 43 | 63 | 22 | 15 |
| 3 | 4-NPPE | 24 h | 50 | 46 | 9 | 45 |
| 4 | 4-NPPE | 2 h | 5 | 49 | 31 | 20 |
| 5 | 4-NPPE | 5 h | 17 | 54 | 24 | 22 |
| 6 | 4-NPPE | 9 h | 22 | 46 | 24 | 30 |
| 7 | 4-NPPE | 24 h | 46 | 47 | 20 | 33 |
| 8 | 4-NPPE ^b | 3 days | 0 | – | – | – |

^a SEC record area; ^b room temperature.

(MW < 1 000) and proved that the polymers are strongly prevailing products in all cases.

Contrary to the results obtained with MoCl₅- or MoOCl₄-based catalysts⁸, there are only small differences in polymer yields in PdCl₂ polymerizations of individual monomers. For 3- and 4-NPPE, the yields achieved with PdCl₂ are comparable with those obtained with Mo-based catalysts; for 2-NPPE, however, the yield achieved with PdCl₂ is significantly higher than the best result obtained with Mo catalyst (24% for the MoOCl₄ + Me₄Sn catalyst system⁸). PdCl₂ catalyst does not seem so sensitive to the steric effect of NO₂ group in *ortho* position. However, PdCl₂ requires different reaction conditions than Mo catalysts, in particular higher temperatures and prolonged reaction times (*cf.* 60 °C and 8 h for Mo catalysts⁸). It is seen from the time dependence experiment (Nos 4–7, Table I), that even at 85 °C the reaction proceeds slowly and prolonged time is necessary to obtain a good yield. The slight difference in polymer yield and molecular weight distribution (*vide infra*) between experiments No. 3 and No. 7 in Table I may be due to the different regime in the early stages of the reaction (see Experimental). At room temperature (No. 8, Table I) no methanol-insoluble product was obtained even after 3 days of reaction.

All poly(nitrophenyl prop-2-yn-1-yl ether)s prepared with PdCl₂ catalyst are soluble in DMF, DMSO and NMP. Their molecular-weight characterization was performed by SEC in NMP and the results are given in Figs 1 and 2. In Fig. 1, the SEC chromato-

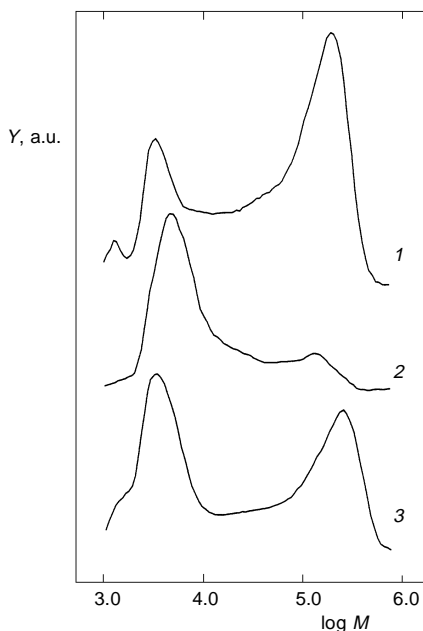


FIG. 1

SEC records (in NMP) of: 1 poly(2-NPPE) (sample No. 1, Table I), 2 poly(3-NPPE) (sample No. 2, Table I) and 3 poly(4-NPPE) (sample No. 3, Table I). *Y* detector response, *M* molecular weight

