

3 Thermo-Oxidative Degradation

3.1 Poly(ethylene terephthalate) (PET)

The mechanism developed originally by Bolland and Gee [1] to explain the thermal oxidation of rubbers and polyolefins has been successfully applied to the same situation in various polymers. A generalised form of the reaction sequence may be set out as follows:

Chain initiation



Chain propagation



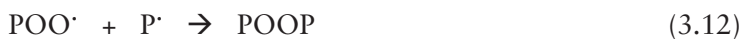
Chain branching



Degradation and Stabilisation of Aromatic Polyesters



Chain termination



As a rule, commercial polymers of all types contain catalyst residues and externally introduced functional groups (e.g., hydroperoxides) from manufacturing and processing which can sensitise the matrix to thermal oxidation. The exact nature of the initiating reactions (3.1) to (3.3) is not, even now, fully understood. It is generally assumed that primary radicals are formed through the action of heat and mechanical stress. In the case of PET, mechanical stress and the labile nature of the hydrogens α to the ester groups (and where such structures feature as 'impurities' α to ether links) towards direct abstraction by oxygen (reaction (3.2)) may provide the most likely point of initiation.

Reaction (3.4) is fixation of an oxygen molecule onto an alkyl radical. It is generally a very fast reaction if the concentration of oxygen in the polymer is moderate-to-high; this rapidly transforms alkyl radicals into peroxy radicals. It is essentially reaction (3.5) that will determine the rate of oxidation of the polymer, the rate being a function of the bond strength of the C-H bond broken and the stability of the alkyl

radical formed. These factors, along with the reaction temperature, determine the kinetic chain length, i.e., the mean number of oxidative cycles (reactions (3.4 and (3.5)) before termination occurs.

The chain-breaking reactions consist of the monomolecular reaction (3.6a), the pseudo-monomolecular reaction (3.6b) and the bimolecular reaction (3.7). They show the decomposition of hydroperoxide groups. The pure thermal decomposition of hydroperoxide involves high activation energies, especially the monomolecular reaction (3.6a). In the case of molten PET, the temperature is more than sufficient to bring such reactions into play. Decomposition of hydroperoxide is efficiently catalysed by various metal ions which may be present in the polymer as catalyst residues, or as part of additive packages. This is especially the case with metal ions that exhibit more than one stable oxidation state. Such catalysed reactions are equivalent to reaction (3.7) but are much faster.

The radicals formed in the initiation, propagation and chain-branching steps can not only fix oxygen and abstract hydrogen, they may also be subject to monomolecular decomposition processes. This type of reaction leads to chain scission and, as a consequence, to a decrease in the molecular weight of the polymer.

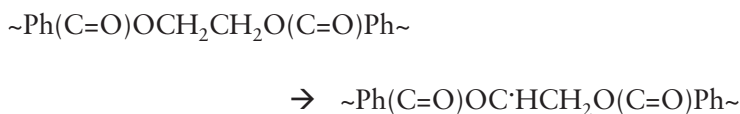
The chain termination reactions (3.10)–(3.13) are bimolecular reactions leading to the destruction of two radicals each. As a rule, in the presence of a sufficient amount of oxygen, only reactions (3.10) and (3.11), involving peroxy radicals, need be considered. Termination reactions (3.12) and (3.13) become increasingly important with reduction in the amount of oxygen available. Bimolecular reactions such as (3.10a), (3.12) and (3.13) give rise to branching and crosslinking. This can give rise to increases in molecular weight and possible gel formation.

Studies of the thermal oxidation of PET have been carried out by various authors over several years [2–20].

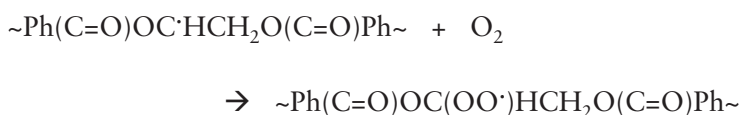
An early overall oxidation scheme for PET was compiled by Buxbaum [3]. From his own, and earlier observations, he deduced that the

