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PAPER

Halogen-free ultra-high flame retardant polymers through enzyme catalysis†

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Over the past few years, the use of certain types of halogenated flame retardant additives such as decabromodiphenylether has come under intense scrutiny due to their toxicity, environmental persistence and bio-accumulation. There is an immediate need for the development of non-toxic alternative flame retardant materials and fire resistant polymers with comparable or better efficacies, obtained using benign synthetic approaches. Enzymatic polymerization is being used increasingly as an environmentally friendly alternative method for the synthesis of functional materials including polymers and additives. Here, we report a biocatalytic synthesis of a new class of thermally stable, ultra-fire resistant polyphenols based on deoxybenzoins. In calorimetric studies, these polyphenols exhibit very low heat release capacities (comparable to NomexTM) and form a large amount of carbonaceous char rendering them suitable for flame retardant applications.

1. Introduction

Production of polymeric materials continues to increase annually, with more than 30 billion pounds of polymers being produced in the US alone in 2010.¹ Due to their low specific gravity and ease of processability, polymers are ideal candidates for a variety of electrical, electronic, structural, optical and medical applications.² In spite of their versatility of use, a significant drawback of most synthetic polymers is their inherent flammability. This necessitates the use of additives to ensure fire safety in most applications. Halogenated flame retardants (FR), decreases flame propagation primarily through quenching of reactive radicals in the flame zone. Phosphorus-based additives facilitate the formation of thermally insulating char layer or exhibit intumescence upon combustion.^{3,4} Metal hydroxides decompose through an endothermic process causing dilution in the flame zone in addition to releasing water thus preventing flame propagation and creating a less flammable product.⁵ The current production

levels of FR additives are at 1.5 million metric tons per year with a 3% annual growth rate.

The majority of the commercially used FR are based on halocarbons, antimony trioxide, phosphorous-based compounds and metal oxides. Though halogenated FR compounds lower the rate of flame propagation, some of them are also toxic⁶ and give out toxic products and/or generate corrosive gases during combustion that threaten both air and water ecosystems.⁷ They are known to be carcinogenic, causing damage to the immune, reproductive, nervous, and endocrine systems.⁸ In addition, they pose serious risk of secondary poisoning in the food chain. There is also concern about exposure of infants to select halogenated FR through human breast-feeding.^{9,10}

While small molecule-based FR (including halogenated varieties) provide a convenient means of reducing flammability, they also leach out of the polymer matrix leading to a variety of serious health and environmental problems.¹¹ With increasing reports on the detrimental effects of these halogenated FR, there is an imminent need for the development of a new class of FR using environmentally friendly methods of production. This will minimize their overall impact on human health and our environment. With the European Union banning the use of some classes of halogenated FR,¹² development of effective non-halogenated FR has gained paramount importance.

Non-toxic, inherently fire-retardant polymers based on *p*-phenylene heterocycles, modified siloxanes and phosphonates can be used directly in applications that require fire resistance.¹³ Alternatively, these polymers can also be used as FR additives. Research on 1,1-dichloro-2,2-(4-hydroxyphenyl)ethane (BPC), a commercially used halogenated flame retardant, indicate that the high char yields observed (upon burning) is due to the formation of diphenylacetylene derivatives¹⁴ which help in cutting off supply of oxygen, thereby preventing further degradation/

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Fig. 1 Structures of substituted phenol monomers.

burning of the polymer. The char-forming abilities of these substituted phenols have been gainfully utilized for the synthesis of polyphosphonate-phenol copolymers. Substituted phenols like 4,4'-bishydroxydeoxybenzoin (BHDB) and 4-methoxy,4'-hydroxydeoxybenzoin (MHDB) have been used as co-monomers to form polyphosphonate-phenol conjugates with good processability and solubility in common polar organic solvents such as chloroform and *N,N*-dimethylformamide (DMF). Several copolymers of BHDB with arylates¹⁵ and phosphonates¹⁶ have been studied and exhibit enhanced char formation and low heat release capacities (HRC).

However, the synthetic route adopted for obtaining these flame retardant polymers involve the use of toxic reagents and solvents, which are not environment friendly. Hence, BHDB and MHDB or hydroxybenzoins in general can serve as attractive starting materials for the synthesis of polymeric phenols with good flame retardant ability.

