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New Monomers and Polymers via Diels-Alder Cycloaddition

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Summary: The series of new bis(naphthalic anhydrides) was prepared through Diels-Alder cycloaddition. The Diels-Alder cycloaddition was used as a synthetic route to new phenylated monomers as well as to polymers. All polymers synthesized revealed to be soluble in a wide range of organic solvents such as toluene,THF, chloroform, and displayed high thermostability. Therefore, they can be processed easily and are promising candidates for advanced coating systems as well as for electrooptical applications.

Keywords: Diels-Alder polymers, gel-permeation chromatography, isomers, phenylated polyphenylenes, synthesis

Introduction

The Diels-Alder reaction[1,2,3] has proven of outmost importance in synthetic organic chemistry. In addition to its major role in the total synthesis of natural products,[4,5] the [2+4]cycloaddition has also achieved considerable impact on synthesis of polymers. Due to the increasing interest in practical applications of the obtained materials,[6,7,8] Diels-Alder polymerization is very active field of polymer chemistry. Here we introduce the Diels-Alder reaction as a simple route to new monomers for synthesis of polynaphthoylenebenzimidazoles and polynaphthylimides as well as directly to polyphenylenes. Polyphenylenes (PPs)[9-11] polynaphthylimides (PNIs)[14-16] and polynaphthoylenebenzimidazoles (PNBIs)[12,13] represent the important group of thermally stable polymers. However, the application of these polymers is limited by their high glass transition temperature and poor solubility in organic solvents. A successful approach to

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overcome such difficulties consisted in the incorporation of phenyl substituents into the polymers chain and was applied earlier by some of us and other authors for different classes of polymers.[15-19] However, active demand for these polymers with valuable properties defines the necessity of diversification.

Experimental Section

^{1}H and ^{13}C NMR chemical shifts were obtained using a Bruker AMX 400 spectrometer (deuterated solvents as the internal standard) and expressed in parts per million (ppm). FTIR spectra were recorded on Perkin-Elmler 1720 X. Thermogravimetrical measurements were carried out on Perkin-Elmler TGA-4; the heating rate was 10°/min. GPC analyses were accomplished on a Waters SEC, equipped with a PPS gel column using polystyrene standards. Detection was achieved with a diffraction index detector.

1,3-diphenylacetone, 4-bromo-1,8-naphthalic anhydride, phenylacetylene, p-diethynylbenzene, benzidine, 3,3'-diaminobenzidine were commercially available. The synthesis of starting bis-α-diketones was performed according to literature.[20] The bis(cyclopentadienone)s 1 a–c were synthesized by methods analogous to those already published in the literature[21] and used without further purification.

1a ^{13}C NMR (400 MHz, chloroform-d, 25°C): δ=200.01 (C=O of cyclopentadienone), 154.69, 152.59, 137.11, 136.41, 132.33, 130.00, 128.84, 128.41,128.19, 128.11,127.95, 127.41, 127.10,126.91, 126.36,125.13

^{1}H NMR (400 MHz, chloroform-d, 25°C): δ=7.59 (m, 4H), 7.28-7.21 (br, 22H), 7.19 (t, 4H), 7.05 (d,4H), 6.94 (d, 4H)

Yield: 89%

1b ^{13}C NMR (400 MHz, chloroform-d, 25°C): δ=200.01 (C=O of cyclopentadienone), 154.73, 152.70, 137.37, 136.54, 132.41, 130.11, 128.97,128.49, 128.31, 128.13,128.09, 127.56, 127.21, 127.02, 126.44, 125.21

^{1}H NMR (400 MHz, chloroform-d, 25°C): δ=7.59 (m, 4H), 7.28-7.21 (br, 22H), 7.19 (t, 4H), 7.05 (d,4H), 6.94 (d, 4H)

Yield: 87%

1c ^{13}C NMR (400 MHz, chloroform-d, 25°C): δ=199.73 (C=O of cyclopentadienone), 195.21

(C=O of benzophenone), 154.03, 152.80, 137.57, 136.62, 132.66, 130.32, 130.01, 130.03, 129.99, 129.57,129.25, 129.05,128.66, 128.10, 127.98, 127.77,127.54, 126.32, 125.32
^{1}H NMR (400 MHz, chloroform-d, 25°C): δ=7.59 (m, 4H), 7.28-7.21 (br, 22H), 7.19 (t, 4H), 7.05 (d,4H), 6.94 (d, 4H). Yield: 89%
4-phenyl-ethynylenenaphthalic anhydride was synthesized according to [22].