Degradation and Stabilisation of Aromatic Polyesters

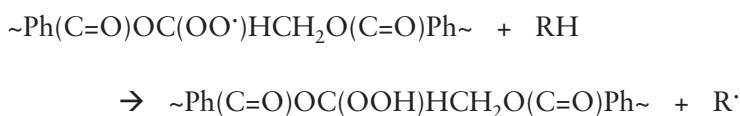
hydrogens most vulnerable to abstraction, and hence to initiation of free radical processes, were those α to the ester group in the polyester backbone:



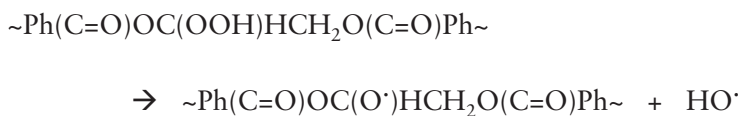
In the presence of oxygen, the alkyl radical formed will rapidly react with oxygen to form a peroxy radical:



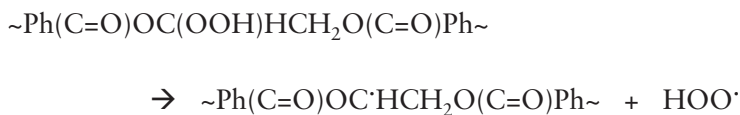
The peroxy radical will then abstract hydrogen from the same or another polymer chain to form a hydroperoxide:



The next stage posited is scission of the hydroperoxide which, in theory, can take place in one of two ways: O-O bond scission to form an alkoxy macroradical and HO \cdot , or C-O bond scission to form an alkyl macroradical and HOO \cdot :

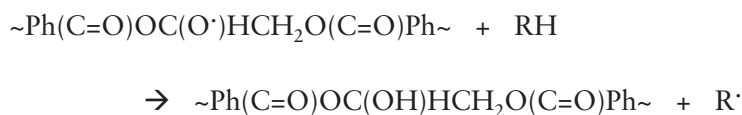


Or

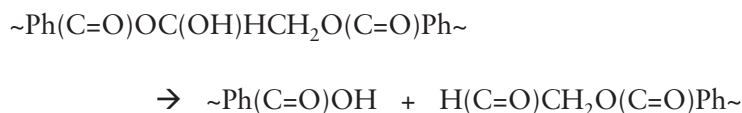


Thermo-Oxidative Degradation

The macroalkoxy radical may then abstract a hydrogen to form a hydroxyl group, and this species can then undergo chain scission via a cyclic intermediate to form an acid chain end and an aldehyde chain end:

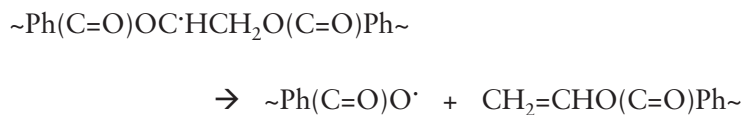


then



The aldehydic chain end may then be oxidised to a carboxylic acid.

The alkyl macroradical may also undergo chain scission, allegedly via a homolytic route:



and



From this description of the primary oxidation processes in PET and the related chain scissions, we see that the main difference between aerobic and anaerobic degradation is the appearance of aldehyde groups as chain ends, in addition to the previously encountered acid and unsaturated chain ends.

Looking at one of the likely following stages of reaction – the formation of low molecular weight fragments from chain ends – each

Degradation and Stabilisation of Aromatic Polyesters

chain end may now react via three general reactions: concerted ester pyrolysis (CEP), transesterification/hydrolysis (TH) and oxidation (OX). The last reaction may take several forms. Likely reactions that may occur (in theory) are described in the following paragraphs.

Chain ends available for further reaction include:

$\sim\text{Ph}(\text{C}=\text{O})\text{OCH}_2\text{CH}_2\text{OH}$	Hydroxyl
$\sim\text{Ph}(\text{C}=\text{O})\text{OH}$	Acid
$\sim\text{Ph}(\text{C}=\text{O})\text{OCH}=\text{CH}_2$	Unsaturated
$\sim\text{Ph}(\text{C}=\text{O})\text{OCH}_2(\text{C}=\text{O})\text{H}$	Aldehyde

Likely evolved species may be:

a) Hydroxyl



This can further react by 'dimerisation' to form 1,4-dioxane, or can form 2-methyl-1,3-dioxolane. The latter can also possibly break down to two molecules of acetaldehyde.

