PAPER

Revising the mechanism of polymer autooxidation†‡

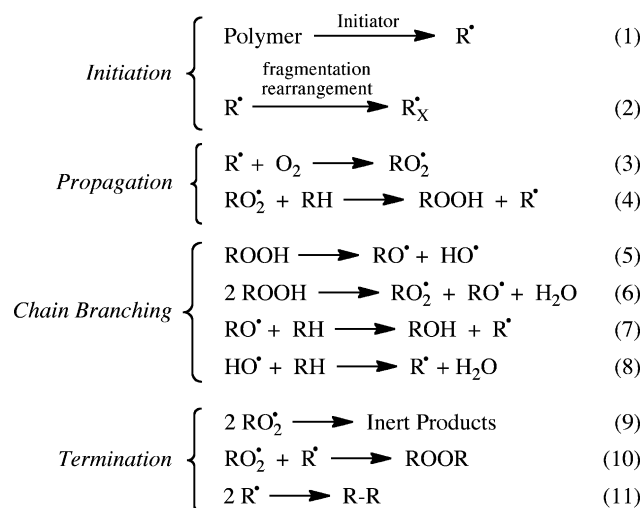**Ganna Gryn'ova, Jennifer L. Hodgson and Michelle L. Coote***

The basic scheme for autooxidation of polymers, originally developed by Bolland, Gee and co-workers for rubbers and lipids, is now widely applied to all types of polymeric materials. According to their scheme, the reaction that makes this process autocatalytic, referred to as the propagation step, is a hydrogen abstraction from the next substrate by the peroxyl radical (ROO$^{\bullet}$ + RH → ROOH + R$^{\bullet}$). In this study, using advanced quantum-chemical methods, we have shown that this step is actually characterised by largely positive Gibbs free energy (10–65 kJ mol^{-1}) for most regular polymers with saturated chains (polypropylene, polyethylene, polyvinyl chloride, polyvinyl acetate, polyurethane, poly(methyl methacrylate) *etc.*) and even some polymers with unsaturated fragments (polystyrene, polyethylene terephthalate). Neither elevated temperature, nor solvation makes this process thermodynamically favourable. Only when the formed radical centre is conjugated with adjacent double bonds (as in polybutadiene) or captodatively stabilised by two suitable functional groups (such as a carbonyl and a lone pair donor such as oxygen or nitrogen), is the propagation step exoergic. Instead, we show that it is the presence of structural defects, such as terminal or internal double bonds, formed either during polymerisation or in the degradation process itself, that is responsible for the autooxidation of most polyesters and most polyalkenes. Recognition of the real mechanism of autooxidation in polymers is a key to developing strategies for the prevention of their degradation.

1. Introduction

The widespread usage of polymer materials in increasingly demanding applications raises the importance of their stabilisation against degradation. Ageing and weathering of polymers results in crucial changes to their properties, and thus dramatically decreases their service life and limits their use. Understanding the mechanisms of polymer degradation is essential for the development of effective stabilisation techniques.[1]

Most polymers and biopolymers are thought to undergo photo- and/or thermo-oxidative degradation under normal conditions (*i.e.*, in the presence of air, water, sunlight, elevated temperatures) *via* an autocatalytic process known as autooxidation. Bolland, Gee and co-workers from British Rubber Producers Research Association (BRPBA) were the first to establish the classic mechanism of polymer autooxidation, which now forms the basis of the modern theory of autooxidation.[2,3] The process includes

initiation, chain propagation, chain branching and termination stages, generally represented by the equations in Scheme 1.

$$\text{Initiation} \begin{cases} \text{Polymer} \xrightarrow{\text{Initiator}} \text{R}^{\bullet} & (1) \\ \text{R}^{\bullet} \xrightarrow[\text{rearrangement}]{\text{fragmentation}} \text{R}^{\bullet}_{X} & (2) \end{cases}$$

$$\text{Propagation} \begin{cases} \text{R}^{\bullet} + \text{O}_2 \longrightarrow \text{RO}_2^{\bullet} & (3) \\ \text{RO}_2^{\bullet} + \text{RH} \longrightarrow \text{ROOH} + \text{R}^{\bullet} & (4) \end{cases}$$

