Smart Polymers

DOI: 10.1002/anie.201005456

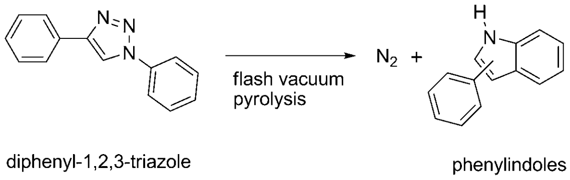
Thermally Induced Structural Transformation of Bisphenol-1,2,3-triazole Polymers: Smart, Self-Extinguishing Materials**

Beom-Young Ryu and Todd Emrick*

In modern organic polymer chemistry, step- and chain-growth polymerization methods are critically important for the fabrication of high-volume and specialty plastics, foams, gels, and rubbery materials. Such materials have enabled new applications that have transformed society.[1] Despite the many advances realized through polymer chemistry, many imperfections remain problematic, often associated with aging and cracking of the material, and leaching of additives.[2] Environmental contamination and bioaccumulation of additives, such as plasticizers, anti-oxidants, and flame-retardants, are particularly problematic.[3] Added inorganic salts compromise the physical and mechanical properties of polymers, while halogenated flame retardant additives are bio-accumulative, and thus threaten the environment and human health.[4] Organic/polymer chemistry advances that address this additives problem are needed urgently, and will be beneficial in terms of both materials performance and safety.

Specific to the area of polymer flammability is the need for novel polymers that exhibit non-flammable properties in the absence of additives. Key to discovering inherently non-flammable polymers is a mechanistic organic understanding of polymer decomposition. Structurally simple hydrocarbon polymers like polyethylene combust readily and completely. Other polymers, especially aromatic structures, possess decomposition mechanisms that prevent complete combustion. For example, polymers based on bisphenol C (BPC)[5] lose Cl_2 to generate a carbene, then rearrange to diphenylacetylenes that, at high temperature, aromatize and char. We adapted this concept to totally halogen-free materials, by developing a new class of deoxybenzoin polymers, which at high temperature undergo dehydration, conversion to diphenylacetylenes, and aromatization/char.[6] The charring event is critically important for precluding further oxidative combustion, by providing a self-extinguishing mechanism.

We recently took interest in the insights reported by Gilchrist and co-workers on the conversion, by flash vacuum pyrolysis, of bisphenyl-1,2-3-triazoles to phenylindoles and nitrogen gas (Scheme 1).[7,8] This organic structural rearrangement provides a new opportunity in polymer synthesis and materials applications, but to our knowledge there is no prior report on the synthesis of polymers containing BPT in the backbone. Here we describe the synthesis of BPT-containing aromatic polyesters by step-growth polymerization, giving *para-* and *meta*-linked structures. Characterization of the BPT-polymers produced in this work revealed exceptional examples of high performance materials, thus representing new opportunities in additive-free, non-flammable macromolecular materials chemistry.



Scheme 1. Thermally induced structural rearrangement of diphenyl-1,2,3-triazole.

Scheme 2 shows our preparation of BPT-containing aromatic polyesters from the corresponding BPT monomer precursors. The phenyl azide and trimethylsilylethynyl (TMSE) precursors to monomers **1** and **2** were connected by copper catalyzed click cycloaddition,[9] using CuBr and 2,2′-bipyridyl, in polar solvents such as DMF, to give the desired bis-phenolic triazole structures. Recrystallization from acetic acid/water gave 4-BPT (**1**) and 3-BPT (**2**) in 60–70% yield, in sufficiently pure form to use directly in polymerization chemistry.

