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Effect of dual functional ionic liquids on the thermal degradation of poly(vinyl chloride)

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Abstract

The short-term thermal stability of PVC on addition of functional ionic liquids (ILs) based on phosphonium and pyridinium cations, and a docusate anion, was studied using FTIR, TGA-MS and TGA-FTIR. The thermal stability of PVC plasticized with these ILs is reduced and the activation energy for thermal degradation for the first step of PVC degradation lowered, relative to neat PVC. This feature is not dependent on the thermal stability of the IL itself, as their addition to neat PVC did not result in increased thermal stability of the resin. Analysis of the gases evolved during thermal degradation showed that there is no variation in the mechanism of PVC degradation in the presence of ILs, the only difference observed is that HCl is evolved at lower temperatures for PVC-ILs samples. The ILs had no effect on the second step of the thermal degradation of PVC. The decrease in the thermal stability of PVC-ILs is associated with two different effects: firstly, the anion weakens the C-H bond while the cation forms complexes and weakens the C-Cl bond; second, the IL interaction with the polymer chains partly substitutes the interaction between the polymer chain and heat stabilizers (e.g. stearates) added to the PVC compound. In this way, the latter tends to be expelled from the bulk polymer, thus not being available for PVC stabilization at high temperature. Heat stabilizer migration is related to the solvating power of the ILs: the higher the solvating power, the higher the migration of heat stabilizer, the lower the thermal stability of the polymer.

1. Introduction

Polyvinyl chloride (PVC) is commonly used in medical devices and packaging due to its biocompatibility, transparency, durability, gloss, good chemical resistance, and suitability for various sterilization methods and relatively low cost. It comprises 25%

of all plastics used in medical applications, such as in blood, plasma and intravenous fluid bags and tubing, catheters, gloves and aprons.[1] PVC without any additives is a rigid polymer with limited function, where plasticization is crucial to soften the polymer for processing and application. In order to plasticise PVC, plasticizers are added to the formulation. However, a family of plasticisers commonly used in PVC medical devices, phthalate esters, has been considered a health risk for vulnerable patients and neonates due to their potential endocrine-disrupting effects and development of toxicity.[2,3] Ionic liquids (ILs) have been proposed as one of the new alternative plasticizers for PVC owing to their low volatility, high versatility and good thermal stability.[4,5] Studies have shown that ILs can act as a plasticizer for PVC by reducing the glass transition temperature and elastic modulus[6-8], increase elongation at break[5], reduce ultimate tensile strength[9-11], and decrease viscosity.[12] As the cationic and anionic components of ILs can be tailored for different functions, this can result in dual or multiple functional ILs.[6] Thus when added into a polymer matrix, ILs can act as additives having dual/multiple functional properties. Previously we have shown that 1-ethypyridinium docusate (IL1) and tributyl(2-hydroxyethyl) phosphonium docusate (IL2) exhibited both a plasticizing and antibacterial effect for different medical grade PVCs.[7, 8]. Indeed, we have shown[7, 8] that a decrease of Tg (glass transition temperature), a general reduction of ultimate tensile strength (U.T.S.) and Young's modulus were observed for all PVC systems with increasing addition of ILs as well as DOP (dioctyl phthalate).

It is necessary for the IL added to PVC to be thermally stable at high temperature (~ 200 ℃), during the shaping (moulding or extrusion) and/or the sterilization of medical devices. Thus, the thermal degradation of not only the ILs, but also the IL-filled PVC must be investigated.