OX (via alkoxy radical)



This structure is most probably unstable, and may rearrange into two molecules of formaldehyde. A less likely reaction would be further oxidation to form glycolic acid.



Thermo-Oxidative Degradation

As already noted in previous discussions, vinyl alcohol rapidly isomerises to acetaldehyde. The latter can be oxidised to acetic acid under certain conditions.

CEP $\text{CH}_2=\text{CHOH}$; vinyl alcohol

b) Acid

Acid ends are created via most of the reactions undergone by other chain end types to split off small molecules. Transition states, particularly via potential homolytic pathways, may undergo further scission to produce gaseous products such as CO and CO_2 . This can occur during ongoing reaction of non-acid chain ends, and by reaction of the existing acid chain ends. Several reactions may then occur on the phenyl radicals formed, including hydrogen abstraction (aromatic chain end), reaction with hydroxyl radicals (phenolic chain end), and reaction with another alkyl radical (chain extension or crosslinking).

c) Unsaturated

TH $\text{CH}_2=\text{CHOH}$; vinyl alcohol

CEP $\text{HC}\equiv\text{CH}$; acetylene

Not energetically favoured because the required β -hydrogen is attached to an unsaturated group.

OX (via alkoxy radical) $\text{CH}_2=\text{C}=\text{O}$; ketene

Unstable compound, which may further react.

OX (via alkyl radical) $\text{HC}\equiv\text{CH}$; acetylene

Overall, the oxidation of unsaturated chain ends in PET requires abstraction of a hydrogen from an unsaturated group. This reaction is not favourable, especially given the high concentration of more labile hydrogens available.

Degradation and Stabilisation of Aromatic Polyesters

d) Aldehyde

TH HOCH₂(C=O)H; 'hydroxyacetaldehyde'

CEP CH₂=C=O; ketene

This process would require transfer of an aldehydic hydrogen in a cyclic transition state, a process which is almost certainly less likely even than abstraction of hydrogen from an unsaturated site. If the aldehydic chain end is oxidised *in situ* to an acid, then it cannot take part in this type of reaction because a β hydrogen is not available for transfer.

OX (via alkoxy radical) H(C=O)(C=O)H; glyoxal

Could be further oxidised to glyoxilic acid or oxalic acid.

OX (via alkyl radical) CH₂=C=O; ketene

Overall, taking into account the theoretical considerations stated above and available laboratory data, acetaldehyde remains the major volatile product from PET during thermal degradation/oxidation. Of the proposed products mentioned above, we cannot be certain which one is important: few have been identified in studies to date. Many of the initially derived small-molecule species may undergo further reaction, or reaction with other species in or on the polymer.

From a practical standpoint, the other problem with oxidative degradation of PET besides evolution of tainting species such as acetaldehyde is polymer discoloration. As already noted, Buxbaum [3] suggested that discoloration could be due to unsaturated polymeric species such as vinyls and aldol derivatives, at least in the case of thermal degradation. An extensive study of the yellowing of PET under thermal and thermo-oxidative conditions was carried out by Edge and co-workers [11]. They concluded that coloured species were due to hydroxylation of the terephthalate ring, followed

by formation of unsaturated ester species, and to the formation of quinonoid-type structures.

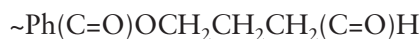
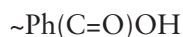
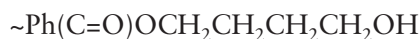
Both this study and later work by Botelho and co-workers [13] showed that, unlike polyolefins, the thermo-oxidative degradation of PET involves non-oxidative thermal degradation processes, especially in the early stages. The overall thermo-oxidative process in PET is therefore extremely complex. Recent studies [19, 20] using state-of-the-art mass spectroscopic techniques have provided further evidence for the role of hydroxylated terephthalate fragments in PET discoloration.

Oxidative degradation of PET can also result in crosslinking and gel formation [4–6].

3.2 Poly(butylene terephthalate) (PBT)

Few studies have been carried out specifically on the thermo-oxidative degradation of PBT [12, 13, 21], and it is generally considered that the oxidation pathway is very similar to that described in the section on PET.