General Procedure for the Synthesis of Bis(naphthalic Anhydride)s 2a-c.

A 50 cm^3 Schlenk tube was charged with a suspension of 1,4-bis(2,4,5-triphenylcyclopentadienone-3 –yl)arylenes (1a-c), 4-phenylethynylenenaphthalic anhydride and diphenylether and then degassed by a serried freeze-pump-thaw cycles to remove O_2. The reaction was carried out for 7 hours at 240°C, with stirring under argon atmosphere. After the reaction was complete (check by TLC and changing the color from deep purple to yellow) the solution was precipitated into methanol, filtered off, washed with an excess of methanol, and dried in vacuo at 80°C for 24 h.

2a ^{13}C NMR (400 MHz, chloroform-d, 25°C): δ= 160.36, 160.16 (C=O of anhydride), 147.72-116.14 (C_{arom});^{1}H NMR (400 MHz, chloroform-d, 25°C): δ=8.87 (d, 2H, J=8.1), 8.70 (d, 2H, J=8.1), 8.61 (d, 2H, J=8.1), 7.60-7.66 (t, 2H), 7.32 (d, 2H), 6.87-6.40 (br, 44H)
Elemental analysis $C_{90}H_{54}O_6$(found/calc.,%): C 87.77/87.78; H 4.96/4.42.
Yield: 83%

2b ^{13}C NMR (400 MHz, chloroform-d, 25°C): 160.42, 160.21 (C=O of anhydride),146.34-115.41(C_{arom}); ^{1}H NMR (400 MHz, chloroform-d, 25°C): δ=8.40 (d, 2H, J=8.1), 8.30 (d, 2H, J=8.1), 8.19 (d, 2H, J=8.1), 7.63-7.55 (t, 2H), 7.43 (d, 2H), 6.83-6.53 (br, 48H)
Elemental analysis $C_{96}H_{60}O_6$(found/calc.,%): C 86.42/88.19; H 4.77/4.47
Yield: 74%, mp =380-408°C (DSC)

2c ^{13}C NMR (400 MHz, chloroform-d, 25°C): δ=196.19, 196.14, 196.09 (C=O of benzophenone), 160.53, 160.33 (C=O of anhydride),147.54-116.59 (C_{arom})
^{1}H NMR (400 MHz, chloroform-d, 25°C): δ=8.42 (d, 2H, J=8.1), 8.32 (d, 2H, J=8.1), 8.22 (d, 2H, J=8.1), 7.60-7.66 (t, 2H), 7.43 (d, 2H), 7.14-6.50 (br, 48H)
Elemental analysis $C_{97}H_{60}O_7$ (found/calc.,%): C 87.37/87.24; H 4.60/4.37
Yield: 91%

General Procedure for the Synthesis of Polyphenylenes 3b-c

A 50 cm^3 Schlenk tube was charged with a suspension of 1,4-bis(2,4,5-triphenylcyclopentadienone-3 –yl)arylenes (1b-c) (1 eq.), freshly sublimated p-diethynylbenzene (1 eq.) and diphenylether and then degassed by a serried freeze-pump-thaw cycles to remove O_2. The common concentration of the starting compounds was 0.7 mol/l. The reaction was carried out for 72 hours at 240°C, with stirring under argon atmosphere. After the reaction was complete the clear viscous yellow solution was precipitated into methanol, filtered off, washed with an excess of methanol, and dried under vacuum at 80°C for 24 h.