Limited studies on the thermal properties of ILs and blends of ILs and PVC have been published.[6, 8, 10, 11, 13] For ILs, two major factors are found to affect their thermal properties: 1) IL structure; for instance the length of the alkyl group and, cation and anion type; and 2) influence of the environment and impurities, such as heating rate, sample weight, apparatus and pan type, gas flow rate and the presence of oxygen.[13] While the thermal properties of PVC-IL samples have also been studied[7, 8, 10, 11, 14], determination of their thermal degradation products has not. The endless possible combinations of IL cation and anion make it impossible to predict the thermal properties of particular ILs without detailed experiments, further complicated by the degradation mechanism and products of the polymer. Generally, it is reported that addition of any plasticizer regardless of whether it is phthalate or IL, can reduce the thermal stability of polymers.[5, 7] However, phthalates and ILs have very different thermal stability, the latter more stable than the former. Therefore, while it could be expected that the thermal stability of PVC-phthalate systems are slightly lower than that of neat PVC, due to the lower thermal stability of phthalate plasticizer, a similar effect observed for PVC-IL systems, which has been reported in literature[5-8], needs to be investigated further.

In this paper, we report the short-term thermal stability of PVC when blended with two different dual functional ILs studied using TGA. The activation energy for degradation were calculated and compared with and without IL addition. Degradation products of both ILs and the PVC-IL samples were also measured using TGA-GC-MS and TGA-FTIR. Potential interactions between the ILs and PVC have been further studied in order to understand the effect of ILs on the thermal stability of plasticized PVCs.

2.   Experimental

2.1 Synthesis, Processing and Characterization of Materials

A rigid PVC formulation containing 0 to 30wt% of IL, were prepared by extrusion, using a co-rotating twin screw micro-extruder (MiniLab Thermo Haake). The formulation consists of PVC resin (K value =60), PVC additive package containing stearate-based heat stabiliser and either IL. The synthesis of both ILs, processing conditions of PVC-IL samples and thermogravimetric analysis (TGA) run conditions for both ILs and the PVC-IL samples were described in our previous work.[8] Hereafter, we refer to 1-ethypyridinium docusate and tri-*n*-butyl(2-hydroxyethyl) phosphonium docusate as IL1 and IL2, respectively.

FTIR spectra of PVC-IL samples prior to pyrolysis were acquired in single-bounce attenuated total reflectance mode (Spectrum 100 FTIR-UATR, Perkin-Elmer), which utilizes a diamond-coated zinc selenide crystal as the internal reflection element. 128 accumulated scans were acquired, within the wavelength range of 4000-650 cm^{-1} at a resolution of 4 cm^{-1}.

The gases evolved during thermal degradation of PVC-IL samples up to 800 °C under an inert atmosphere (nitrogen or helium) were analysed by coupling TGA with either FTIR (Nicolet Nexus 670) or quadrupole mass spectrometer (Thermo Electron MD 800), using transfer lines heated at 250 °C. The time delays between release and detection of gaseous compounds has previously been shown to be about 2 minutes for TGA/MS analyses and about 1 minute for TGA/FTIR analyses[15]. The MS spectra were acquired in the range from 35 to 150 a.m.u to avoid the influence of nitrogen and oxygen while FTIR spectra were acquired every 60 sec in the range from 4000 to 400 cm^{-1}.

2.2 Calculation of Activation Energy

The activation energy for each thermal degradation step of the ILs, PVC and PVC-IL samples were calculated based on the Friedman method[16]. The thermal decomposition kinetics related to TGA weight loss data can be represented by the kinetic equation:

$$\frac{d\alpha}{dt} = Z{\cdot}(1-\alpha)n \cdot e^{-E_a/(RT)} \tag{1}$$

where α is the weight loss of degraded polymer at time t, $d\alpha/dt$ indicates the decomposition rate or weight loss rate, Z denotes the frequency factor, n is the decomposition reaction order, E_a is activation energy, R represents the universal gas constant (8.3134 J/mol·K), and T is absolute temperature (K).

Applying the Friedman model, equation 1 in the natural logarithmic differential form becomes:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln Z + n{\cdot}\ln(1-\alpha) - E_a/(RT) \tag{2}$$

From a plot of Ln($d\alpha/dt$) or Ln(1-α) against 1/T, the value of $-E_a/R$ or $E_a/(nR)$ can be determined from the slope, and Z can be calculated from equation 1. R^2 in fitting Ln(1-α) and Ln ($d\alpha/dt$) used was 0.96 or higher. The results are listed in Table 1.