grams of poly(2-NPPE), poly(3-NPPE) and poly(4-NPPE) (Nos 1, 2 and 3, respectively, Table I) are given. These chromatograms show broad molecular-weight distributions with two distinct maxima: in the low (3 000–5 000) and high-molecular-weight region (150 000–270 000). While for poly(2-NPPE) and poly(4-NPPE), the high-molecular-weight maxima are well developed, for poly(3-NPPE) this maximum is only weak. Time dependence experiments (polymerization of 4-NPPE, Nos 4–7, Table I) showed an additional (weak) maximum in the central region of molecular weight (at about 15 000) for the lower reaction times (Fig. 2). It is evident that individual peaks of chromatograms in Figs 1 and 2 were not baseline-separated. In order to quantify the individual polymer fractions, we divided the area of each SEC record into three parts corresponding to low-, medium- and high-molecular-weight regions according to the limits given in Table I. The percentages of thus obtained polymer fractions are listed in Table I from which the following conclusions can be drawn: (i) the high-molecular-weight fraction decreases in the following series: poly(2-NPPE) > poly(4-NPPE) > poly(3-NPPE); (ii) in the time course of 4-NPPE polymerization, the percentage of low-molecular-weight polymer fraction in the product remains approximately unchanged, the medium-molecular-weight fraction decreases, but the high-molecular-weight fraction continuously rises.

Time evolution of molecular-weight distribution (polymerization of 4-NPPE, Fig. 2) suggests the presence of at least two different kinds of important catalytic centres in the polymerization system, responsible for the formation of low- and high-molecular-weight polymer fractions, respectively. The nature of catalytic species of both types is not apparent. In olefin polymerizations induced by Pd(II) compounds, monomer insertion in the Pd–C bond is assumed¹⁶. For polymerization of substituted acetylenes, the same reaction mode is very probable. Catalytic centres resulting from the reaction of PdCl₂ with DMF and/or monomers may differ in both the Pd oxidation state and the

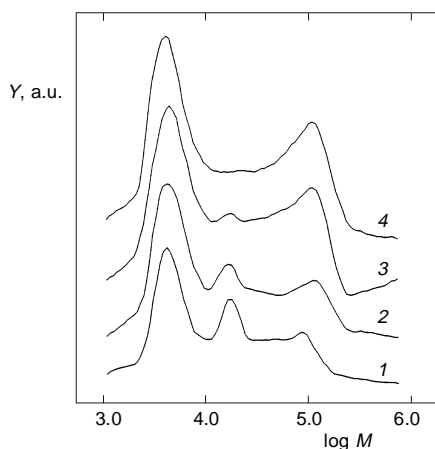


FIG. 2
SEC records (in NMP) obtained in the course of polymerization of 4-NPPE. Polymerization times: 1 2 h, 2 5 h, 3 9 h, 4 24 h (samples Nos 4–7, Table I). *Y* detector response, *M* molecular weight

kind of ligands in the Pd coordination sphere. The differences in molecular-weight distribution of poly(2-NPPE), poly(3-NPPE) and poly(4-NPPE) in Fig. 1 may probably reflect differences in concentrations of distinct types of catalytic centres formed in the presence of individual monomers.

Polymers prepared were characterized by IR, UV-VIS and NMR spectroscopy. IR spectra of poly(2-NPPE), poly(3-NPPE) and poly(4-NPPE) prepared with PdCl₂ were practically identical with IR spectra of corresponding polymers prepared with Mo-based catalysts, reported previously⁸. No significant differences were also revealed between individual poly(4-NPPE) listed in Table I. Always, the absence of bands corresponding to $\nu(\equiv\text{C}-\text{H})$ and $\nu(\text{C}\equiv\text{C})$ vibrations (3 270–3 245 cm⁻¹ and about 2 125 cm⁻¹, respectively) in polymers confirms the complete transformation of monomer triple bond. On the other hand, the bands characteristic of the CH₂ group (2 932, 2 982 cm⁻¹), NO₂ group (1 540–1 522 and about 1 355 cm⁻¹) and phenyl ring affected by NO₂ substitution (3 120–3 030 cm⁻¹, about 1 610, 1 585 and 1 490 cm⁻¹ and between 875 and 700 cm⁻¹) give evidence for the presence of nitrophenoxymethyl pendant groups in polymers. UV-VIS spectra of poly(2-NPPE), poly(3-NPPE) and poly(4-NPPE) (together with spectra of corresponding monomers) are shown in Fig. 3. Intensive bands in the UV region take their origin mainly from transitions in substituted phenyl rings of the pendant groups. The VIS part of spectra must be ascribed to $\pi-\pi^*$ transition in polyacetylenic main chain with a broad distribution of effective conjugation length.

