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End-Functionalized π-Conjugated Oligomeric Materials for Photoelectrical Applications

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Summary: Soluble poly(diphenylacetylene)s (PDA) capped with PhCO– groups (PDA-C) and Ph_2C= groups (PDA-P) were prepared via McMurry reductive coupling of benzil and carbonyl-olefin exchange reaction of tetraphenylethene and benzil, respectively. Fluoren-9-ylidene groups have been introduced into PDA by the McMurry coupling of PDA-C with fluoren-9-one and via copolymerization of benzil and fluoren-9-one. The oligomers prepared are stable in air, soluble in a variety of solvents. They can be processed by casting to form good-quality thin films suitable for measurements of electrical and optoelectrical properties.

Keywords: conjugated polymers; oligomers

Introduction

Poly(vinylene)s derived from monosubstituted acetylenes are the first large group of π–conjugated organic materials which showed impressive electrical and optoelectrical properties. However, these polymers have insufficient stability under electrical and optical loading as well as low stability in air, which is the main drawback preventing them from practical use [1-8]. On the other hand, fully substituted polyvinylenes, such as poly(diphenylacetylene)s (PDA) introduced by Masuda and coworkers [4,9], are sufficiently stable in air; however, unsubstituted PDAs prepared by their procedures are insoluble in any solvent, and ring-substituted PDAs, which are soluble, do not show desired electrical and optoelectrical properties. The procedures of Masuda et al. consist in the chain polymerization of diphenylacetylene with $TaCl_5$- and $NbCl_5$-based catalysts, which is not controlled as to the polymer molecular weight. It seems that a too high molecular weight of the so obtained PDAs is the main reason for their insolubility. Since polymers of low-to-medium molecular weights are usually soluble and, in addition, it is well known that various oligomeric conjugated oligomers show functional properties that are good

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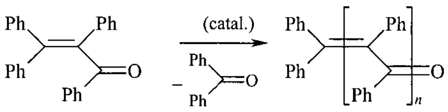
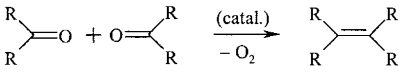
enough for their applications as materials in construction of electronic and optoelectronic devices [10], it seems useful to find a synthetic path to soluble and processable low-molecular-weight PDAs.

We have tried to accomplish such synthesis by using Masuda's catalyst systems at low diphenylacetylene/catalyst ratios and various temperatures; however, we always obtained high-molecular-weight, insoluble PDA. Also attempts to prepare processable PDAs by using tungsten dinuclear complexes containing unbridged quadruple bonds [11] were unsuccessful. Thus, it seems that formation of growing species is too slow compared with the propagation in these systems, which does not allow to synthesize low-molecular-weight PDAs in that way. More than ten years ago, Jossifov et al. [12-15] used the carbonyl-olefin exchange reaction, which reminds of the McMurry reaction [16], for preparation of various conjugated polymers. They prepared PDA from diphenylethane-1,2-dione (benzil) and 1,1,2,2-tetraphenylethene and from 1,2,3,3-tetraphenylprop-2-en-1-one using WCl_6, $MoCl_5$ and $WOCl_4$ in combination with $AlCl_3$ as catalysts, which, however, must be used at high monomer/catalyst mole ratios ranging from 0.1 to 1 to achieve a good yield of polymer. According to the results obtained and the mechanism proposed by Jossifov [14,15], the carbonyl-olefin exchange reactions give soluble PDAs with benzoyl (Ph-CO) and diphenylmethylidene ($Ph_2C=$) end groups. In principle, the carbonyl-olefin exchange reaction can also be used for additional end-group modification of PDAs. In the present contribution we report the preparation of soluble PDAs capped with Ph-CO, $Ph_2C=$, and fluoren-9-ylidene end groups by combining the carbonyl-olefin exchange reaction and McMurry reaction.