In this context, enzymatic polymerization using oxidoreductases can serve as an attractive alternate route to chemical routes for the synthesis of polyphenols. Enzymatic polymerization reactions can be carried out in aqueous conditions or mixed solvent systems. In the past, we have demonstrated the use of oxidoreductases for the polymerization of phenols,¹⁷ anilines¹⁸ and pyrroles.¹⁹ This biocatalytic approach offers a completely benign and versatile synthetic route to the synthesis of novel materials with properties comparable to or better than those obtained using chemical synthesis.²⁰ Here we report the polymerization of deoxybenzoins under predominantly aqueous conditions (near-neutral pH) and room temperature to produce polymers with superior flame retardant properties and processability. Although the monomers (deoxybenzoins) are produced using chemical methods, the polymers produced are thermally stable and are not expected to leach out into the environment during use or when blended into other polymers.

2. Experimental

2.1 Materials

BHDB and MHDB monomers (shown in Fig. 1) were synthesized by using a reported procedure.²¹ Phenol (99.99%) and Horseradish Peroxidase (HRP-Type II, RZ = 1.9) were purchased from Sigma-Aldrich (St Louis, MO). Hydrogen peroxide was diluted with de-ionized water to a stock solution of 0.3% (w/v). This diluted H₂O₂ solution was used for polymerization. All other chemicals were of reagent grade or better, and used without further purification. 100–500 molecular weight cellulose ester dialysis membranes were obtained from Spectra/Por Biotech.

Fig. 2 Proposed scheme for enzymatic polymerization of BHDB-MHDB using HRP.

Fig. 3 Proposed scheme for enzymatic copolymerization of BHDB-MHDB with phenol using HRP.

2.2 Synthetic procedure

2.2.1 Synthesis of homopolymers. Polymerization of BHDB was carried out in mixtures of pH 7 phosphate buffer and DMF (80 : 20) as shown in Fig. 2. The insolubility of BHDB in water necessitated the use of an organic solvent in small amounts. The reaction mixture is prepared by the addition of 5 mM BHDB to the buffer solution, followed by the addition of 3 mg of HRP. The polymerization is initiated by the addition of 5 mM, 0.3% H₂O₂ in small aliquots over a period of one hour. The polymerization is complete in 3 hours and the final product is isolated using dialysis and lyophilization. Polymerization of MHDB was done using a pH 8 phosphate buffer and DMF (80 : 20) combination. The synthesis procedure was similar to that of BHDB.

2.2.2 Synthesis of copolymers. Copolymerization of MHDB and BHDB with phenol was carried out using the method similar to the homo-polymerization in mixtures of pH 7 or pH 8 phosphate buffer and DMF (80 : 20), respectively (Fig. 3). The reaction mixture is prepared by the addition of 5 mM phenol and then 5 mM MHDB to the buffer solution, followed by the addition of 3 mg of HRP. The addition of phenol increases the solubility of the monomer in the reaction mixture. The polymerization is initiated by the addition of 5 mM, 0.3% H₂O₂ in small aliquots over a period of one hour. The polymerization is

complete in 3 hours and the final product is isolated using dialysis and lyophilization.

2.3 Characterization

The molecular weight of the polymers formed using this biocatalytic polymerization was determined using an Agilent 1100 series Gel Permeation Chromatography system with a Refractive Index Detector. The compounds were dissolved in DMF (mobile phase) and were run at 1 mL min⁻¹ flow rate. Fourier Transform Infrared (FTIR) spectroscopy measurements were carried out on a Thermo Scientific Nicolet 4700 FTIR with a Smart Orbit Attenuated total reflectance (ATR) accessory. The thermal stability of the monomeric and polymeric samples were analyzed using a thermogravimetric analyzer (TGA Q50, V6.7). Approximately 10 mg of the samples were weighed in platinum pans and heated up to 700 °C at a rate of 10 °C min⁻¹. All the samples were run under a constant nitrogen flow of 10 mL min⁻¹. Pyrolysis combustion flow calorimetry was done at Trace technologies LLC, New Jersey. Samples were heated at 1 °C s⁻¹ until decomposition was completed (maximum temperature 900 °C). Typical sample sizes were about 3 mg. The samples were tested in triplicate and the results averaged.