¹H and ¹³C NMR spectra of poly(2-NPPE), poly(3-NPPE) and poly(4-NPPE) are given in Fig. 4. In ¹H NMR spectra (Fig. 4a), broad peaks in the region 3.5–5.5 ppm are ascribed to OCH₂ group and broad bands between 6.0 and 8.5 ppm to aromatic protons.

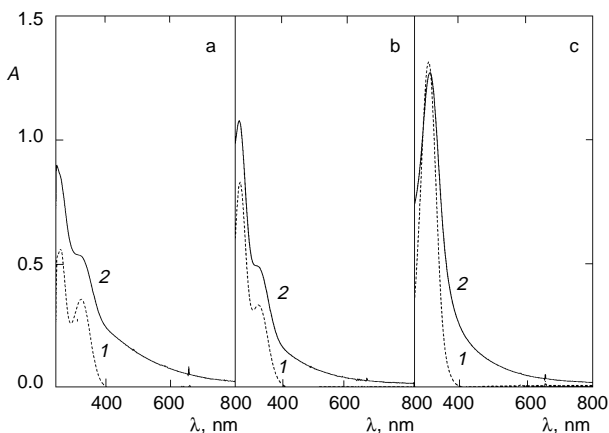


FIG. 3

UV-VIS spectra of: 1 2-NPPE and 2 poly(2-NPPE) (a); 1 3-NPPE and 2 poly(3-NPPE) (b); 1 4-NPPE and 2 poly(4-NPPE) (sample No. 3, Table I) (c). DMSO, $c = 0.3$ mg/ml, $l = 0.1$ cm

Olefinic protons of the main chain are supposed to be very broad and to lie in the last region overlapped by signals of aromatic protons. The line broadening in these spectra indicates a high irregularity of all polymers measured (irregularity with respect to head-to-tail and head-to-head monomer linkages and/or *cis/trans* configuration of the main-chain double bonds). ^{13}C NMR spectra (Fig. 4b) consist of OCH_2 broad and low-intensity peaks in the range 63–75 ppm (probably doublets) and peaks of aromatic carbons assigned according to the corresponding monomers (for numbering the peaks in Fig. 4b, see the numbering in Scheme 1). The main-chain carbon-atom signals are less intensive and manifest themselves by base line elevation in the region 130–150 ppm. The splitting of bands corresponding to OCH_2 groups is visible in ^1H NMR spectra of all poly(nitrophenyl prop-2-yn-1-yl ether)s in Fig. 4a and has been also reported for other poly(phenyl prop-2-yn-1-yl ether)s¹⁷. A similar splitting seems to be present also in ^{13}C NMR spectra. It may be considered as a result of hindered rotation of bulky phenoxymethyl groups in polymer molecules. However, neither IR nor NMR spectra allow to draw any reliable detailed information about the conformation of the main chain giving no data sufficient for construction of any conformation models.

Polymerization and Copolymerization of 3-Diethylaminophenyl Prop-2-yn-1-yl Ether

Table II shows the results of polymerization experiments with 3-DEAPPE. Its homopolymerization provides a very good yield of a black polymer soluble in CHCl_3 , NMP