Polymerization via carbonyl-olefin exchange reaction



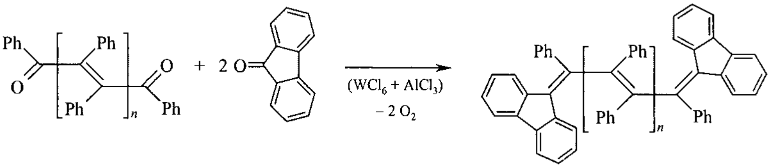
McMurry reaction

Experimental

General. Benzil (diphenylethane-1,2-dione), tetraphenylethene, tungsten hexachloride (WCl_6), aluminium trichloride ($AlCl_3$), chlorobenzene dried over molecular sieve, 1,4-dioxane for fluorescence measurements (all Aldrich), fluoren-9-one (Fluka) and methanol and sodium hydroxide (both Lachema, Czech Republic) were used as supplied. Toluene (Lachema, Czech Republic) was distilled from P_2O_5 and kept over molecular sieve. Size exclusion chromatography (SEC) analyses of polymers were made on a TSP (Thermo Separation Products, Florida, USA) chromatograph equipped with a UV detector operating at 254 nm and a series of two PL-gel columns (Mixed B and Mixed-C, Polymer Laboratories Bristol, UK, THF eluent, flow rate 0.7 mL min^{-1}); molecular weight values based on polystyrene standards are reported. IR spectra were measured on a Nicolet Magna IR-760 spectrophotometer using the diffusion reflectance method. UV-VIS absorption spectra were recorded on a double beam Perkin Elmer 340 spectrophotometer and steady-state photoluminescence spectra on a SPEX Fluorolog 3-11 instrument using polymer solutions in 1,4-dioxane.

Polymerization and copolymerization reactions were carried out under dry argon atmosphere in chlorobenzene or toluene using the following concentrations of reactants: $[WCl_6]_0 = [AlCl_3]_0 = 0.5$ M; $[\text{monomer}]_0 = 0.5$ M or 1 M. The monomer or a mixture of monomers was dissolved in particular solvent (25 mL) at 60 °C, then thermostatted at a desired temperature, weighed amounts of powdered $AlCl_3$ and WCl_6 were added under stirring and the resulting mixture was allowed to react for a given time 1 – 6 h. The reaction was terminated by adding aqueous NaOH (50 mL, 40 % w/w) under shaking, the organic phase was separated and washed with distilled water till the neutral reaction. The product was precipitated by adding methanol (100 mL), separated by centrifugation, four times reprecipitated from toluene/methanol and dried in vacuum to constant weight. PDA with terminal $=CPh_2$ groups (hereinafter denoted as PDA-P) was prepared by reacting a mixture of benzil and 1,1,2,2-tetraphenylethene, PDA with terminal benzoyl groups (PDA-C) by reacting only benzil as monomer. A copolymer of benzil and fluoren-9-one prepared using the latter procedure is denoted PDA-F.

End-capping of PDA-C with fluoren-9-one. PDA containing fluoren-9-ylidene end groups, PDA-FM, was prepared by a modification of PDA-C using the reaction of the oligomer with fluoren-9-one. Solid WCl_6 (0.1 g, 0.253 mmol) and solid $AlCl_3$ (0.05 g, 0.375 mmol) were added under argon to a solution of PDA-C (100 mg) of $M_w = 1\,290$ and fluoren-9-one (50 mg, 0.277 mmol) in chlorobenzene (13 ml), the suspension was heated up and stirred for 3 h at 100 °C. Then the mixture was cooled down to room temperature and worked up as described above ($M_w = 1\,410$).



Results and Discussion

Polymerization data summarized in Table 1 clearly show that the studied reaction is rather complex; nevertheless, some qualitative conclusions can be drawn. As can be seen, a longer reaction time and mainly a higher reaction temperature and higher monomer concentration have generally a positive effect on the yield and M_w of the benzil homopolymer and copolymer. Also, the influence of the solvent used for the polymerization is evident. In general, higher yields as well as higher molecular weights are obtained in chlorobenzene rather than in toluene.