3b η_{red}=0.93 dl/g (N-MP, 25°C)

Yield: 93%, M_w =192.300 g • mol^{-1} (GPC)

3c η_{red}=0.82 dl/g (N-MP, 25°C) Yield: 91%, M_w=207600 g • mol^{-1} (GPC)

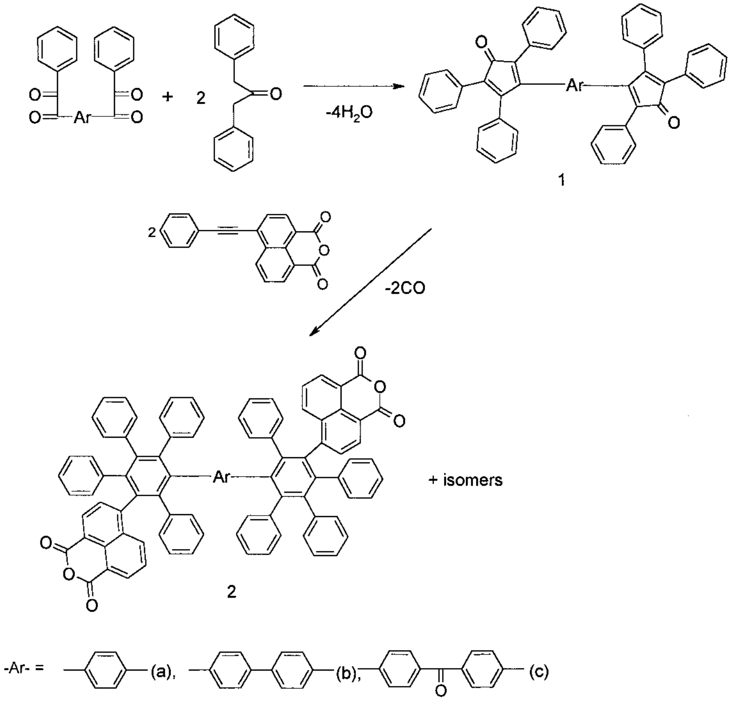
General Procedure for Synthesis of Polynaphthylimides 4a-c and Polynaphthoylene-benzimidazoles 5a-c

The three-necked flask equipped with argon inlet and a stirrer was charged with a corresponding di- or tetraamine (0.01mol), phenylated bis(naphthalic anhydride) (0.01 mol), benzoic acid (0.01 mol), benzimidazole (0.01 mol) and molten phenol. Temperature was raised stepwise from 40°C to 170°C. Reaction was carried out for 20 hours. Reaction mixture was precipitated into ethanol, filtered off, extracted by means of Soxhlet extractor and dried under vacuum at 120°C for 24 h.

Results and Discussions

Monomers

For the preparation of new processable PNI's and PNBI's highly phenylated bis(naphthalic anhydrides) (BNA's) were used as starting materials. The synthetic route leading to BNAs involved the Knoevenagel reaction of different bis(α-diketones) with a two-fold molar amount of 1,3-diphenylacetone to result phenylated bis(cyclopentadienones). At the next stage these compounds have been reacted with a two-fold molar amount of 4-(phenylethynylene)naphthalic anhydride under Diels-Alder conditions.



Scheme 1

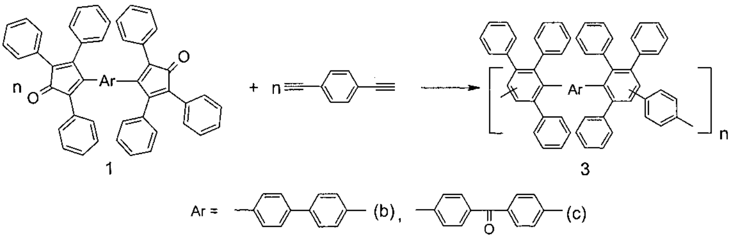
Phenylated BNA's obtained by this route are not individual compounds, but mixtures of isomers. In some cases, it is necessary to separate the isomers to prepare ordered polymers, but in our research we escaped that because polyheteroarylenes based on the mixture of isomeric monomers are less ordered and exhibit improved solubility and enhanced free volume, useful for low dielectric constant materials applications. All reactions were running smoothly and resulted in desired products with high enough yield. Even the use of less reactive 4-(phenylethynylene)naphthalic anhydride containing non-terminal ethynylene groups (instead of very active terminal ethynylic compounds) in the Diels-Alder cycloaddition did not lead to dramatic reduction of the product yield. The conversion of the reactions was checked by TLC and by reaction mixture color changing from deep purple to yellow-brown, indicating the depletion of bis(cyclopentadienone) in the Diels-Alder reactions. The compositions of the