PeakFit software (v4, AISN Software Inc.) was used to separate overlapped peaks in the DTA data. Peak deconvolution was carried out using Gaussian and Lorentzian functions with area as amplitude. The co-efficient of determination (R^2) for the separated peaks was 0.99 or higher.

Results and Discussion

The TGA curves of neat PVC, IL1, IL2 and the PVC-IL samples have already been reported elsewhere[8]. It is clearly evident that the onset of thermal degradation, as well

as the thermal stability up to 350°C of PVC-IL2 samples are lower than that of neat PVC, even though the thermal stability of IL2 itself is higher than that of PVC. Moreover, no significant differences can be observed for different IL2 content. A different trend was observed for the PVC-IL1 samples, as the difference in thermal stability is significant only for sample containing 30wt% IL1. These trends can be better understood by comparing the experimental TGA curves and those calculated (i.e. the TGA curves obtained as a weighted sum of the neat components), as shown in Figure 1. The thermal stability of the PVC-IL2 samples is always much lower than expected for temperatures up to 350°C. To further study this behaviour, the kinetic parameters for thermal degradation of PVC, both ILs and PVC-IL samples were calculated using the Friedman method. The Friedman plot is one of the most widely used methods to estimate the degradation kinetics of polymers, and it has been used to calculate the kinetic parameters of PVC upon pyrolysis previously[17, 18]. It is a differential method usefully applied to obtain apparent kinetic parameters, in which the calculated activation energy for thermal degradation varies with the degree of conversion, while mathematical approximations are not necessary[18]. Figures 2 show the Friedman plots of the first and second degradation steps for PVC and PVC-IL samples in an nitrogen atmosphere. Both ILs display only one degradation step, and are included in both figures for comparison. Furthermore, Table 1 lists the kinetic parameters calculated for each degradation step, the onset degradation (at 95% weight loss) for each sample and the maximum weight loss for each degradation rate. PVC control samples were found to have activation energies with values similar to those reported in the literature[18], within the range 135-209 kJ/mol and 218-267 kJ/mol for the first and second degradation steps, respectively. A significant decrease in the activation energy with respect to the PVC control sample was observed for all PVC-

IL samples for the first degradation step, concomitant with the lower onset of degradation temperature for all PVC-IL samples. The addition of IL1 and IL2 to PVC resulted in an approximate 60-80 kJ/mol and 90-130 kJ/mol lower activation energy, respectively. In contrast, the change in activation energy for the second degradation step were considerably lower, approximately 15-60 kJ/mol and 20-40 kJ/mol difference in the activation energy calculated for PVC-IL1 and PVC-IL2, respectively. Compared to literature values (218-267 kJ/mol)[18], the values obtained for the activation energy for the second degradation step were lower in this study. The Friedman method is known to give more accurate results for single degradation processes but not multiple processes or overlapped thermal decomposition therefore, an error was expected[16, 17]. The reaction order (n) values calculated in this study were higher (2.59-8.42) than the values reported in the literature (0.46-1.54)[18], for two reasons: firstly, neat PVC resins were used in the studies reported in the literature[17, 18] instead of PVC formulation(s) as used in this study; and second, multiple reactions may have occurred simultaneously, leading to one or more complicated reactions. The latter is supported by multiple overlapped peaks observed in the DTA curves, the list of peaks isolated/de-convoluted using PeakFit are shown in Table S1 (see Electronic Supplementary information, ESI).