Table 1. Polymerization data for poly(diphenylacetylene)s

No.	Monomer (mole ratio)	[WCl$_6$]/ [monomer(s)]	*T*, °C	*t*, h	Solvent	Yield %	M_w
1	B	1	60	1	PhCl	nd[b)]	690
2	B	1	60	2	PhCl	nd[b)]	740
3	B	1	60	3	PhCl	48	1 200
4	B	1	60	6	PhCl	53	1 300
5	B	1	100	3	PhCl	49	1 400
6	B	0.5	100	1	PhCl	91	2 500
7	B	0.5	100	3	PhCl	93	3 600
8	B	1	131	3	PhCl	~100	7 200 [a)]
9	B	1	60	3	toluene	57	350
10	B	0.5	60	3	toluene	81	1 400
11	B + T (1:1)	1	25	6	PhCl	33	690
12	B + T (1:1)	1	25	48	PhCl	93	2 100
13	B + T (1:1)	1	60	6	PhCl	25	650
14	B + T (1:1)	1	80	6	PhCl	38	830
15	B + T (1:1)	1	100	6	PhCl	91	2 200
16	B + T (2:1)	1	60	3	toluene	51	410
17	B + T (1:1)	1	60	3	toluene	30	460
18	B + T (1:2)	1	60	3	toluene	22	510
19	B + T (1:0.8)	0.7	60	1	toluene	60	1 100
20	B + F (1:1)	1	80	3	PhCl	23	1 100
21	B + F (1:1)	0.5	80	3	PhCl	48	7 900
22	B + F (1:1)	0.5	80	3	toluene	52	1600
23	F	1	80	6	PhCl	12	2 900

[a)] Molecular weight of a soluble fraction of the polymer (ca. 8 % of the isolated polymer).
[b)] not determined
B – benzil, T – tetraphenylethene, F – fluoren-9-one.

Using the observed effects of reaction conditions, the character of the prepared PDAs can be tuned from short-chain oligomers to almost insoluble polymers formed under reflux of the solvent (Table 1, entry No. 8).

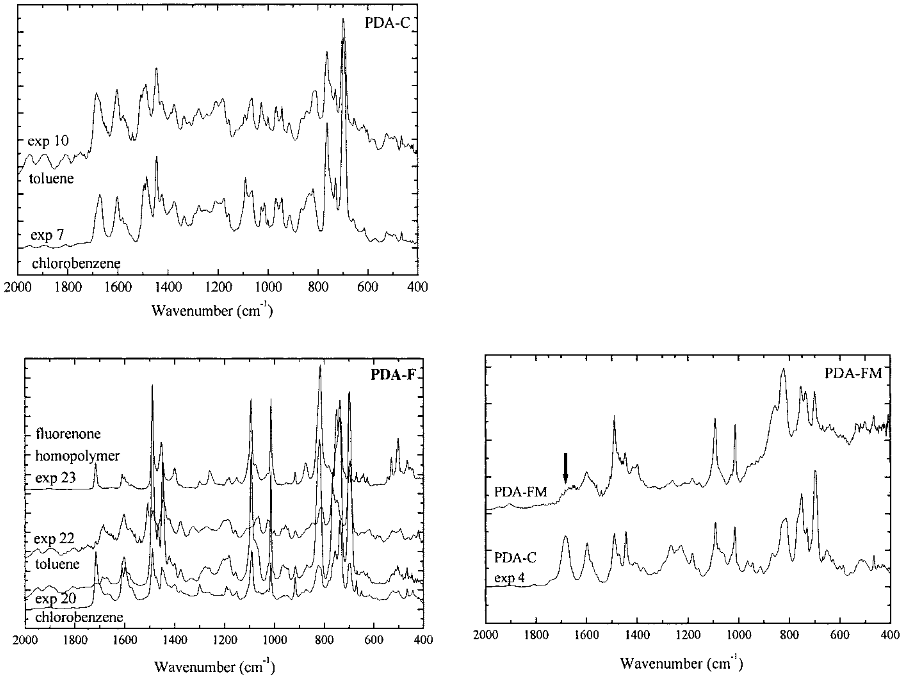


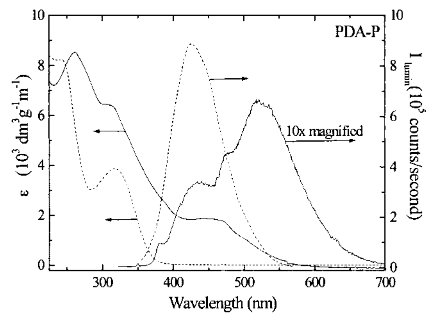
Figure 1. - IR spectra of selected PDA oligomers acquired by diffusion reflectance method.