3. Results and discussion

3.1 BHDB–MHDB homopolymers

Substituted polyphenols are ideal candidates for enzyme polymerization, due to their very low oxidation potentials.²² Peroxidase-catalyzed synthesis of several substituted phenols using various methods have been summarized in multiple review articles.^{23–25} It was expected that peroxidase catalyzed polymerization of BHDB and MHDB, if successful, would yield polymers with good char forming and radical scavenging properties.

To explore this possibility, in the current study, all reactions were carried out in 10 mL scale. The reaction pH was fixed at 7 and 8 for BHDB and MHDB, respectively, after optimization for maximum yields. Oxidoreductases, exhibit significant substrate inhibition problems caused by rapid addition of the substrate (the oxidant) resulting in very low yields. Therefore the oxidant (H₂O₂ in this case) is usually added slowly in multiple aliquots.²⁶ However, it was reported that enzymatic polymerization of phenols using H₂O₂ as the oxidant required a one-shot addition of large quantities of H₂O₂ to generate sufficient amount of radicals that can facilitate propagation of the polymerization.¹³ In contrast, we observed that the polymerization of BHDB and MHDB did not proceed to good yields with one-shot addition of H₂O₂. We optimized the H₂O₂ addition to aliquots of 85 µL (0.83 mmol) over 10 minute intervals to get products in good yields. In all cases the reactions go to completion within 6 hours, forming a dark brown solution. Dialysis through 500 MW cut-off bags helped remove unreacted monomer. The dialyzed reaction mixtures were lyophilized to give the final product. The resulting products were soluble in common organic solvents like DMF and chloroform. It is acknowledged that use of 20% organic media (DMF) is not preferable from the environmental standpoint and the process cannot be considered as completely benign. But DMF is necessary to obtain polyphenols

Table 1 GPC analysis of enzymatically synthesized BHDB–MHDB homopolymers and copolymers

Molar ratios (benzoins : phenol)	BHDB-co-phenol		MHDB-co-phenol	
	Yield (%)	Mn (Da)	Yield (%)	Mn (Da)
100 : 0	68	5400	65	4800
99 : 1	75	6220	73	5440
95 : 5	81	8400	77	7040
90 : 10	90	11 360	84	9650
80 : 20	65	10 340	54	6600

with reasonable molecular weights. Other less toxic polar solvents are being currently evaluated as alternatives to DMF.

3.2 BHDB-phenol–MHDB-phenol copolymers

A major limiting factor in obtaining higher yields in these reactions was the initial solubility of BHDB and MHDB monomers in the reaction mixture. In order to increase the solubility of the monomers, phenol was introduced as a co-monomer into the reaction mixture. Phenol also acts as a spacer between the MHDB or BHDB units in the resulting polymer. It was found that reaction conditions similar to those adopted for the BHDB–MHDB homopolymer synthesis produced maximum yields. The ratio of the phenol to benzoin monomers in the feed was varied and product yields calculated as shown in Table 1. Clearly, the introduction of phenol has helped in significant improvement of reaction yields from 65 to 90% in both cases. This is because of the higher solubility of an unsubstituted phenol at a neutral–near-neutral pH, facilitating a more homogeneous system at the initial stages of the reaction. However, the improvement in reactions yields saturates at 90 : 10 molar ratios of the co-monomer and phenol. Phenol concentration higher than 10% in the feed results in a product with low yields and higher values of HRC.

3.3 Polymer characterization

3.3.1 Molecular weight. The molecular weights of the homopolymers and copolymers based on BHDB and MHDB are shown in Table 1. The molecular weights of the copolymers increased with the increase in phenol concentration in the feed as shown in Table 1. This can be attributed to the higher solubility of the co-monomer in buffer solutions.

3.3.2 Chemical structure (FTIR–ATR analysis). Homopolymers and copolymers of BHDB and MHDB were analyzed by FTIR–ATR spectroscopy to investigate the chemical structure of the synthesized compounds. Fig. 4 displays the transmittance FTIR spectra of BHDB and MHDB-based polymers respectively. The IR traces of the homopolymers of BHDB and MHDB (black and red curves in Fig. 4) are typical of polyphenols previously reported in the literature. Characteristic vibrations at 3300–3500 cm⁻¹ and 1170–1230 cm⁻¹ are attributed to the O–H and C–O–C stretching respectively. Pronounced vibrations at 1660 cm⁻¹ are due to C=O stretching of the carbonyl groups from the repeat unit of the polymer backbone. For the copolymers based on BHDB and MHDB (blue and green curves in

Fig. 4 FTIR spectra of HRP catalyzed BHDB and MHDB homo and copolymers.