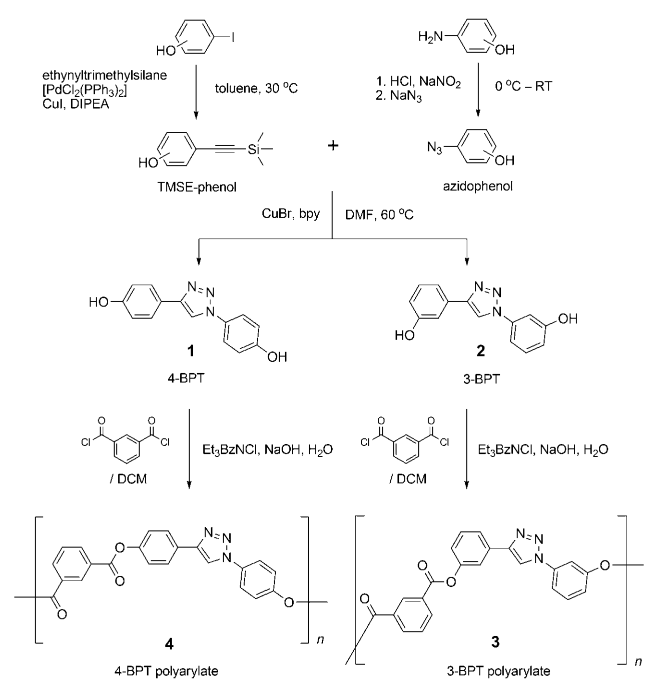
BPT-containing polymers were prepared by interfacial polycondensation of BPT monomers **1** or **2** with isophthaloyl dichloride as the difunctional comonomer, benzyltriethylammonium chloride as the phase-transfer catalyst, and CH_2Cl_2 as the organic phase. Typical of interfacial polymerization, a film was seen to develop in the stirring heterogeneous reaction mixture during the course of the polymerization, indicating successful polymer formation at the fluid–fluid interface. The 4-BPT aromatic polyesters isolated from this reaction (65% yield on ca. 1-gram scale) were found to be poorly soluble in common solvents (e.g., THF, DMF, and NMP), making spectroscopic characterization difficult. Thus, we performed the interfacial polymerization experiments using bisphenol A (BPA) as a comonomer with BPT and isophthaloyl chloride,

---

[*] Dr. B.-Y. Ryu, Prof. Dr. T. Emrick
Polymer Science and Engineering
University of Massachusetts
120 Governors Drive, Amherst, MA 01003 (USA)
Fax: (+1) 413-545-0082
E-mail: tsemrick@mail.pse.umass.edu

[**] The authors acknowledge the financial support of the Federal Aviation Administration (FAA-09-G-013), and the member companies and organizations of the Center for UMass-Industry Research on Polymers (CUMIRP) that support anti-flammable polymer research, including Boeing, Sabic-Innovative Polymers, Kydex, Inc., and the U.S. Army. Facilities support from the NSF Materials Research Science and Engineering Center (DMR-0820506) is also acknowledged.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201005456.



Scheme 2. Synthetic procedures for BPT polymers. bpy = bipyridine, Bz = benzoyl, DCM = dichloromethane, 4-BPT = 1,4-bis(4-hydroxyphenyl)-1,2,3-triazole, 3-BPT = 1,4-bis(3-hydroxyphenyl)-1,2,3-triazole.

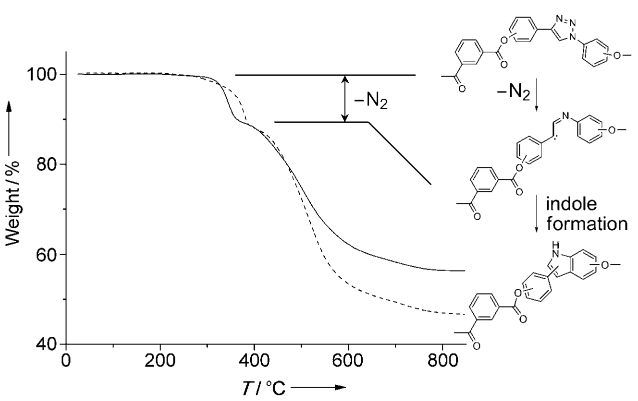


Figure 1. TGA thermograms of 3-BPT polyarylates (——) and 4-BPT polyarylates (– – –) (heating rate 10 °C min^{-1} in N$_2$).

in attempts to improve the solubility and processability of the BPT-containing materials. However, these copolymers proved only partially soluble, and also difficult to characterize. Nonetheless, thermal characterization of these 4-BPT polymers (which does not require solubility) was particularly promising, revealing exceptionally low heat release capacities (HRC) of $< 50\,\mathrm{J\,g^{-1}\,K^{-1}}$, and total heat releases (THR) of $< 7\,\mathrm{kJ\,g^{-1}}$. This data, obtained by pyrolysis combustion flow calorimetry (PCFC),[10] an oxygen consumption technique, places these novel BPT aromatic polyesters in the ultra-low flammability category, despite the absence of additives.