In an attempt to understand the effect of ILs on thermal degradation of PVC, the gases evolved during degradation were analysed by means of FTIR and MS. The degradation of PVC takes place in two steps. It is well known that the first step of PVC thermal decomposition is de-hydrochlorination (-HCl). Loss of HCl leaves a residue of a conjugated polyene structure that can undergo further pyrolysis to yield a vast array of hydrocarbons. The most abundant volatile pyrolysate from PVC (other than HCl) is benzene as well as some anthracenes and naphtalenes[19]. Benzene

formation, which occurs nearly concurrently with the evolution of HCl is due to the cleavage of a cyclo-hexadiene intermediate which yields benzene plus radical chain ends[19]. Considering the FTIR spectra of the gases released during the first step of thermal degradation (under inert atmosphere) of neat PVC sample, the typical absorbance peaks of HCl ($3050-2650cm^{-1}$), benzene (above $3000cm^{-1}$) and some hydrocarbon compounds (below $3000cm^{-1}$) can be observed, see Figure 3(a). Moreover, CO_2 ($2300-2400cm^{-1}$ and $677cm^{-1}$), formed by reaction of released HCl and $CaCO_3$, the latter a filler contained in the PVC additives package, can be observed. Mass spectra of neat PVC show the same results: during the first step of degradation, HCl is the main product released (m/z= 36, 38) with benzene (m/z = 78, 50, 51, 52), CO_2 (m/z = 44) and a hydrocarbon (m/z = 56, 41) are also detected (ESI, Figure S1). During the second PVC degradation step (Figure 3(b)) aromatic and aliphatic hydrocarbons are released (peaks above and below $3000cm^{-1}$, respectively), and peaks at $1300cm^{-1}$ and $3020cm^{-1}$ are associated with methane. Similar results were obtained when the mass spectra are considered. Linear and branched saturated aliphatic chains (m/z= 43, 57, 41) as well as cyclic (m/z = 41, 56, 69), allylic (m/z = 55, 69) and aromatic compounds (m/z 91, 92, 78) are released. Also, some chlorinated hydrocarbons (m/z= 43, 41, 63) were detected (ESI, Figure S1). The gases evolved during IL1 degradation (Figure 3(b), ESI Figure S2) are hydrocarbon chains, both saturated and un-saturated (IR absorbance around $3000cm^{-1}$, m/z = 41, 53, 55, 56, 70); sulphur dioxide (SO_2) (IR absorbance in the range $1300-1400cm^{-1}$, m/z = 48, 64), pyridine (IR absorbance above $3000cm^{-1}$ and around $700cm^{-1}$, m/z = 79, 52) and ester compounds (IR absorbance at $1750cm^{-1}$). The degradation of IL2 takes place through the evolution of aliphatic chains (IR absorbance around $3000cm^-$

[1], m/z = 43, 55, 57, 69, 70) as well as SO_2 and ester compounds coming from the same anion, i.e. docusate (Figure 3(b), ESI Figure S3).

The analysis of the gas evolved during the first degradation step of the PVC-IL samples show that they are merely the sum of the gases evolved during degradation of PVC and ILs alone (Figure 4). The first compound that is released for these samples is HCl, as in the case of neat PVC, the only difference is the HCl is evolved at lower temperatures from the PVC-ILs samples (especially those containing IL2) than that of neat PVC. During the second degradation step of PVC-ILs samples no contribution of the ILs was observed, at temperatures higher than 450 °C, i.e. the ILs were already fully degraded. Therefore, we can assess that the ILs, mainly IL2, have a catalytic effect on the thermal degradation of PVC, although they do not change the mechanism of degradation. In order to further investigate this hypothesis, we compare the experimental and expected (i.e. the calculated TGA curves) thermal stability of several mixtures comprising PVC resin, additives and ILs as well as their precursors (the PVC compounds are obtained by pre-mixing a PVC resin with an additives package, comprising a filler, $CaCO_3$, and processing aids, e.g. stearate based heat stabiliser). The results (Figure 5) show that there is a negative interaction between ILs (mainly IL2) and the PVC resin, i.e. the experimental thermal stability of this mixture is much lower than that expected, while no significant deviations were observed for the additives-IL systems.