BNA's as well as intermediate bis-cyclopentadienones were confirmed by elemental analysis, H^1 and C^{13}NMR and FTIR spectroscopy. In the FTIR spectra of the bis-cyclopentadienones there are very intense absorption bands of the C=O vibration in the range of 1700-1720 cm^{-1} . Also in the FTIR spectrum of bis-cyclopentadienone **1(c)** together with absorption band at 1710cm^{-1} there is a carbonyl mode at 1660 cm^{-1}. In the ^{13}C NMR spectra of all cyclopentadienones there is characteristic resonance of the carbonyl carbon of the cyclopentadienone at about δ=200 ppm. Besides in ^{13}C NMR spectrum of **1c** there is a band at 196 ppm of carbonyl carbon of benzophenone moiety. ^{1}H NMR spectra of the bis(cyclopentadienone)s comprised the proton signals just in aromatic region. ^{13}C NMR spectra of bis(naphthalic anhydrides) **2 a-c** displayed characteristic signals of unequal carbons of anhydride moiety at 160.3 and 160.5 ppm whereas resonance of the carbonyl carbon of cyclopentadienones at 200 ppm disappeared. As well as for 1c the ^{13}C NMR spectrum of 2c included the signals at about 196 ppm are attributed to carbonyl carbon of benzophenone fragment. However, it is worth to note that band at 196 ppm represented three signals (196.19, 196.14, 196.09 ppm) of carbonyl carbon instead of single one as in case of **1c**. This phenomenon should be treated in term of confirmation of the isomer mixture formation in course of Diels-Alder reaction between bis-(cyclopentadienone)s and 4-phenylethynylenenaphthalic anhydride. In general the NMR spectra of dianhydrides were more complex in aromatic regions than bis(cyclopentadionone)'s ones, caused by the increasing number of benzene rings. FTIR spectra of BNA's displayed the absorption bands at about 1730 and 1780 cm^{-1} attributed to C=O vibration of dianhydrides whereas the modes of C=O of cyclopentadienone moiety in the range of 1700 to 1720 cm^{-1} disappeared.

Polymers

A. Polyphenylenes

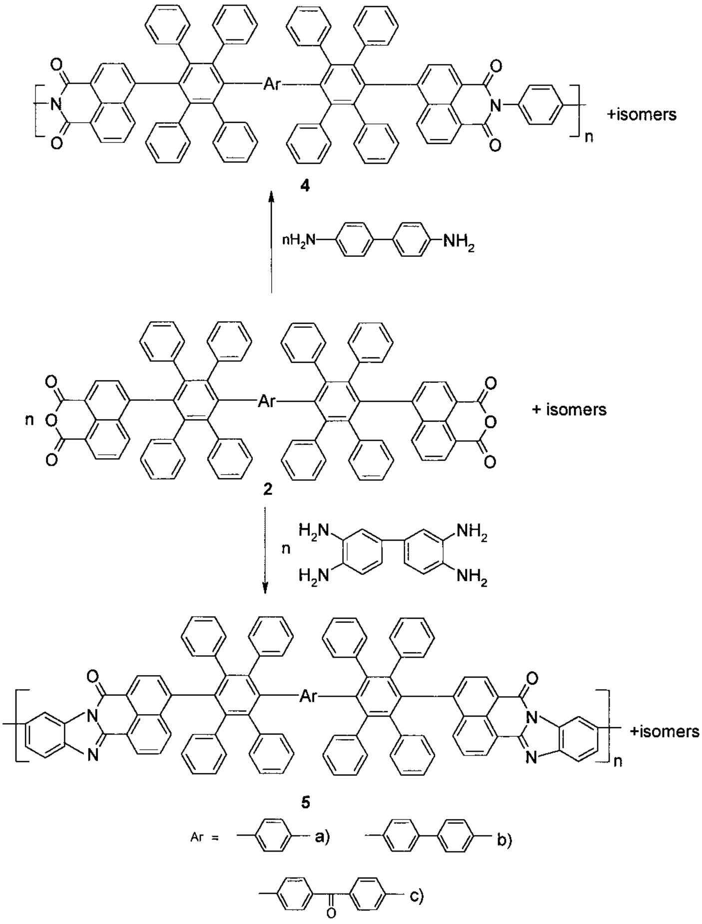
Synthesis of phenylated polyphenylenes was performed from bis(cyclopentadienone)s **1b,c** and p-diethynylbenzene via Diels-Alder reaction. Since earlier the optimal conditions for such synthesis have been found by some of us[23] for bis(cyclopentadienone) **1a** we suggested the using it in the reported experiments to be rather expedient.