Fig. 4), the absorption bands at $780\text{--}870\text{ cm}^{-1}$ are assigned to C–H out-of-plane deformation vibration of substituted benzene nuclei, incorporated by the phenol groups in the polymer. BHDB homopolymer in comparison with BHDB-phenol copolymer shows a greater reduction in intensity of the free OH vibration. Although these FTIR spectra are only semi-quantitative, the relative reduction of peak intensities indicates the possibility of a polymer with greater C–O–C coupling. MHDB-phenol copolymer is more C–O–C coupled than MHDB homopolymer. In the case of the homopolymer, the electron-withdrawing methoxy substituent, predominantly directs the polymerization to proceed *via* C–C coupling. However, in all cases the polymerization appears to proceed through both C–C and C–O–C coupling in the initial stages of the reaction. Preliminary ^1H NMR studies (data provided in ESI†) also indicate the formation of both C–C and C–O–C coupled products. Unambiguous NMR peak assignment has been a challenge due to the formation of multiple types of polymeric products in these reactions leading to peak broadening in the spectra.

3.3.3 Thermal stability and FR properties. Flame retardancy in polymers can be achieved by incorporation of additives that act either in the condensed phase – physical action through char formation (for example phosphorus compounds) – or the gas phase – chemical action through radical scavenging (for example halogenated FR).

The primary motivation for the selection of BHDB and MHDB as candidates for the synthesis of flame retardants was to combine the thermal stability of polyphenols¹³ with the radical scavenging capability of phenolic entities.²⁷ In addition, it was hypothesized that if the aromatic groups were coupled through C–C linkages, the possibility of formation of carbonaceous char is also maximized. It has been previously reported that polyphenols formed *via* C–C linkages exhibit high char yields upon thermal decomposition.²⁸ Several publications and review articles including our group's recently published work on

Fig. 5 Thermogravimetric analysis spectra of MHDB and poly(MHDB) made using HRP.

polyborosiloxanes have also shown that char formation is an important characteristic for an effective FR material.^{3,4,29}

TGA of enzymatically synthesized polyphenols based on BHDB and MHDB is presented in Fig. 5. For all samples, there is an initial weight loss of between 4–6% until approximately $150\text{ }^{\circ}\text{C}$, attributed to loss of water (moisture) absorbed by the sample. The polymers and copolymers of BHDB and MHDB were stable up to $500\text{ }^{\circ}\text{C}$, with char yields greater than 30 and 60% respectively. In addition to the thermal stability, apparent limiting oxygen index values were also determined. Limiting Oxygen Index (LOI) is defined as the minimum concentration of oxygen in a nitrogen–oxygen mixture, required to support downward burning of a vertically mounted test specimen. It is a quality control tool for determining the relative flammability of polymeric materials. The estimated LOI (calculated from van Krevelen's numerical method^{30,31} from the char yields at $800\text{ }^{\circ}\text{C}$) for the samples is shown in Table 2.

Table 2 Char yield and heat release capacities of BHDB and MHDB polymers–copolymers with varying ratios of phenol

Compound	HRC (kJ g^{-1})	Total HR (kJ g^{-1})	Char ^a (%)	Approx. LOI ^b
Poly(BHDB)	15	3.3	51.9	38
Poly(MHDB)	19	2.8	40	34
Poly(phenol)	42	3.1	47.7	37
Poly(BHDB : phenol) ratio: 99 : 1	30	4.5	58.7	41
Poly(BHDB : phenol) ratio: 95 : 5	37	3.9	53.8	39
Poly(BHDB : phenol) ratio: 90 : 10	55	7.2	56	40
Poly(MHDB : phenol) ratio: 99 : 1	46	6.8	55.1	40
Poly(MHDB : phenol) ratio: 95 : 5	46	7.4	54.7	39
Poly(MHDB : phenol) ratio: 90 : 10	53	7.6	59.1	41

^a Char yield calculated from PCFC analysis. ^b Calculated using the equation $\text{LOI} = 17.5 + 0.4(\text{Char})$.