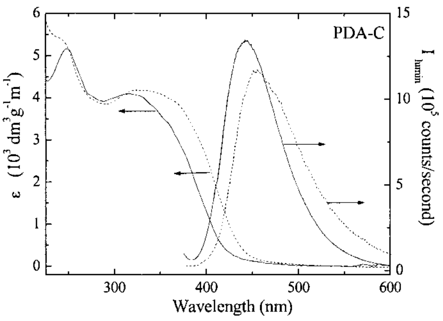
Copolymerization of benzil and fluoren-9-one provided interesting results. We assumed that fluoren-9-one will act as a precursor of terminal units only, introduced to both ends of PDA via the McMurry reaction. However, the observed results surprisingly indicate that fluoren-9-one also acts as a bifunctional monomer, the units of which are also incorporated in the polymer backbones. This suspicion was confirmed by a successful homopolymerization of this monomer (experiment 23). On the other hand, functionalization of the prepared PDA-C gave a polymer, in which terminal carbonyl groups are almost absent being replaced with fluoren-9-ylidene groups (PDA-FM). However, nor in this case can we exclude participation of homopolymerization of fluoren-9-one in the overall reaction.

IR spectra of selected oligomers of all four classes are compared in Figure 1. As can be seen, the band at 1686 cm^{-1}, which is typical of carbonyl groups, is absent in IR spectra of PDA with $=CPh_2$ end groups as expected according to the results of Jossifov [13-15]. However, this band is present in IR spectrum of PDA-F sample prepared in toluene, which proves incomplete end-capping of this polymer with fluoren-9-ylidene units, most probably owing to prevailing incorporation of fluorene units into the polymer backbones. On the other hand, the CO band is practically absent in the IR spectrum of PDA-F prepared in chlorobenzene, which corresponds with the above discussed easier course of the coupling reaction in this solvent. We cannot provide more detailed data on the structure of these copolymers because only poorly resolved NMR spectra were obtained.

In the case of copolymerization of benzil with 1,1,2,2-tetraphenylethene (Table 1, experiments 11-19), we found that an increasing amount of tetraphenylethene in the starting mixture leads to a decrease in the yield of methanol-insoluble polymer (experiments 16-18), which can be ascribed to the preferred formation of non-functionalized benzil homopolymer. According to IR spectra, all copolymers of benzil and tetraphenylethene contain some carbonyl groups, which indicates that, under the used reaction conditions, the McMurry reaction is favored compared with the carbonyl-olefin exchange reaction.

UV-vis absorption and fluorescence spectra of PDA-P oligomers in dioxane solution are presented in Figure 2. PDA prepared in toluene was probably partly contaminated with a very stable complex of the oligomer with the catalyst residues [17], which absorbs in the visible region and, as can be seen from Figure 2, quenches the polymer photoluminescence. Compared with PDA-P, the optical absorption of PDA-C is red-shifted possessing much higher absorbance and broader distribution thus indicating a higher extent of effective π-conjugation in PDA-C. The bathochromic shift of absorption spectra of π-conjugated polymers caused by carbonyl groups was discussed recently [18] as an increase in the effective conjugation length. In addition to the conjugative effect, carbonyl groups introduce $n \rightarrow \pi^*$ electronic transition originating in the nonbonding π-orbitals on the oxygen atom, which is not observed in the spectrum due to much lower absorbance. In absorption spectra of PDA-F, optical transitions centered at 370 nm, typical of fluorene groups, as well as vibronic peaks in the fluorescence emission spectrum centered at 420 nm are clearly visible.