$$\text{Chain Branching} \begin{cases} \text{ROOH} \longrightarrow \text{RO}^{\bullet} + \text{HO}^{\bullet} & (5) \\ 2\,\text{ROOH} \longrightarrow \text{RO}_2^{\bullet} + \text{RO}^{\bullet} + \text{H}_2\text{O} & (6) \\ \text{RO}^{\bullet} + \text{RH} \longrightarrow \text{ROH} + \text{R}^{\bullet} & (7) \\ \text{HO}^{\bullet} + \text{RH} \longrightarrow \text{R}^{\bullet} + \text{H}_2\text{O} & (8) \end{cases}$$

$$\text{Termination} \begin{cases} 2\,\text{RO}_2^{\bullet} \longrightarrow \text{Inert Products} & (9) \\ \text{RO}_2^{\bullet} + \text{R}^{\bullet} \longrightarrow \text{ROOR} & (10) \\ 2\,\text{R}^{\bullet} \longrightarrow \text{R-R} & (11) \end{cases}$$

Scheme 1 Basic Autooxidation Scheme (BAS).

Much attention has been given to developing an understanding of the rich and diverse chemistry of the initiation reactions, and the subsequent rearrangement and fragmentation of the formed radicals in the various types of polymers and biopolymers.[4] However, for most polymers, less is known about the propagation

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† In fond memory of our friend and mentor, Emeritus Professor Athel Beckwith FAA, FRACI, FRS and in recognition of his many distinguished contributions to chemistry.

‡ Electronic supplementary information (ESI) available: Optimised geometries in the form of GAUSSIAN archive entries, corresponding total energies, thermal corrections, zero-point vibrational energies, entropies, free energies and free energies of solvation. See DOI: 10.1039/c0ob00596g

stage. Yet it is this step that is responsible for the autocatalytic nature of the oxidative degradation – transforming what would otherwise be a slow and steady accumulation of damage to a rapidly accelerating failure. The propagation stage in Scheme 1 is almost universally considered to be a part of the basic autooxidation scheme (BAS) for a wide range of polymers, and can be found in many books[5] and journal articles,[6] published over the past 65 years since Bolland's first paper.[2]

However, in the original papers of Bolland, Gee and co-workers[2] the mechanism above was suggested only for a certain class of polymers – namely, rubber and lipids such as ethyl linoleate, ethyl linolenate, methyl oleate, squalene and so forth. Such species contain an activated α-methylenic group that readily reacts with the oxygen (Reaction (3), which has been shown to be thermodynamically favourable even for very stable radicals[3,7,8]) to form the corresponding peroxyl radical, which then readily abstracts hydrogen from the next substrate (Reaction (4)), because the formed radical centre is stabilised by the conjugation with the adjacent double bonds (see Scheme 2). The heat of this reaction, according to Hess' law, is equal to the difference between the R–H and ROO–H bond dissociation energies (BDEs). For example, the heat of hydrogen abstraction from 1-butylene by 1-butylene peroxyl radical (R^1=H and R^2=CH$_3$ in Scheme 1) is 351–360 = –9 kJ mol^{-1} (values of the BDEs are taken from ref. 9); taking into account entropy changes, the overall Gibbs free energy of the reaction is –10.7 kJ mol^{-1}. Therefore the propagation step in this case is thermodynamically favoured according to the second law of thermodynamics. Naturally, the heat of reaction would be expected to be negative in all similar cases, including the lipids mentioned above.
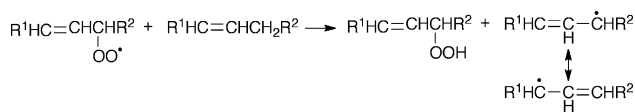
Scheme 2 The hydrogen abstraction from the unsaturated polymer chain by a peroxyl radical with consequent formation of hydroperoxide and stable polymeric radical.

Nevertheless, it is often overlooked that, based on the experimental gas phase BDEs, Reaction (4) is either disfavoured for a broad range of functional groups, or its thermodynamic

Table 1 Values of ROO–H BDEs (kJ mol^{-1}) for a set of hydrocarbon hydroperoxides, available in the literature

Hydroperoxide	Ref. 9[a]	Ref. 13[b]	Ref. 14[a]
CH$_3$OO–H	370.3 ± 2.1	360 ± 1	368.2 ± 4.2
CH$_3$CH$_2$OO–H	354	358 ± 1	355.6 ± 8.4
(CH$_3$)$_2$CHOO–H	356	356 ± 1	N/A
(CH$_3$)$_3$COO–H	344	354 ± 1	351.5 ± 8.4

[a] Experimental measurements; [b] Isodesmic calculations using CBS-methods.