Taking the same theoretical approach to the likely low molecular weight products, the following processes are the most probable from the available end groups:



Degradation and Stabilisation of Aromatic Polyesters

1. Hydroxyl



As evidenced by laboratory studies, this product may then relatively easily cyclise to form tetrahydrofuran (THF). Some workers have also suggested that THF could be formed directly from the hydroxyl chain end via a cyclic intermediate.



Unlike the situation in PET, there is no likely rearrangement to form an aldehyde in this case. Potentially, this species might react with an acid end group to produce an 'extra' unsaturated chain end. The likelihood of this will depend on the volatility of the unsaturated alcohol (boiling point (bp) = 112 °C) and its miscibility/solubility in the polymer.

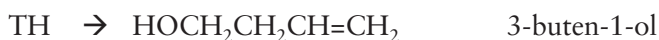


Oxidation of the hydroxyl end group could alternatively form 3-buten-1-ol. It is also possible for the hydroxyaldehyde to further oxidise to form 4-hydroxybutyric acid.

2. Acid

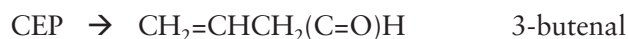
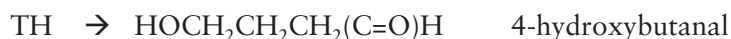
As for PET

3. Unsaturated



Alternatively, the last reaction may produce additional 1,3-butadiene. The unsaturated aldehyde, if formed, could further oxidise to vinylacetic acid.

4. Aldehyde



Alternatively, the last reaction could produce additional 3-butenal. The dialdehyde, if formed, could further oxidise to form succinic acid.

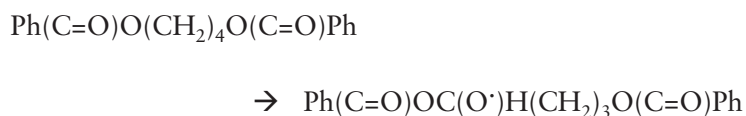
From investigations of non-oxidative degradation, the main products posited from PBT are 1,3-butadiene, THF, 1,4-butanediol and 4-vinylcyclohexane (dimer of butadiene), as well as carbon oxides and water. Potential minor products, as suggested in this theoretical examination, in some way resemble those of PET, with hydroxy acids, hydroxy aldehydes, dialdehydes and diacids. Unlike PET, the above examination reveals the possibility of the formation of unsaturated species such as acids, alcohols and aldehydes which are not possible with PET. One can regard ketene as an unsaturated aldehyde, and acetaldehyde can be derived from an unstable unsaturated alcohol.

As it is known that a cyclic ether (THF) may be formed during degradation and from the 1,4-butanediol by-product, the 1,4-diacid and hydroxyacids noted above could therefore also cyclise, leading to formation of succinic anhydride and γ -butyrolactone. Further studies are required to investigate if any of these possible products occur in the thermo-oxidation of PBT.

A study of the oxidation of butylene benzoate as a model compound for PBT was undertaken by Botelho and co-workers [13] and several products identified by gas chromatography-mass spectrometry

Degradation and Stabilisation of Aromatic Polyesters

(GC-MS). Initial reactions involved abstraction of a hydrogen from a methylene group alpha to an ester group. This was followed by oxidation, formation of hydroperoxide, and homolytic scission of the hydroperoxide to form an alkoxy radical. This can be summarised as:



The formed alkoxy radical could then react in three ways:

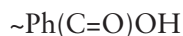
- a) H-abstraction \rightarrow $\text{Ph}(\text{C}=\text{O})\text{OC}(\text{OH})\text{H}(\text{CH}_2)_3\text{O}(\text{C}=\text{O})\text{Ph}$ {I}.
- b) O-C bond scission \rightarrow $\text{Ph}(\text{C}=\text{O})\text{O}^\cdot + \text{H}(\text{C}=\text{O})(\text{CH}_2)_3\text{O}(\text{C}=\text{O})\text{Ph}$.
The carboxy radical will then abstract a further hydrogen to form $\text{Ph}(\text{C}=\text{O})\text{OH}$ {II}. The aldehydic fragment then having aldehydic H abstracted there from and passing through an oxidation/hydroperoxidation/alkoxy radical formation/H-abstraction cycle to form $\text{Ph}(\text{C}=\text{O})\text{O}(\text{CH}_2)_3(\text{C}=\text{O})\text{OH}$ {III}; or through a series of reactions starting with loss of carbon dioxide to eventually form benzoic acid {II}.
- c) C-C bond scission \rightarrow $\text{Ph}(\text{C}=\text{O})\text{O}(\text{C}=\text{O})\text{H}$ {IV} + $\cdot\text{CH}_2(\text{CH}_2)_2\text{O}(\text{C}=\text{O})\text{Ph}$. The alkyl radical fragment may then go through a series of reactions to again form benzoic acid {II}.