Similar comparisons were made using the IL precursors, i.e. ethylpyridinium bromide, sodium docusate and tri-*n*-butyl(2-hydroxyethyl) phosphonium chloride (Figure 6). Negative interactions were found mainly for phosphonium chloride and, to a lesser extent, ethylpyridinium bromide. No effect was observed for sodium docusate.

In a recent paper[20], Glas et al. used several ILs (different to those used in this study) to study the de-hydrochlorination of PVC for recycling purposes. Although the IL concentration these authors used was much higher than that used in our work (PVC was generally 5wt% of the PVC-IL mixture), they found that the onset temperature for de-hydrochorination of un-stabilized PVC was lower for a phosphonium rather than a nitrogen containing IL because of the higher swelling ability of the former. This is probably because phosphonium ILs are excellent media for dissolving polymers, thus giving very good solvation of the polymer chains and making the Cl atoms more accessible for removal. Considering data from other published literature[5, 6, 10], it seems that, generally in PVC-IL systems there is a correlation between the solvating power of the IL towards PVC (inferred from the decrease in glass transition temperature) and the catalytic effect on de-hydrochlorination, i.e. the higher the solvating power the lower the thermal stability. Glas et. al also found that for a stearate stabilized PVC (like the one used in this study) the stabilizer has only a minor effect under these harsh conditions, since the rate of de-hydrochlorination is now only slightly affected by the presence of heat stabilizer[20]. In a previous paper, we have shown that the thermal stability of PVC plasticized with dioctyl phthalate (DOP), whose effectiveness is well known owing to the good solvent ability toward PVC, is very similar to that of neat PVC[21]. Therefore, we can infer that the decrease in thermal stability due to the use of ILs as plasticizers is related not only to their solvent ability but also to other aspects, for example, their potential for interference with the efficacy of carboxylates used as heat stabilizers. Indeed, these stabilizers would act differently. Strong basic carboxylates derived from metals such as K, Ca, or Ba, have little or no Lewis acidity and act mostly as HCl scavengers (secondary stabilizers). Whilst carboxylates derived from metals such as Zn and Cd, are stronger Lewis acids and

could form covalent carboxylates. These carboxylates not only scavenge HCl, but also substitute carboxylate for allylic chlorine atoms (primary stabilizers)[21]. Therefore, in PVC-IL systems, the IL anion will weaken the C-H bond while the cation can form complexes and weaken the C-Cl bond. Moreover, the IL interaction with PVC chains most likely will partially substitute the interaction between the polymer chain and heat stabilizer. In this way, carboxylates tend to be expelled from the bulk of the polymer, and are thus no longer available for polymer protection at relatively high temperatures. Indeed, it is well known that in plasticized PVC there can be a loss of additives due to their faster migration to the surface depending on the mutual solubility and diffusion properties of the components of the PVC formulation[22].

In this framework, considering the FTIR spectra of the surface of the PVC-IL2 samples (Figure 7), a very high concentration of carboxylates was detected (peaks at $1539 cm^{-1}$ and $1576 cm^{-1}$ are derived from zinc and calcium carboxylates, respectively)[23], with respect to neat PVC, although the concentration of carboxylates in both formulations as well as the processing conditions used were the same. In particular, more Zn- than Ca-carboxylate was expelled to the surface of the polymer and the concentration expelled was higher when the IL2 content was increased. This we propose is due to the substitution of the interaction between Zn-carboxylate-PVC with the interaction between IL2 and PVC. Consequently, the Zn stabilizer is no longer effective in substituting carboxylate for allylic chlorine atoms, resulting in PVC degradation initiated at lower temperatures. For the PVC-IL1 samples, carboxylate peaks can be identified (Figure 7). However, there is no difference between migration of Ca- or Zn-carboxylate with increasing IL1 content. It is probable that the destabilizing effect in this case is less important because of the lower solvating power of IL1 towards PVC with respect to IL2, as we have already shown[7, 8]. Therefore,

more Zn-carboxylate is still active in coordinating with the polymer, reducing the number of allylic chlorine atoms, thus delaying degradation. It should also be noted that this migration effect is due to the ionic nature of the ILs themselves, since no migration of carboxylates was determined in the same PVC system plasticized with dioctyl phthalate (DOP) (ESI, Figure S3).