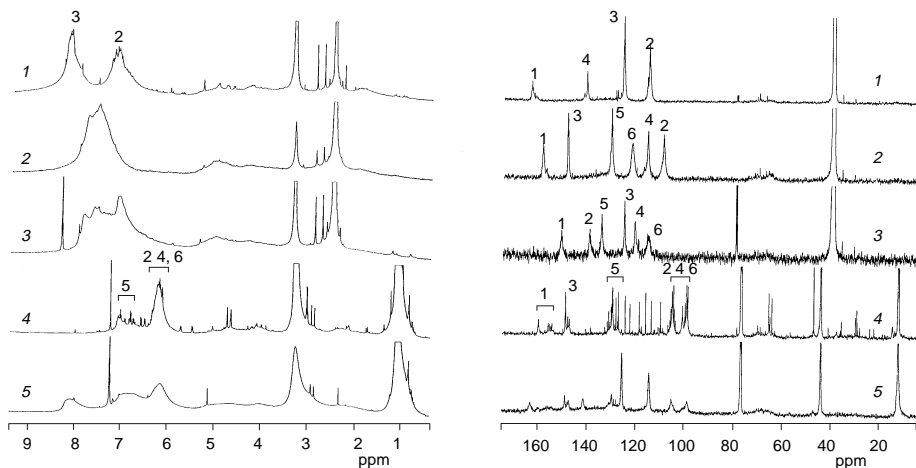


FIG. 4

^1H NMR spectra (a) and ^{13}C NMR spectra (b) of poly(NPPE)s in $\text{DMSO}-d_6$, and poly(3-DEAPPE) and copolymer of 3-DEAPPE with 4-NPPE in CDCl_3 . 1 Poly(4-NPPE) (sample No. 3 Table I), 2 poly(3-NPPE), 3 poly(2-NPPE), 4 poly(3-DEAPPE), 5 copolymer (sample No. 2, Table II). Solvent and impurities lines (ppm) in: ^1H NMR 2.5; 3.4 (H_2O); 7.25; 2.89 and 2.73 (DMF) and ^{13}C NMR 40; 77

and in THF. Although insoluble in methanol, this polymer could not be isolated from the reaction mixture *via* precipitation into methanol; instead, water had to be used. According to SEC in NMP, poly(3-diethylaminophenyl prop-2-yn-1-yl ether), [poly(3-DEAPPE)] (Table II, No. 1) has a bimodal molecular-weight distribution in which the low-molecular-weight fraction ($M_n = 4\ 200$, $M_w = 5\ 400$) strongly prevails. High-molecular-weight fraction ($MW > 100\ 000$) makes only about 10 wt.% of the polymer. Poly(3-DEAPPE) spectra (IR (Fig. 5), UV-VIS (Fig. 6) and NMR (Fig. 4)) are consistent with the polymer structure given in Scheme 1. Complete disappearance of IR bands and NMR signals at $3\ 270$ and $2\ 110\ \text{cm}^{-1}$, at $2.48\ \text{ppm}$ (^1H) at $78.96\ \text{ppm}$ and at $75.06\ \text{ppm}$ (^{13}C) as a result of polymerization proves the polymerization to proceed by transformation of the monomer $\text{C}\equiv\text{C}$ bond. Enhanced absorbances of polymer at $\lambda > 325\ \text{nm}$ due

TABLE II

Results of polymerization and copolymerization of 3-diethylaminophenyl prop-2-yn-1-yl ether with PdCl_2 . Initial catalyst concentration $10\ \text{mmol/l}$, DMF, $85\ ^\circ\text{C}$ (F initial molar fraction of 4-nitrophenyl prop-2-yn-1-yl ether in the comonomer feed, f molar fraction of 4-nitrophenyl prop-2-yn-1-yl ether units in copolymer)

| No. | Monomer | F | f | Polymer yield, % ^a | M_n^d | M_w^d |
|-----|-------------------------------|------|-----|-------------------------------|------------|------------|
| 1 | 3-DEAPPE ^b | 0 | 0 | 76 | $4\ 200^e$ | $5\ 400^e$ |
| 2 | 3-DEAPPE, 4-NPPE ^b | 0.5 | 0.3 | 40 | $3\ 500^f$ | $9\ 200^f$ |
| 3 | 3-DEAPPE, 4-NPPE ^c | 0.75 | 0.5 | 52 | $3\ 000^f$ | $7\ 900^f$ |

^a Relative to the total initial mass of comonomers; ^b initial 3-DEAPPE concentration $0.5\ \text{mol/l}$; ^c initial 3-DEAPPE concentration $0.25\ \text{mol/l}$; ^d without high-molecular-weight (minor) fraction if any; ^e in NMP; ^f in THF.