Thermogravimetric analysis (TGA) of the 4-BPT polyarylates showed a two-step weight loss curve (about 12 % weight loss at 300–400 °C), which would be expected from the initial structural rearrangement (resulting in loss of N$_2$), and a 47 % char yield (i.e., residual mass after burning) at 850 °C (Figure 1). Taken together, this outstanding set of thermal properties compelled us to investigate routes to more soluble, processable BPT-containing polymers, without resorting to the addition of flexible hydrocarbon chains that would improve solubility, but also markedly increase the heat release, and reduce char yield.

In order to increase the processability of BPT-containing polymers without compromising their exceptional thermal properties, 3-substituted BPT polyarylates were prepared. This was intended to exploit the kinked (and thus less rigid) structure of the *meta*-substituted 3-BPT framework, relative to the linear, *para*-substituted, 4-BPT case. Under interfacial polymerization conditions similar to those used for 4-BPT, the yields of isolated 3-BPT/isophthaloyl chloride aromatic polyesters, and their copolymers with BPA, were in the 85–90 % range. Fortunately, the solubility of the 3-BPT polymers was improved markedly over the 4-BPT materials, exhibiting excellent solubility in *N*-methyl-2-pyrrolidone (NMP) (ca. 100 mg mL^{-1}). Moreover, 1:1 3-BPT:BPA copolyarylates exhibited solubility in DMF, tetrachloroethane (TCE), and NMP. The 3-BPT/BPA copolymer compositions tracked closely to the monomer ratio introduced to the organic phase at the outset of the polymerization (as confirmed by ^{1}H NMR spectroscopy).

The molecular weights and polydispersity indices (PDIs) of the 3-BPT polymers were estimated by gel permeation chromatography (GPC) against polystyrene calibration standards, eluting with NMP (0.05 M of LiCl) at 80 °C. The 3-BPT polymers isolated from five different reaction batches showed number-average molecular weights ($\overline{M_n}$) in the range of 9800–10 900 g mol^{-1}, weight-average molecular weights ($\overline{M_w}$) in the range of 27 600–30 900 g mol^{-1}, and PDIs of 2.5–2.9. Similar molecular weights were achieved in the 3-BPT/BPA copolymerizations, for example $\overline{M_n} = 7800$ g mol^{-1}, $\overline{M_w} = 17\,900$ g mol^{-1}, and PDI = 2.3.

Like the 4-BPT materials, 3-BPT-containing polymers and copolymers exhibited TGA curves that showed a two-step weight loss, reflecting loss of nitrogen (N$_2$) associated with conversion of the triazole moieties to indoles (Figure 1). Interestingly, we observed that the char yield of the 3-BPT polymer at 850 °C was significantly higher (56 %) than the 4-BPT materials (47 %). We attribute the higher char yield of the *meta*-linked 3-BPT polymers to its lower crystallinity and closer proximity of the phenyl rings, making it better suited for thermally induced aromatization than the *para*-substituted structures. An analogous *para* vs. *meta* effect is seen in the commercial aromatic polyamides poly(*p*-phenylene terephthalamide) (Kevlar) and poly(*m*-phenylene terephthalamide) (Nomex). Kevlar is highly crystalline, has excellent thermal stability (decomposition > 500 °C), and high char yield, but heat release values significantly higher than those of Nomex (Nomex char yield = 43 % and heat release capacity = 99 J g^{-1} K^{-1}; Kevlar char yield = 38 % and heat release capacity = 363 J g^{-1} K^{-1}).[11] Clearly the *meta*-substitution provides a distinct advantage with regards to these key thermal properties, for both the commercial high performance polyamides and the novel BPT structures described here.

Figure 2 shows FT-IR spectra of 3-BPT polyarylate ($\overline{M}_w = 30\,900\ \mathrm{g\,mol^{-1}}$), before and after heating to 350 °C for 10 min. Notable changes in the FT-IR spectrum were seen after heating, between 1700 and 1000 $\mathrm{cm^{-1}}$. Triazole signals at 1475 $\mathrm{cm^{-1}}$ and 1035 $\mathrm{cm^{-1}}$ (triazole ring stretching vibrations), were noticeably absent after heating, indicating the anticipated thermally induced structural transformation. The new IR signal at 1435 $\mathrm{cm^{-1}}$ (phenylindole skeletal vibrations) reflects the expected formation of phenylindole groups. In addition, at these high temperatures, we expect some ester bond degradation occurred, as noted by the appearance of a carboxylate signal at 1670 $\mathrm{cm^{-1}}$ in the spectrum. Pyrolysis gas chromatography–mass spectrometry (GC-MS) characterization of 3-BPT polyester **3**, run at 400 °C for 6 min, revealed a gradual loss of N_2 and CO_2 in the 4–10 min time-frame, and a sharp peak of isophthaloyl fragments at 24 min (see Supporting Information).