CONCLUSIONS

The thermal stability of PVC plasticized with IL1 and IL2 is lower than neat PVC, with a marked effect on the first degradation step, de-hydrochlorination. This phenomenon is not dependent on the thermal stability of the IL itself, since the use of very thermally stable ILs does not increase the thermal stability of PVC-IL blends. This was confirmed from the significant reduction in the activation energy calculated for thermal degradation combined with initiation of weight loss at lower temperature.

Even though the high reaction order values (n) determined using the Friedman method, employed to calculate the activation energy for thermal degradation, indicated multiple simultaneous reactions, the analysis of the gases evolved during degradation showed that there was no variation in the mechanism of degradation in the presence of ILs. The only difference is that HCl is evolved at lower temperatures for PVC-ILs samples and the ILs had no effect on the second PVC degradation step. The decrease in the thermal stability of PVC-ILs relative to neat PVC is a contribution from two different effects: firstly, the IL anion weakens the C-H bond while the cation can form complexes and weaken the C-Cl bond. Second, the interaction between the ILs and polymer chains partially substitutes the interaction between polymer chains and heat stabilizer. This results in carboxylates being expelled from the bulk polymer, and not readily available to stabilise the PVC resin at high temperature. Heat stabilizer migration is

related to the solvating power of the ILs: the greater the solvating power, the more effective the migration of heat stabilizer, the lower the thermal stability of the polymer.
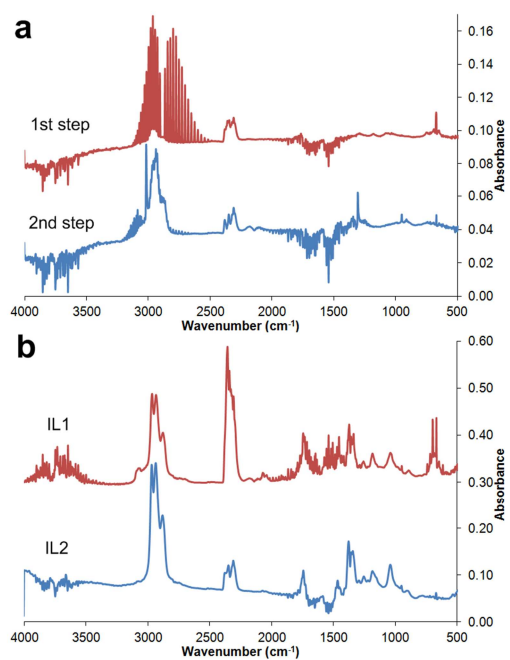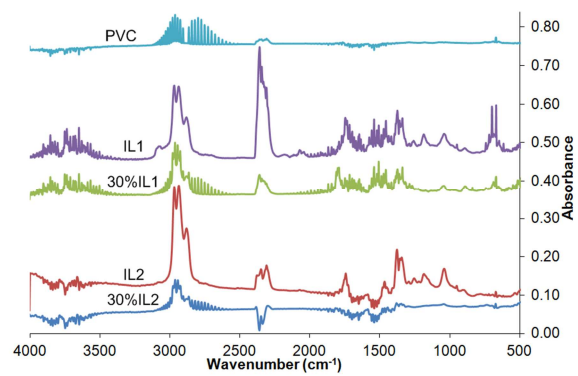
References