Species with numbers in parentheses are those identified by the authors.

Studies on the effect of the level of acid end groups present on the thermo-oxidative stability of PBT [12] noted that increased carboxyl content lowered stability; this behaviour matches that of PET.

3.3 Poly(trimethylene terephthalate) (PTT)

Very little has been published in thesis form [22] or in the literature [23, 24] relating to the thermo-oxidation of PTT. A theoretical consideration of the likely small molecule by-products from thermal degradation and oxidation may provide useful information. Available end groups are:



a) Hydroxyl



Under these circumstances, PTT would be expected to behave more like PBT than PET. Allyl alcohol is relatively stable, and there does not appear to be a likely driving force for it to rearrange to an aldehyde. There is potential for this species to form an ester with an acid chain end, thus forming an additional unsaturated chain end.



Alternatively, oxidation could lead to formation of additional allyl alcohol. The aldehyde could further oxidise to 3-hydroxypropanoic acid.

Degradation and Stabilisation of Aromatic Polyesters

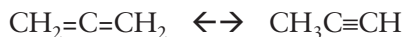
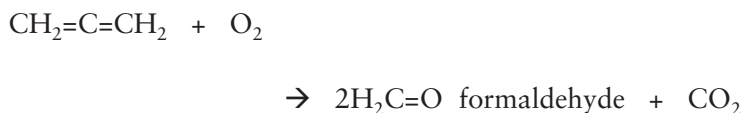
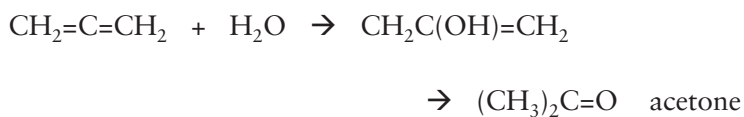
b) Acid

As for PET

c) Unsaturated



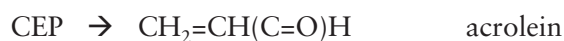
In this case we have, unlike PBT and more like PET, the requirement for abstraction of a hydrogen from an unsaturated carbon during chain scission via the proposed 6-membered cyclic intermediate. It is difficult to be certain whether this product will form. The potential for resonance stabilisation of the intermediate is difficult to assess; the allyl radical and allyl ions show some resonance characteristics, but it is also known that in the final compound the two double bonds are orthogonal, i.e., there is no interaction between them. Allene is extremely volatile (bp = -34°C), but it is also quite reactive with water and oxygen and can, under certain circumstances, form a resonance structure with methyl acetylene:



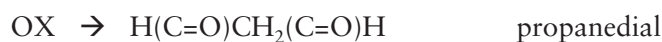
Alternatively, oxidation of this end group could lead to the formation of more allene. The potential formation of acrolein is interesting because

this has been noted in the literature as a by-product during PTT synthesis [22]. Potentially it could also further oxidise to acrylic acid.

d) Aldehyde



An alternative route to acrolein is possible. If aldehyde ends are present in a PTT sample (possibly by prior oxidation during manufacture or processing), then further oxidation is not required to produce acrolein.



Alternatively, acrolein may also be formed by oxidation of the aldehyde chain end. Propanedial, if formed, could potentially further oxidise as far as malonic acid.

Studies by Wang and co-workers [23] indicated a three-step process for the degradation of PTT in air:

Step 1: Degradation of chains into smaller fragments by an initial end-chain scission.

Step 2: Oxidation of small fragments into volatile products.