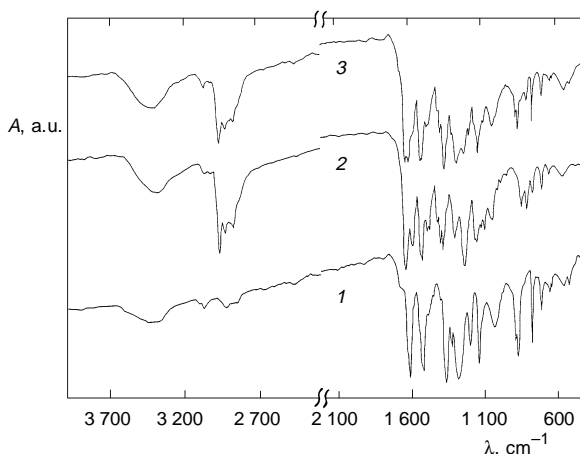


FIG. 5

IR spectra: 1 Poly(4-NPPE) (sample No. 3 Table I), 2 poly(3-DEAPPE), 3 copolymer of 4-NPPE with 3-DEAPPE (sample No. 2, Table II)

to the double-bond-conjugated main chain are clear in comparison with UV-VIS spectrum of the monomer. The bands characteristic of diethylaminophenoxy groups are evident in the IR spectrum of polymer (mainly bands of ethyl groups in the $2\,800$ to $3\,000\text{ cm}^{-1}$ region, aromatic ring vibration at $1\,607$ and $1\,500\text{ cm}^{-1}$, C–O and C–N vibrations at $1\,266$ and $1\,200\text{ cm}^{-1}$). The signals in ^1H NMR spectra were assigned to the polymer as follows: signal at 1.14 ppm to CH_3 , at 3.30 ppm to N-CH_2 , broad signal at $3.6\text{--}5.2\text{ ppm}$ to O-CH_2 , and signal at $5.8\text{--}7.2\text{ ppm}$ to aromatic protons as indicated by numbers in the spectrum (Fig. 4a). The olefinic proton signal must be also present in this last region but, like in the previous cases, it is supposed to be broad and overlapped by the signals of aromatic protons. In ^{13}C NMR spectrum, CH_3 signal is located at 12.6 ppm , N-CH_2 signal at 44.3 ppm , O-CH_2 signal at $60\text{--}75\text{ ppm}$, and the positions of signals of aromatic carbons are indicated by numbers (Fig. 4b). Tertiary and quaternary carbons of the polymer main chain are expected at about 125 ppm and 135 ppm , respectively, but they are probably very broad and hardly visible. In ^1H NMR as well as in ^{13}C NMR, the sharp lines and slightly elevated base line in the aliphatic region indicate the presence of some impurities (probably low oligomers and/or side products of initiation reactions).

Using mixtures of 3-DEAPPE and 4-NPPE as a comonomer feed (experiment No. 2 and No. 3, Table II) brown copolymers precipitated from methanol after termination which were completely soluble in NMP and CHCl_3 . Copolymer from experiment No. 2 is completely soluble in THF, copolymer from No. 3 contains a small amount of THF-insoluble fraction. Their IR and NMR spectra (Figs 5 and 4) exhibit all bands characteristic of pendant groups of both monomeric units. The spectra together with the differences in solubility of copolymers and corresponding homopolymers give evidence that copolymers were really formed in copolymerization experiments. The SEC records in NMP and THF show bimodal molecular-weight distribution for both copolymers. The minor, high-molecular-weight fraction has molecular weight about $1 \cdot 10^6$ for both

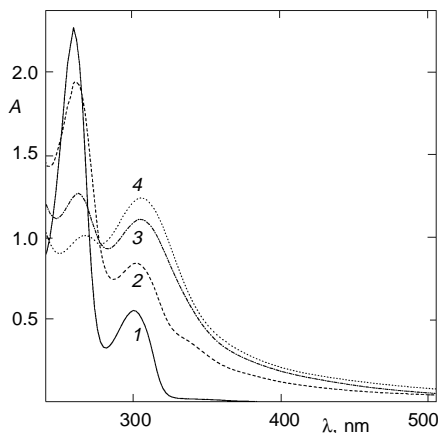


FIG. 6
1 UV-VIS spectra of 3-DEAPPE, 2 poly(3-DEAPPE), and copolymers of 4-NPPE with 3-DEAPPE 3 (sample No. 2, Table II), 4 (sample No. 3, Table II). THF, $c = 0.3\text{ mg/ml}$, $l = 0.1\text{ cm}$