1. K. Z. Hong, *J. Vinyl Addit. Technol.*, 1996, **2**, 193-197.
2. J. A. Tickner, T. Schettler, T. Guidotti, M. McCally and M. Rossi, *Am. J. Ind. Med.*, 2001, **39**, 100-111.
3. U. Heudorf, V. Mersch-Sundermann and J. Angerer, *Int. J. Hyg. Envir. Heal.*, 2007, **210**, 623-634.
4. M. Rahman and C. S. Brazel, *Prog. Polym. Sci.*, 2004, **29**, 1223-1248.
5. M. Rahman and C. S. Brazel, *Polym. Degrad. Stabil.*, 2006, **91**, 3371-3382.
6. A. M. A. Dias, S. Marceneiro, M. E. M. Braga, J. F. J. Coelho, A. G. M. Ferreira, P. N. Simoes, H. I. M. Veiga, L. C. Tome, I. M. Marrucho, J. M. S. S. Esperanca, A. A. Matias, C. M. M. Duarte, L. P. N. Rebelo and H. C. de Sousa, *Acta Biomater.*, 2012, **8**, 1366-1379.
7. S. Y. Choi, H. Rodriguez, H. Q. N. Gunaratne, A. V. Puga, D. Gilpin, S. McGrath, J. S. Vyle, M. M. Tunney, R. D. Rogers and T. McNally, *RSC Adv.*, 2014, **4**, 8567-8581.
8. S. Y. Choi, H. Rodriguez, A. Mirjafari, D. F. Gilpin, S. McGrath, K. R. Malcolm, M. M. Tunney, R. D. Rogers and T. McNally, *Green Chem.*, 2011, **13**, 1527-1535.
9. D. J. Kinnear, C. P. McCoy, D. S. Jones, G. P. Andrews, S. P. Gorman and K. Bica, *J. Pharm. Pharmacol.*, 2010, **62**, 1322-1323.
10. L. X. Hou and S. Wang, *Polym. Bull.*, 2011, **67**, 1273-1283.
11. S. Wang and L. Hou, *Iran. Polym. J.*, 2011, **20**, 989-997.
12. S. Marceneiro, Q. Hu, A. M. A. Dias, I. Lobo, I. Dias, E. de Pinho, M. Graca Rasteiro and H. C. de Sousa, *Ind. Eng. Chem. Res.*, 2014, **53**, 16061-16071.
13. C. Maton, N. De Vos and C. V. Stevens, *Chem. Soc. Rev.*, 2013, **42**, 5963-5977.
14. H. Katano and T. Tsukatani, *B. Chem. Soc. of Jpn.*, 2010, **83**, 190-194.
15. A. Lorenzetti, M. Modesti, S. Besco, D. Hrelja and S. Donadi, *Polym. Degrad. Stabil.*, 2011, **96**, 1455-1461.
16. X. S. Wang, X. G. Li and D. Y. Yan, *Polym. Degrad. Stabil.*, 2000, **69**, 361-372.
17. A. Marcilla and M. Beltran, *Polym. Degrad. Stabil.*, 1995, **48**, 219-229.
18. R. Miranda, J. Yang, C. Roy and C. Vasile, *Polym. Degrad. Stabil.*, 1999, **64**, 127-144.
19. R. P. Lattimer and W. J. Kroenke, *J. Appl. Polym. Sci.*, 1980, **25**, 101-110.
20. D. Glas, J. Hulsbosch, P. Dubois, K. Binnemans and D. E. De Vos, *ChemSusChem*, 2014, **7**, 610-617.
21. R. Bacalogulu, M. H. Fisch, J. Kaufhold and H. J. Sander, in *Plastics Additives Handbook*, eds. H. Zweifel, R. D. Maier and M. Schiller, Hanser Gardner Publishing, 6th edn., 2009, pp. 439-440.
22. G. Wypych, in *Handbook of Plasticizers*, ed. G. Wypych, ChemTec Publishing, Toronto, Canada, 2004, pp. 171-177.

23.   R. Benavides, M. Edge, N. S. Allen, M. Mellor, H. Harvey and G. Schmets, *Polym. Degrad. Stabil.*, 1996, **53**, 319-327.