Step 3: Decomposition of initially stable structures formed in 1 and 2, probably to form crosslinked residues.

In a study on PTT recycling, Ramiro and co-workers [24] noted that the structure of the polymer did not change despite lowering of molecular weight. This suggests that chain-end scission is probably the correct first step. They noticed that, despite the lack of 'new' structures, the polymer did yellow considerably. This was a paradoxical observation unless the colour is attributable to small fragments or polymerised unsaturated species.

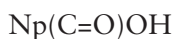
3.4 Other Aromatic Polyesters

Botelho and co-workers [25] made a comparative study of the thermo-oxidative degradation of poly(ethylene naphthalate) (PEN) and poly(butylene naphthalate) (PBN). The mechanism of the degradation of model compounds for these two polymers was similar in many ways to that noted for the terephthalate equivalents [13].

GC-MS analysis of the oxidation of ethylene dinaphthalate revealed the following products (where Np denotes a naphthalene ring system):



whereas butylene dinaphthalate gave:



CO and CO₂ were not detected, unlike with the terephthalate equivalents.

The thermo-oxidation of PEN and PBN leads to yellowing, with the latter discolouring faster than the former. For both polymers, yellowing is related to oxygen uptake, indicating that this discoloration is due to

oxidative reaction(s). Compared with their terephthalate equivalents, these polymers discolour much more quickly, although the rate of oxidation appears to be lower. This may be accounted for by the greater extinction coefficients likely with oxidised derivatives of the naphthalene ring system.

Carboxylic acid end groups and anhydrides were detected in oxidised samples of these polymers, so it is proposed that the oxidation mechanism is very similar to that of the model compounds.

The oxidation stability of poly(butylene isophthalate-*co*-terephthalate) copolyesters has been shown to decrease steadily with isophthalate unit content [26]. As expected, GC-MS analyses show that oxidation takes place mainly in the butylene units, through the same mechanism as before. Small-molecule products of a copolyester containing 25 mol% isophthalate included THF, butyrolactone, 3-buten-2-one, 2-propenal, and various other cyclised and carbonyl fragments, along with acetic acid. As has been observed for most polyesters, thermal and thermo-oxidative reactions occur simultaneously, and the lower stability of butylene-isophthalate units is most probably responsible for the lower overall stability of copolymers containing this structure, even under the oxidation conditions used.

Studies have also been carried out on the oxidation of copolymers of terephthalic acid and 1,4-butanediol with aliphatic diacids such as adipic acid [27] and succinic acid [28]. No specific information was revealed on the details of the reaction mechanism. It was assumed that the butylene unit would remain the point of initial oxidative attack.

In the case of poly(4-hydroxybenzoate) [29], thermo-oxidative degradation occurs only at very high temperature and even then only slowly. From the data available, it would appear that oxidation occurs at chain ends, and that reduction in molecular weight is brought about essentially by a depolymerisation process. This conjecture is backed by the fact that, even at 75% weight loss, the chemical composition of the remaining polymer is virtually unchanged.

Degradation and Stabilisation of Aromatic Polyesters

A few studies have been made on polyarylates (i.e., copolymers of hydroxybenzoic acid with other ester-forming co-condensates), some of which provided information on oxidative degradation [30–32]. As might be expected, in the case of a hydroxybenzoate-*co*-ethylene terephthalate, the two parts of the copolymer degrade separately: the PET first via the usual pathways, and the hydroxybenzoate unit later by a ‘depolymerisation’ route with the formation of phenol and carbon dioxide.

References

1. J.L. Bolland and G. Gee, *Transactions of the Faraday Society*, 1946, **42**, 236.
2. I. Gomory, O. Mejnek and J. Stimel, *Journal of Polymer Science*, 1962, **59**, 1, 71.
3. L.H. Buxbaum, *Angewandte Chemie International Edition*, 1968, **7**, 3, 182.
4. K. Yoda, A. Tsuboi, M. Wada and R. Yamadera, *Journal of Applied Polymer Science*, 1970, **14**, 9, 2357.
5. D.L. Nealy and L.J. Adams, *Journal of Polymer Science: Polymer Chemistry Edition*, 1971, **9**, 7, 2963.
6. P.A. Spanniger, *Journal of Polymer Science: Polymer Chemistry Edition*, 1974, **12**, 4, 709.
7. J.D. Cooney, M. Day and D.M. Wiles, *Journal of Applied Polymer Science*, 1984, **29**, 3, 911.
8. J. Friedrich, I. Loeschke, H. Frommelt, H.D. Reiner, H. Zimmermann and P. Lutgen, *Polymer Degradation and Stability*, 1991, **31**, 1, 97.
9. K.S. Seo and J.D. Cloyd, *Journal of Applied Polymer Science*, 1991, **42**, 3, 845.