Fig. 6 PCFC analysis of commercial polymers in comparison with BHDB and MHDB homo and copolymers.

Pyrolysis combustion flow calorimetry (PCFC) analysis. PCFC is a method reported by Walters and Lyon to measure the HRC and total heat release of polymer materials through an oxygen consumption calorimetric technique.³² It is a Federal Aviation Administration patented technology for evaluation of flame retardancy of polymer materials. This test requires very small sample size and the test procedure is quite straightforward. The heat release values obtained using this method correlates closely to other large-scale techniques such as cone calorimetry, oxygen bomb and TGA/GC-MS.³³

Table 2 shows the HRC values of the enzymatically synthesized homopolymers and copolymers of BHDB and MHDB. The high char yields could be attributed to the formation of diphenylacetylene derivatives during the degradation of these polymers.¹⁰ Homopolymers of BHDB and MHDB exhibit the lowest HRC ($<20 \text{ kJ g}^{-1}$) reported for these types of polymeric materials. A very low total heat release also indicates that these polymers are promising candidates for flame retardant applications. This result was not totally unexpected, as chemically synthesized BHDB copolymers with arylates and phosphonates have shown superior thermal properties with HRC values ranging between $75\text{--}200 \text{ kJ g}^{-1}$.^{11,12} However, enzymatic approach has enabled the 'clean' synthesis of polymers of BHDB and MHDB with better HRC than previously reported BHDB-based copolymers. The introduction of an unsubstituted phenol into the system tends to increase the HRC value by about 30 kJ g^{-1} with respect to the homopolymers, which is a very marginal increase.

Poly(BHDB) and its copolymers have a lower HRC and higher char yield in comparison to their poly(MHDB) counterparts as shown in Table 2. This can be explained by the higher concentration of radical scavenging phenolic groups in BHDB-based polymers. The total HR values of MHDB-based polymers (except for the MHDB homopolymer) are also higher. Even in the case of poly(MHDB) homopolymer the total HR is only marginally lower than that of poly(BHDB).

Comparison of enzymatically synthesized polyphenols to commercial commodity and engineering polymers (Fig. 6)³² clearly indicates that these new polymers belong to the ultra-high fire resistant category. A systematic study of the decomposition products of these materials will lead to deeper understanding of their degradation pathway. This in turn will help in designing new materials based on polyphenols with improved FR properties.

4. Conclusions

Homopolymers and copolymers of BHDB and phenol as well as MHDB and phenol were synthesized using enzyme catalysis. These biocatalyzed reactions were carried out at room temperature in predominantly aqueous environment following the fundamental principles of green processing. The use of a co-monomer (phenol), helped improve the yields and molecular weights of the final products. This new class of homopolymers exhibit superior thermal stability, extremely low HRC ($<20 \text{ kJ g}^{-1}$) and high char yields upon combustion. The copolymers exhibit slightly higher HRC values of about 50 kJ g^{-1} . The heat release values for both the homopolymers and the copolymers of enzymatically synthesized BHDB and MHDB are extremely low, indicating that these polymers are ultra-fire resistant materials, comparable to NomexTM and TeflonTM. Efforts are underway to blend these polymers into common plastics such as polypropylene to impart FR properties to these commodity polymers.

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Notes and references

- G. L. Nelson, A. B. Morgan and C. A. Wilkie, *Fire and Polymers V: Materials and Concepts for Fire Retardancy*, ACS Symposium Series, 2009, 1–7.
- Plastic Applications Database, 2005, Knovel.
- T. Kashiwagi, 25th International Symposium on Combustion, Pittsburgh PA, 1994, 1423–1437.
- C. E. Anderson, D. E. Ketchum and W. P. Mountain, *J. Fire Sci.*, 1988, **6**, 390–410.
- R. Rothon, *Effects of Particulate Fillers on Flame Retardant Properties of Composites: Particulate-Filled Polymer Composites*, Rapra Technology Ltd., Shawbury U. K., 2003, vol. 6, pp. 271–273.
- K. D'Silva, A. Fernandes and M. Rose, *Crit. Rev. Environ. Sci. Technol.*, 2004, **34**, 141–207.