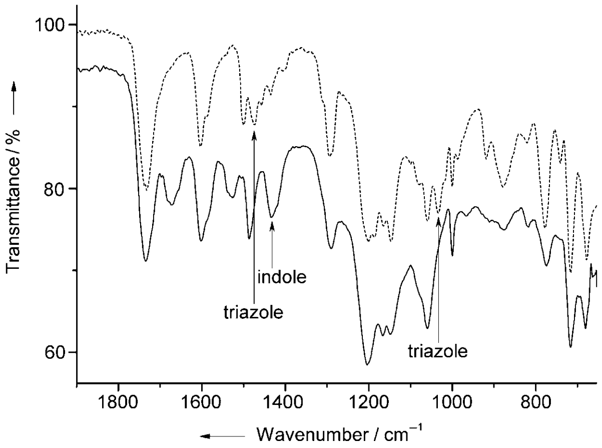


Figure 2. FT-IR spectra of 3-BPT polymer **3** (-----), and the same polymer after heating at 350 °C for 10 min (——).

PCFC characterization of these 3-BPT aromatic polyesters exhibited a HRC of 23 $\mathrm{J\,g^{-1}\,K^{-1}}$ and THR of 4.5 $\mathrm{kJ\,g^{-1}}$. Such low heat release values for hydrocarbon-based polymers are rare (lower even than inorganic-based polyphosphazenes[11]), and these values for BPT structures rank very close to those of the aromatic polyimide Kapton, one of the few commercialized ultra-low flammability polymers (Table 1). We also note that BPA/3-BPT copolymers, having an equimolar BPA:BPT ratio, gave a HRC of 102 $\mathrm{J\,g^{-1}\,K^{-1}}$, and THR of 11.3 $\mathrm{kJ\,g^{-1}}$. Thus, entries 2 and 4 of Table 1 show that interrupting the BPT homopolymer structure with BPA units removes the influence of the *meta*- vs. *para*-substitution seen for the BPT homopolymers. Nonetheless, it is remarkable to observe that inserting 50 % BPT as a comonomer in the classic BPA polymeric structure leads to a 400 % reduction in HRC from BPA-only structures (i.e., compare entries 1 and 4 in Table 1). In a small-scale flame test (Figure 3) performed in our laboratories, conducted by placing a thin film (2 × 0.5 × 0.025 cm) of 3-BPT polyarylate in a propane torch flame at a 45° angle for 5–10 s, the film was seen to extinguish immediately (i.e., self-extinguish) following removal from the flame, with little smoke evolution. In a propane torch flame, 3-BPT polyarylates charred immediately, and the char maintained its shape during the course of the test (i.e., without dripping).

Table 1: Heat release capacity (HRC), total heat release (THR), and charring properties of BPT-containing polymers and commercial high-performance materials.

Entry	Polymer	HRC [$\mathrm{J\,g^{-1}\,K^{-1}}$]	THR [$\mathrm{kJ\,g^{-1}}$]	Char [%][b]
1	BPA polyarylate	456 ± 13	17.7 ± 0.5	26
2	4-BPT/BPA (50/50)	95 ± 4	12.0 ± 0.5	38
3	4-BPT	46 ± 5	6.8 ± 0.3	47
4	3-BPT/BPA (50/50)	102 ± 5	11.3 ± 0.4	44
5	3-BPT	23 ± 3	4.6 ± 0.2	56
6	Kevlar[a]	363 ± 2	8.8 ± 0.5	38
7	Nomex[a]	99 ± 0.5	6.6 ± 0.2	43
8	Kapton[a]	14	4.0	66

[a] Data taken from the references.[11] [b] Data obtained from TGA at 850 °C in nitrogen (heating rate 10 °C $\mathrm{min^{-1}}$).

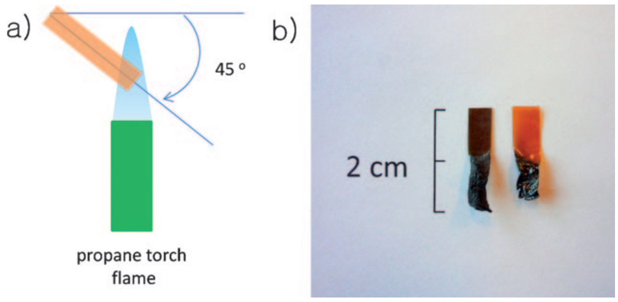


Figure 3. a) Small-scale flame test configuration. b) Samples after the test (left: 3-BPT polyarylate; right: Kapton).