Scheme 2

Thus, the polycycloaddition was carried out in Shlenk tube under argon atmosphere in diphenylether at 240°C. The change of the color from magenta to yellow indicating the accomplishment of the reaction was observed after 7-9 hours depending on bis(cyclopentadienone)s used. However the time of reaction was expanded to 72 hours to achieve the maximum of molecular weight. The polymers remained to be soluble during the reaction time and were isolated by precipitation into methanol, intensively washed with hot ethanol and dried. Polyphenylenes were obtained with yields above 90 %, demonstrating a very high conversion of monomers. The ^{1}H NMR, ^{13}C NMR, FT-IR spectroscopy where used for characterization of the new polymers. In the FT-IR spectra of new polymers there are no ν bands at 2100 cm^{-1} of ethynyl moiety and at 1710cm^{-1} of carbonyl of cyclopentadienone. Also the signals of cyclopentadienone carbonyl carbon ($\approx$200 ppm) and ethynyl carbon ($\approx$90 ppm) could not be detected in the ^{13}C NMR spectra. The ^{13}C NMR and ^{1}H NMR spectra of the polymers were rather complex in the aromatic region and did not significantly depend on bis(cyclopentadienone)s used. The molecular weights of the polymers were determined by gel-permeation chromatography calibrated with respect to polystyrene standards. The weight-average molecular weight M_w was determined to be 192.300 g • mol^{-1} for **3b** with a polydispersity index M_w/M_n of about 2.6 and of 207600 g • mol^{-1} for **3c** with a polydispersity index M_w/M_n=3.5. The polymers were found to be readily soluble in toluene, THF, 1,4-dioxane, chloroform, N,N-dimethylformamid, N-methylpyrrolidone. The unique solubility of polymers should be attribute both to formation of meta- and para- coupling in course of Diels-Alder polycycloaddition and to bulky phenyl substituents. High molecular weights of polymers obtained combined with solubility in a wide range of solvents makes their use in coatings systems very promising.

Thermogravimetric analysis (TGA) reflects the high thermal stability of polymers **3b** and **3c** in air. The thermograms displayed starting weight loss of 10% at 450-470°C (ΔT=4.5°/min) and at 600-610 °C (ΔT=20°/min) for polyphenylenes **3b** and **3c**. Thermal degradation started even at high temperature in argon atmosphere.



Scheme 3

B. Polynaphthylimides and Polynaphthoylenebenzimidazoles

There was revealed that disorder in polymer chains facilitates the solubility of polymers as well as a presence of phenyl substituents. Because one of the research goal was the synthesis of soluble high-molecular weight polymers we did not attempt to separate the isomers of bis(naphthalic anhydrides) **2a-c** and used the isomer mixture in synthesis of polynaphthoylenebenzimidazoles and polynaphthylimides.