- 7 M. Alaei and R. J. Wenning, *Chemosphere*, 2002, **46**, 579–582.
- 8 J. E. Haddow, G. E. Palomaki, W. C. Allan, J. R. Williams, G. J. Knight, J. Gagnon, C. E. O’Heir, M. L. Mitchell, R. J. Hermos and S. E. Waisbren, *N. Engl. J. Med.*, 1999, **341**, 549–555.
- 9 S. Jianwen, M. Pereas, J. Winkler, P. Vista, M. McKinney and D. Kopec, *Chemosphere*, 2002, **46**, 697–707.
- 10 V. J. Pop, J. L. Kuijpers, A. L. van Baar, G. Verkerk, M. M. van Son, J. J. de Vijlder, T. Vulsma, W. M. Wiersinga, A. H. Drexhage and H. L. Vader, *Clin. Endocrinol.*, 1999, **50**, 149–155.
- 11 A. F. Grand and C. A. Wilkie, *Fire Retardancy of Polymeric Materials*, Marcel Dekker, New York, 2000.
- 12 The European Parliament and the European Council: Off. J. Eur. Union, 2003, Directive 2002/96/EC of 27.
- 13 S. Bourbigot and S. Duquesne, *J. Mater. Chem.*, 2007, **17**, 2283–2300.
- 14 A. C. L. M. van der Waals, A. J. H. Klunder, F. R. van Buren and B. Zwanenburg, *J. Mol. Catal. A: Chem.*, 1998, **134**, 179.
- 15 K. A. Ellzey, T. Ranganathan, J. Zilberman, E. B. Coughlin, R. J. Farris and T. Emrick, *Macromolecules*, 2006, **39**, 3553.
- 16 T. Ranganathan, J. Zilberman, R. J. Farris, E. B. Coughlin and T. Emrick, *Macromolecules*, 2006, **39**, 5974.
- 17 F. F. Bruno, R. Nagarajan, P. Stenhouse, K. Yang, J. Kumar, S. K. Tripathy and L. A. Samuelson, *J. Macromol. Sci., Part A: Pure Appl. Chem.*, 2001, **A38** (12), 1417–1426.
- 18 W. Liu, J. Kumar, S. K. Tripathy, K. J. Senecal and L. A. Samuelson, *J. Am. Chem. Soc.*, 1999, **121**, 71–78.
- 19 R. M. Bouldin, S. Ravichandran, R. Gharwal, S. Nagarajan, J. Kumar, F. Bruno, L. A. Samuelson and R. Nagarajan, *Synth. Met.*, 2011, **161**, 1611–1617.
- 20 S. Kobayashi and A. Makino, *Chem. Rev.*, 2009, **109** (11), 5288–5353.
- 21 N. P. Buu-hoi, M. Sy and N. D. Xuong, *Bull. Soc. Chim. Fr.*, 1956, **44**, 629.
- 22 C. Li and M. Z. Hoffman, *J. Phys. Chem. B*, 1999, **103**, 6653–6656.
- 23 H. Uyama and S. Kobayashi, *Adv. Polym. Sci.*, 2006, **194**, 51–67.
- 24 M. Reihmann and H. Ritter, *Adv. Polym. Sci.*, 2006, **194**, 1–49.
- 25 M. Ayyagari, J. A. Akkara and D. L. Kaplan, *Acta Polym.*, 1996, **47**, 193–203.
- 26 J. A. Nicell and H. Wright, *Enzyme Microb. Technol.*, 1997, **21**, 302.
- 27 N. Blanc, D. Hauchard, L. Audibert and E. A. Gall, *Talanta*, 2011, **84** (2), 513–518.
- 28 G. F. L. Ehlers, R. K. Fisch and W. R. Powell, *J. Polym. Sci., Part A-1*, 1969, **7** (10), 2931–2953.
- 29 R. Mosurkal, R. Kirby, W. S. Muller, J. W. Soares and J. Kumar, *Green Chem.*, 2011, **13**, 659–665.
- 30 D. W. van Krevelen, *Properties of Polymers: Their Correlation with Chemical Structure*, Elsevier, Amsterdam, Netherlands, 1990.
- 31 D. W. van Krevelen, *Polymer*, 1975, **16**, 615–620.
- 32 R. Lyon and R. N. Walters, *J. Anal. Appl. Pyrolysis*, 2004, **71**, 27–46.
- 33 R. Lyon and R. N. Walters, Final Report, FAA, 2002, DOT/FAA/AR-01/11.