samples (SEC in THF). For sample No. 3, this fraction makes about 20% of the whole SEC record area, while for sample No. 2, its amount is negligible (~2%). Molecular-weight characteristics of the major, low-molecular-weight fractions (determined in THF using PL 1000 column) are given in Table II. Composition of copolymers was determined from ^1H NMR spectra (using CH_3 bands) and the results are presented in Table II. It can be seen that both copolymers are enriched in 3-DEAPPE monomeric units compared with the compositions of comonomer feeds used for copolymerizations, *i.e.* 3-DEAPPE is more readily incorporated into copolymer chains. Increasing 4-NPPE fraction in the comonomer feed from 0.5 to 0.75 leads to an enhanced amount of the high-molecular-weight copolymer fraction. Therefore, the composition of low- and high-molecular-weight fractions may differ: the high-molecular-weight fraction may be enriched by 4-NPPE units. UV-VIS spectra of 3-DEAPPE, poly(3-DEAPPE) and both copolymers are shown in Fig. 6. The long-wavelength tails of UV-VIS spectra of the copolymers (Fig. 6) do not differ significantly suggesting the approximately same distribution of effective conjugation length in both copolymers, probably very similar to that of poly(3-DEAPPE).

In the supernatants, after poly(3-DEAPPE) and copolymers isolation, a mixture of low-molecular-weight products ($\text{MW} < 1\ 000$) was revealed by SEC in THF. However, no monomer(s) were found (IR, GC), contrary to the experiments in which NPPEs were homopolymerized. This indicates that oligomerization and/or other monomer transformation reactions take place in considerable extent in the reaction systems containing 3-DEAPPE.

It may be noted that Mo-based catalyst, which showed high activity in 4-NPPE homopolymerizations⁸, failed in copolymerization of 4-NPPE with 3-DEAPPE. Using the $\text{MoOCl}_4/3\ \text{Me}_4\text{Sn}$ catalyst system in benzene (60 °C, 6 h, initial MoOCl_4 concentration 3 mmol/l, initial 4-NPPE concentration equal to initial 3-DEAPPE concentration, 80 mmol/l), only homopolymer of 4-NPPE was obtained in the yield of 5%. Evidently, the used Mo-based catalyst does not tolerate amino group in 3-DEAPPE.

CONCLUSIONS

PdCl_2 in DMF is an active catalyst for homopolymerization of 2-, 3- and 4-NPPEs as well as 3-DEAPPE. It provides soluble polymers of the polyacetylene type having phenoxymethyl pendants groups with nitro or diethylamino substituents. Molecular-weight distribution is bimodal having the first maximum in the low-molecular-weight region (3 000–5 000) and the second maximum in the high-molecular-weight region (above 100 000). The ratio of these fractions depends strongly on the starting monomer. Although bimodal molecular-weight distributions of products have already been reported for olefin polymerizations with alkylpalladium complexes¹⁶, to our knowledge, they have not been observed in acetylene polymerizations.

Copolymers of 3-DEAPPE with 4-NPPE soluble in common solvents such as CHCl_3 and THF were prepared with PdCl_2 in DMF. The copolymer containing 50% of 4-NPPE monomeric units has bimodal molecular-weight distribution with major fraction of $M_n = 3\ 000$ and minor fraction of molecular weight about $1 \cdot 10^6$; the copolymer containing 30% of 4-NPPE monomeric units has M_n of 3 500. To our knowledge, they are the first examples of soluble acetylene-type copolymers bearing both nitro and dialkylamino substituents on pendant groups (the copolymer of 4-nitrophenylacetylene with 4-dimethylaminophenylacetylene was only partly soluble⁷). The good solubility of the copolymers prepared makes possible a subsequent study of their physical properties (e.g., in thin layers).

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