To better understand these novel BPT-containing structures as materials, we generated preliminary data associated with their mechanical properties. Specimens for tensile tests ($\overline{M}_w = 30\,900\ \mathrm{g\,mol^{-1}}$, $T_g = 195$ °C) were prepared by thermal pressing at 240 °C. The ultimate strength, tensile modulus, and extension at break of 3-BPT/isophthaloyl chloride polymers were measured on an Instron (Model 5564) as 95 ± 25 MPa, 2.5 ± 0.3 GPa, and 4.5 ± 0.6 %, respectively. These properties, while unoptimized and derived from relatively low molecular weight polymer films, already demonstrate significant mechanical strength, with tensile strength intermediate between commercial BPA polyarylate (i.e., Ardel, 69 MPa) and a commercial liquid crystalline aromatic copolyester (i.e., Xydar, 110–135 MPa).[12] We expect that the mechanical properties of BPT-polyarylates (and other BPT-containing structures) will improve as higher molecular weight samples are prepared and utilized. Figure 4 a shows a 3-BPT polymer sample ($\overline{M}_n = 10\,900\ \mathrm{g\,mol^{-1}}$, $\overline{M}_w = 30\,900\ \mathrm{g\,mol^{-1}}$, 2 × 0.5 × 0.025 cm) as a thin, flexible film after processing by pressing at 240 °C. Moreover, we were intrigued to see that low molecular weight versions of BPT polymer **3** (i.e., $\overline{M}_n = 3200\ \mathrm{g\,mol^{-1}}$, $\overline{M}_w = 5730\ \mathrm{g\,mol^{-1}}$) readily formed fibers from the polymer melt (at 260 °C), by simply pulling the material with tweezers from the hot stage of a melting point

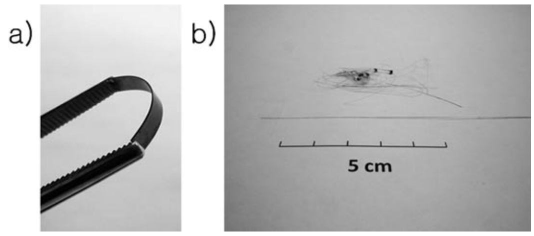


Figure 4. a) 3-BPT polymer film formed by hot-pressing. b) 3-BPT fibers pulled from the melt.

apparatus (Figure 4b). We anticipate that blending of these structures with other fiber-forming polymers will permit additional opportunities in fiber-based applications. Finally, we note that the 3-BPT structures prepared so far are advantageous for their amenability to both solution and thermal processing, and do not require special processing conditions of polybenzoxazoles and polyimides, or polymer precursors as in the case of Kapton.

In summary, we synthesized novel BPT monomers and polymers by click cycloaddition and interfacial polycondensation, and investigated their heat release and mechanical properties. This work shows that BPT homopolymers and copolymers are viable candidates for applications in which ultra-low flammability materials are needed. Further added benefit is derived from having such exceptional thermal properties without requiring additives of any sort. The *meta*-linked 3-BPT structures are particularly promising for their combined thermal properties and facile processibility, and we envisage this concept adding value across a range of polymer materials that can accommodate BPT within the structure.

Received: August 31, 2010

Keywords: aromatic polyesters · click cycloaddition · smart polymers · thermally responsive materials · triazoles

---

[1] a) M. P. Stevens, *Polymer Chemistry: An Introduction*, Oxford University Press, New York, **1990**; b) G. Odian, *Principles of Polymerization*, Wiely, New York, **2004**.

[2] J. Murphy, *Additives for Plastics Handbook*, Elsevier, New York, **2001**.

[3] a) A. Blum, B. N. Ames, *Science* **1977**, *195*, 17–23; b) M. D. Gold, A. Blum, B. N. Ames, *Science* **1978**, *200*, 785–787; c) L. Fishbein, *Carcinog. Mutagens Environ.* **1985**, *5*, 75–93; d) J. de Boer, P. G. Wester, H. J. C. Klamer, W. E. Lewis, J. P. Boon, *Nature* **1998**, *394*, 28–29; e) R. C. Hale, M. J. La Guardia, E. P. Harvey, M. O. Gaylor, T. M. Mainor, W. H. Duff, *Nature* **2001**, *412*, 140–141; f) M. Rahman, C. S. Brazel, *Prog. Polym. Sci.* **2004**, *29*, 1223–1248; g) B. Gómara, L. Herrero, J. J. Ramos, J. R. Mateo, M. A. Fernandez, J. F. Garcia, M. J. Gonzalez, *Environ. Sci. Technol.* **2007**, *41*, 6961–6968; h) A. Blum, *Science* **2007**, *318*, 194b.