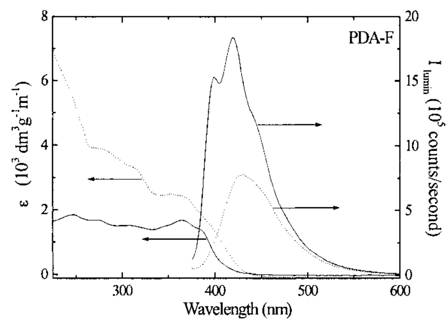


Figure 2. UV-vis absorption spectra and photoluminescence emission spectra of dioxane solutions of the PDAs prepared in chlorobenzene (dashed lines) and toluene (solid lines). Excitation wavelength 320 nm for PDA-P prepared in chlorobenzene, 366 nm in all other cases.

Conclusions

Although the application of the McMurry reaction to preparation of special polymers was already described [7,8], we extended this procedure to synthesis of telechelic soluble oligomers with various functional end-groups. Molecular weight of these oligomers can be controlled by an appropriate choice of reaction conditions. The described method is very simple and provides end-functionalized soluble oligomers in a single step. The resulting materials are film-forming, well processable and they show high stability in air. These properties meet demands of practice for organic materials for optoelectrical measurements and applications. Other end-groups can also be introduced into PDA chains by using these procedures and suitable precursors containing carbonyl and/or diphenylmethylidene end-groups of appropriate reactivity. Furthermore, we have found that fluoren-9-one homopolymerizes in the presence of WCl_6 and $AlCl_3$; however, we did not yet obtain evidence that would enable proposal of a mechanism of this reaction. This interesting new reaction providing a novel material is to be studied more in detail.

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[1] H. S. Nalva, ed., Handbook of Organic Conductive Molecules, Wiley, New York 1996.

[2] J. Sedláček, J. Vohlídal, Z. Grubišič-Gallot, *Makromol. Chem. Rapid Commun.* **1993**, *14*, 51.

[3] J. Vohlídal, D. Rédrová, M. Pacovská, J. Sedláček, *Collect. Czech. Chem. Commun.* **1993,** *58,* 2651.

[4] H. Shirakawa, T. Masuda, K. Takeda in: The Chemistry of Triple-bonded Fumctional Groups (ed. S. Patai), Wiley, New York 1994, Chapter 17, pp. 945-1016.

[5] J. Vohlídal, Z. Kabátek, M. Pacovská, J. Sedláček, Z. Grubišic-Gallot, *Collect. Czech. Chem. Commun.* **1996,** *61,* 120.

[6] Z. Kabátek, B. Gaš, J. Vohlídal, *J. Chromatogr. A* **1997,** *786,* 209.

[7] S. M. A. Karim, R. Nomura, T. Masuda, *Polym. Bull.* **1999**, *43*, 305.

[8] J. Vohlídal, J. Sedláček in: Chromatography of Polymers: Hyphenated and Multidimensional Techniques (ed T. Provder); *ACS Symp. Ser.* **1999**, 731, 263.

[9] A. Niki, T. Masuda, T. Higashimura, *J. Polym. Sci.* **1987**, *25*, 1553.

[10] J. Jortner, M. Ratner, Molecular Electronics; Blackwell Science, Oxford 1997.

[11] K. Mertis, S. Arbilias, D. Argyris, N. Psaroudakis, J. Vohlídal, O. Lavastre, P.H. Dixneuf, *Collect. Czech. Chem. Commun.* **2003,** *68,* 1094.

[12] I. Schopov, C. Jossifov, *Makromol. Chem., Rapid Commun.* **1983**, *4*, 659.

[13] C. Jossifov, I. Schopov, *Makromol. Chem.* **1991**, *192*, 857, 863.

[14] C. Jossifov, *Eur. Polym. J.* **1993,** *29,* 9.

[15] C. Jossifov, *Eur. Polym. J.* **1998,** *34,* 883.

[16] J. McMurry, *Chem. Rev.* **1989,** *89*, 1513.

[17] I. Schopov, L. Mladenova, *Makromol. Chem. Rapid Commun.* **1985,** *6,* 659.

[18] M. Belletete, J.F. Morin, S. Beaupre, M. Ranger, M. Leclerc, G. Durocher, *Macromolecules* **2001**, 34, 2288.