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New Monomers with Trifluoromethyl and Phenylphosphine Oxide Substituents for Polynaphthylimides and Polyperyleneimides

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There is increasing interest in polymers containing fused heterocycles on account of the growing need of advanced technologies in novel materials showing improved thermal, heat, chemical, and photochemical stability, optical transparency, electrographic and other special properties [1]. The introduction of perylene [2] and phenylene [3–5] fragments in the main chains of polymers allows one to impart them electrochromic and electroluminescent properties. However, the majority of polyheteroarylenes have poor solubility in organic solvents, which confines their processing for items manufacture.

In this paper, we describe the synthesis of new soluble polynaphthylimides (PNIs) and polyperyleneimides containing phenylphosphine oxide and trifluoromethyl substituents [6, 7].

The key compounds further used in the synthesis of monomers are 1,1-bis(4-hydroxyphenyl)-1-[3",5"-bis(trifluoromethyl)phenyl]-2,2,2-trifluoroethane (I) prepared by superelectrophilic activation of carbonyl compound [8] (Scheme 1):



Scheme 1.

and bis(4-hydroxyphenyl)phenylphosphine oxide (II) [9] prepared according to Scheme 2:



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Certain characteristics of bis(naphthalic anhydride)s of general formula



Bis(naphthalic anhydride)s were obtained by the reaction of bisphenols of appropriate structure with a twofold molar amount of 4-bromonaphthalic anhydride under conditions of aromatic nucleophilic substitution similarly to [10], Scheme 3:





v unknown bis[(1',8'-dicarboxynaphth-4'-yl)phenoxy]-1-[3",5"bis(trifluoromethyl)phenyl]-2,2,2-trifluoroethane (III)

The experiment resulted in previously unknown bis(naphthalic anhydride)s: dianhydride of 1,1-

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and dianhydride of 1,1-bis{[(1',8'-dicarboxynaphth-4'-yl)phenoxy]phenylphosphine oxide (**IV**).

The reaction was carried out in a medium of freshly distilled DMA with addition of chlorobenzene to remove resulting azeotrope at 150°C for 10 h in an argon flow.

The structure and purity of the dianhydrides were confirmed by the data of elemental analysis (table) and IR spectroscopy.

The IR spectra of compounds III and IV show absorption bands at 1773 and 1736 cm^{-1} correspond-

ing to vibrations of carbonyl groups in the anhydride ring, a band at 1278 cm^{-1} typical for the absorption of ether bond -C-O-C-, and a band at 1595 cm^{-1} corresponding to the absorption of the naphthalene ring.

The bis(naphthalic anhydride)s were used for the synthesis of previously unknown polynaphthylimides.

The synthesis of PNIs was carried out by the reaction of the above dianhydrides with binuclear aromatic diamines containing bridging groups according to Scheme 4:





The reaction was conducted under conditions of high-temperature catalytic polycyclization in phenol. A mixture of benzoic acid and benzimidazole was used as a catalyst, and the synthesis was accomplished under homogeneous conditions at $80-180^{\circ}$ C for 15-20 h in an argon flow.

The IR spectra of resulting polymers show absorption bands at 1670 and 1720 cm⁻¹ typical for the vibrations of six-membered imide rings, a band at 1250 cm⁻¹ typical of the absorption of -C-O-C- ether bond, and a band at 1592 cm⁻¹ corresponding to the absorption of the naphthalene ring.

The obtained PNIs are soluble in such organic solvents as NMP, DMF, DMA, DMSO, and phenolic solvents; their reduced viscosities are within 0.36–

0.84 dL/g (25°C, NMP). According to TGA, degradation onset temperatures are in the range of 470– 500°C, softening points are within 260–290°C; the phosphorus-containing PNIs have higher softening points as compared with the fluorine-containing polymers.

New polynaphthylimides and polyperyleneimides were obtained by the reaction of anhydrides of naphthalene-1,4,5,8-tetracarboxylic and perylene-3,4,9,10-tetracarboxylic acids or dianhydride of 1,3bis(1,8-dicarboxynaphth-4-oyl)benzene with a new diamine, 1,1-bis[4-(4'-amino-2'-trifluoromethylphenoxy)phenyl]-1-[3",5"-bis(trifluoromethyl)phenyl]-2,2,2-trifluoroethane (**V**), which was obtained in several stages according to Scheme 5.



Scheme 5.

The structure of diamine V was confirmed by elemental analysis data and ¹H NMR spectrum. Yield 55-60%. Compound V does not melt according to DSC data.

For $C_{36}H_{21}F_{15}N_2O_2$ anal. calcd. (%): C, 54.15; H, 2.65; N, 3.51.

Found (%): C, 54.10; H, 2.67; N, 3.50.

¹H NMR (400 MHz, DMSO- d_6 , δ , ppm): 5.53 (s, 4H, -NH₂), 6.86 (dd, 2H, H_g), 6.94–6.99 (m, 8H,

 H_d , H_e , H_f), 7.03 (d, 2H, H_c), 7.55 (s, 2H, H_b), 8.27 (s, 1H, H_a).

Integrated intensity ratio of the signals agrees well with the presented formula.

Polynaphthylimides were obtained under the above conditions, while polyperyleneimides were prepared in a chlorophenol medium at 210°C for 10 h according to Scheme 6:



Scheme 6.

The structure of these polymers was also confirmed by the data of IR spectra showing absorption bands at 1670 and 1720 cm⁻¹ typical for the vibrations of sixmembered imide rings, a band at 1250 cm⁻¹ typical for the absorption of ether bond -C-O-C-, and a band at 1592 cm⁻¹ corresponding to the absorption of naphthalene ring.

Polynaphthylimides containing trifluoromethyl groups are soluble in NMP, DMF, DMA, DMSO, and phenolic solvents, while polyperyleneimides are soluble in NMP, chlorophenol, and a phenol–TCE mixture. Reduced viscosity was measured for the obtained polymers (0.46–0.55 dL/g, NMP, 25°C). According to TGA, the onset degradation temperatures of PNIs is in the range of 490–500°C, and softening points are within 270–290°C. Polyperyleneimide does not soften until the onset of degradation (500°C). Preliminary studies showed that solutions of the polymers in NMP exhibited electroluminescent properties in the yellow region of the spectrum.

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