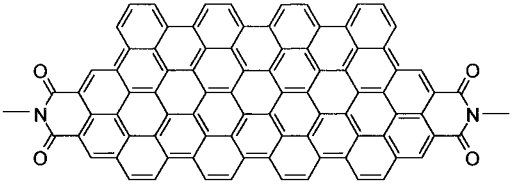
The reactions were performed under high-temperature polycondensation conditions in phenolic solvents using the benzoic acid and benzimidazole as catalysts. Within reaction time all reactions proceeded homogenously and resulted in phenylated polymers demonstrating very high conversion of monomers and extraordinary solubility.

B1. Polynaphthylimides

The polynaphthylimides **4a-c** were characterized by FTIR and NMR spectroscopy. FTIR spectra display ν bands at around 1713 cm^{-1} of the C=O vibration of the naphthylimide cycle. The ^{13}C NMR spectra of polymers show characteristic carbonyl resonances of the naphthylimide moiety at $\delta=164.0$ ppm and 164.4 ppm. Besides, in spectrum of **4c** there is a broad signal at $\delta=196$ ppm attributed to carbonyl carbon of benzophenone fragment. ^{13}C and ^{1}H NMR spectra of **4a-c** in aromatic region were rather complex to reliably assign polymer structure.

Synthesized polymers **4a-c** were predictably soluble in a wide range of organic solvents including N-MP, chloroform, THF. Their molecular weights (M_w) were in the range of 60000 to 121000 g mol^{-1}. Polymers appeared to be extremely thermostable. Thermograms show the starting weight loss of 10% in air at 480-500 **°C** ($\Delta T=4.5°/min$) and at 580-600°C ($\Delta T=20°/min$) for **4a, 4b** and **4c**. T_g of polynaphthylimide **4c** was 398°C whereas for **4a,b** T_g's were not observed before 500°C. Such a phenomenon could be rationalized in terms of new condensed structures formation due to intramolecular oxidative cyclodehydrogenation under the heating of the sample (see Scheme 4).

The presence of the bridge carbonyl fragment in polynaphthylimides **4c** decreased the T_g significantly what is very useful for the processing.



Sheme 4

B2. Polynaphthoylenebenzimidazoles

The polynaphthoylenebenzimidazoles **5a-c** were subjected to FTIR and Raman scattering analysis. FTIR spectra of **5a-c** differed from ones of **4a-c** not significantly and displayed ν bands at around 1702 cm^{-1} of the C=O vibration and weak signals at 1660 and 1551 cm^{-1} attributed to =C=N- group of the naphthoylenebezimidazole cycle. The Raman spectra of polynaphthoylenebenzimidazoles strongly proved the conversion of o-aminonaphthylimide cycles into naphthoylenebenzimidazole ones. In general, the polymers **5a-c** demonstrated the properties very closed to polymers **4a-c.** They proved to be soluble in standard organic solvents, including chloroform and THF and possessed high thermal stability in air in a temperature range of 510-620°C. As well as for **4a,b** we did not observed the T_g's for **5a,b** before decomposition started. For **5c** the T_g was 425°C allowing the processing of this polymer. In all the polymers **5a-c** were more thermostable than **4a-c** to be concerned with more stability of naphthoylenebenzimidazole cycle when compared with naphthylimide one.[24] The molecular weights of polymers (M_w) were determined by gel permeation chromatography and vary from 182000 g mol^{-1} for 5a to 378100 g mol^{-1} for **5c** with polydispersity index 2.1 and 2.55, accordingly.

The mechanical, electrooptical properties of films elaborated from such polymers are in progress.

Conclusion

It appears that the Diels-Alder cycloaddition is a very simple synthetic route to new phenylated monomers and polymers. The target phenylated polymers obtained by using of this method directly (polyphenylenes) or for synthesis of phenylated monomers (polynaphthylimides and polynaphthoylenebenzimidazoles) revealed to be soluble in a wide range of organic solvents such as toluene,THF, chloroform, and displayed high thermostability. Therefore, they can be processed easily and are promising candidates for advanced coating systems as well as for electrooptical applications.

Acknowledges

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