10. F. Villain, J. Coudane and M. Vert, *Polymer Degradation and Stability*, 1994, **43**, 3, 431.
11. M. Edge, R. Wiles, N.S. Allen, W.A. McDonald and S.V. Mortlock, *Polymer Degradation and Stability*, 1996, **53**, 2, 141.
12. D.N. Biriakis and G.P. Karayannidis, *Polymer Degradation and Stability*, 1999, **63**, 2, 213.
13. G. Botelho, A. Queiros, S. Liberal and P. Gijsman, *Polymer Degradation and Stability*, 2001, **74**, 1, 39.
14. M. Dzieciol and J. Trzeczynski, *Journal of Applied Polymer Science*, 2001, **81**, 12, 3064.
15. E.V. Kalugina, T.N. Novotorseva and M.B. Adreeva, *International Polymer Science and Technology*, 2002, **29**, 4, T51.
16. P.K. Fearon, S.W. Biggar and N.C. Billingham, *Journal of Thermal Analysis and Calorimetry*, 2004, **76**, 1, 75.
17. Y.N. Gupta, A. Chakraborty, G.D. Pandey and D.K. Setna, *Journal of Applied Polymer Science*, 2004, **92**, 3, 1737.
18. S.V. Levchik and E.D. Weil, *Polymers for Advanced Technologies*, 2004, **15**, 12, 691.
19. C.F.L. Ciolacu, N.R. Choudhury and N.K. Dutta, *Polymer Degradation and Stability*, 2006, **91**, 4, 875.
20. C.F.L. Ciolacu, N.R. Choudhury, N.K. Dutta and N.H. Voelcker, *Macromolecules*, 2006, **39**, 23, 7872.
21. A. Massa, A. Ecettri, S. Contessa, V. Bugatti, S. Concilio and P. Ianelli, *Journal of Applied Polymer Science*, 2007, **104**, 5, 3071.

Degradation and Stabilisation of Aromatic Polyesters

22. H.L. Traub, *Synthesis and Textile Chemical Properties of Polytrimethyleneterephthalate*, University of Stuttgart, Stuttgart, Germany, 1994. [PhD Thesis]
23. X. Wang, X. Li and D. Yan, *Polymer Degradation and Stability*, 2000, **69**, 3, 361.
24. J. Ramiro, J.I. Eguiazábal and J. Nazábal, *Journal of Applied Polymer Science*, 2002, **86**, 11, 2775.
25. G. Botelho, A. Quieros and P. Gijsman, *Polymer Degradation and Stability*, 2000, **70**, 2, 299.
26. M.S. Chen, S.J. Chang, R.S. Chang, S.M. Chen and H.B. Hsai, *Polymer Degradation and Stability*, 1989, **23**, 3, 239.
27. S. Chang, M. Chen, R.S. Chang, S. Chen and H. Tsai, *Journal of Applied Polymer Science*, 1990, **39**, 2, 225.
28. F. Li, X. Xu, Q. Li, Y. Li, H. Zhang, J. Yu and A. Cao, *Polymer Degradation and Stability*, 2006, **91**, 8, 1685.
29. J. Economy, R.S. Storm, V.I. Matkovic, S.G. Cittis and B.E. Nowak, *Journal of Polymer Science: Polymer Chemistry Edition*, 1976, **14**, 1, 2207.
30. M.C. Gupta and A.K.S. Vishnu, *Journal of Materials Science*, 1984, **19**, 2, 347.
31. X. Li and M. Huang, *Polymer Degradation and Stability*, 1999, **64**, 1, 81.
32. S. Saikrasun and O. Wongkalasin, *Polymer Degradation and Stability*, 2005, **88**, 2, 300.