[4] a) J. W. Lyons, *Chemistry and Uses of Fire Retardants*, Wiley, New York, **1970**; b) G. Camino, A. Maffezzoli, M. Braglia, M. D. Lazzaro, M. Zammarono, *Polym. Degrad. Stab.* **2001**, *74*, 457–464.

[5] a) A. Factor, C. M. Orlando, *J. Polym. Sci. Polym. Chem. Ed.* **1980**, *18*, 579–592; b) H. Zhang, P. R. Westmoreland, R. J. Farris, E. B. Coughlin, A. Plichta, Z. K. Brzozowksi, *Polymer* **2002**, *43*, 5463–5472; c) M. L. Ramirez, R. Walters, R. E. Lyon, E. P. Savitski, *Polym. Degrad. Stab.* **2002**, *78*, 73–82; d) J. L. Jurs, J. M. Tour, *Polymer* **2003**, *44*, 3709–3714; e) K. A. Ellzey, R. J. Farris, T. Emrick, *Polym. Bull.* **2003**, *50*, 235–242; f) S. I. Stoliarov, P. R. Westmoreland, *Polymer* **2003**, *44*, 5469–5475.

[6] a) K. A. Ellzey, T. Ranganathan, J. Zilberman, E. B. Coughlin, R. J. Farris, T. Emrick, *Macromolecules* **2006**, *39*, 3553–3558; b) T. Ranganathan, J. Zilberman, R. J. Farris, E. B. Coughlin, T. Emrick, *Macromolecules* **2006**, *39*, 5974–5975; c) R.-Y. Ryu, S. Moon, I. Kosif, T. Ranganathan, R. J. Farris, T. Emrick, *Polymer* **2009**, *50*, 767–774.

[7] a) T. L. Gilchrist, G. E. Gymer, C. W. Rees, *J. Chem. Soc. Perkin Trans. 1* **1975**, 1–8; b) T. L. Gilchrist, C. W. Rees, C. Thomas, *J. Chem. Soc. Perkin Trans. 1* **1975**, 8–11.

[8] a) E. M. Burgess, R. Carithers, L. McCullagh, *J. Am. Chem. Soc.* **1968**, *90*, 1923–1924; b) W. Kirmse, *Eur. J. Org. Chem.* **2002**, 2193–2256.

[9] a) T. Pirali, R. D. Brisco, S. Tacchi, R. Zaninetti, E. Brunelli, A. Massarotti, G. Sorba, P. L. Canonico, L. Moro, A. A. Genazzani, G. C. Tron, R. A. Billington, *ChemMedChem* **2007**, *2*, 437–440; b) C. Courme, S. Gillon, N. Gresh, M. Vidal, C. Garbay, J.-C. Florent, E. Bertounesque, *Tetrahedron Lett.* **2008**, *49*, 4542–4545.

[10] a) R. N. Walters, R. E. Lyon, *J. Appl. Polym. Sci.* **2003**, *87*, 548–563; b) R. E. Lyon, R. N. Walters, *J. Anal. Appl. Pyrolysis* **2004**, *71*, 27–46; c) R. E. Lyon, R. N. Walters, S. I. Stoliarov, *J. ASTM Int.* **2006**, *3*, 13895.

[11] a) P. A. Havelka-Rivard, K. Nagai, B. D. Freeman, V. V. Sheares, *Macromolecules* **1999**, *32*, 6418–6424; b) C. Q. Yang, Q. He, R. E. Lyon, Y. Hu, *Polym. Degrad. Stab.* **2010**, *95*, 108–115; c) H. R. Allcock, *Phosphorus-Nitrogen Compounds*, Academic Press, New York, **1972**; d) R. E. Lyon, L. Speitel, R. N. Walters, S. Crowley, *Fire Mater.* **2003**, *27*, 195–208.

[12] B. D. Dean, *Polymeric Materials Encyclopedia*, *Vol. 8* (Eds.: J. C. Salamone), CRC, Boca Raton, **1996**, pp. 5902–5909.