probability is at least questionable (Fig. 1). In many cases, the BDEs for R–H are larger than for the corresponding ROO–H bond, and thus the heat of Reaction (4) is positive. In fact, besides the lipids and rubbers themselves, the only other clear case in Fig. 1 where the classic propagation step is likely to be favourable is for the autooxidation of peptides. Even here, the propagation step appears to be favourable only at the backbone αC–H bonds and not the side chains, presumably due to the possibility of captodative stabilisation in the former case. Whilst the favourability of this reaction at the backbone is consistent with extensive theoretical[10] and experimental[11] studies of peptide degradation, the experimental work also implicates peroxide formation at the side chains, which is more surprising given these available gas-phase BDEs.

It should be noted that, in some cases available experimental and theoretical data for BDEs is controversial. For example, according to the BDEs from Ref. 9, Reaction (4) is favoured for polystyrene. However, if one considers the BDE of PhC(CH$_3$)$_2$–H from Ref. 12 (which is equal to 365.6 kJ mol^{-1}), the propagation step would become thermodynamically unfavourable. Another example is the influence of carbon centre hybridisation on the BDE of ROO–H bond (Table 1). Not only is there a noticeable variation (up to 10 kJ mol^{-1}) between the values for the same species, but also the general trend of the decrease in BDE value with the increase of the number of substituents at the carbon centre is not reflected by the data from Ref. 9. Therefore, it is crucial to obtain unified data in order to define the thermodynamic probability of the Reaction (4) for various polymers and biopolymers.

Notwithstanding this uncertainty, the presented experimental data reveals that the autocatalytic degradation of many common
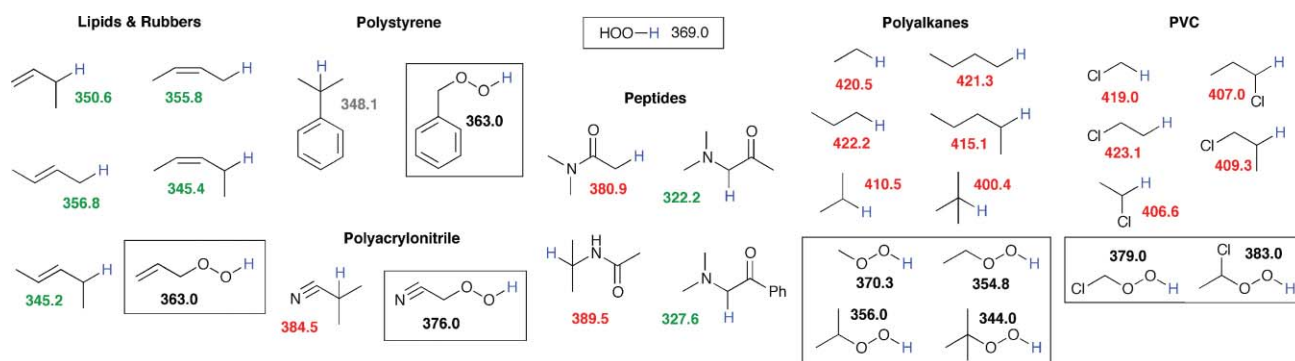

Fig. 1 Experimental gas-phase bond dissociation energies[9] (kJ mol^{-1}) for various R–H and ROO–H bonds, found in the degradation of some common polymers and biopolymers. The abstracted hydrogen is marked in blue. Thermodynamic favourability of Reaction (4), based on the difference between R–H BDEs and corresponding ROO–H BDEs (in black, framed), is reflected by the following colour code: green – strongly favoured; red – strongly disfavoured; grey – questionable.

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polymers is unlikely to proceed *via* the propagation step of the BAS. Indeed, Bolland himself emphasised limited application of his mechanism in his later *Nature* paper[15] on photosensitised oxidation of alcohols: *"In many respects the above mechanism resembles those established for the autooxidation of unsaturated hydrocarbons and aldehydes. The completely different kinetic behaviour results from the fact that the peroxy-radicals are incapable of abstracting hydrogen from further alcohol molecules"*. Ingold and coworkers[16] in their studies of hydrogen abstraction by peroxyl radicals have also indicated the selectivity of this reaction depending on the structure of substrate. Benson[7] has shown that Reaction (4) of the propagation step is characterised by positive change of the enthalpy for saturated hydrocarbons. Bertin and coworkers in their recent paper[17] have established using both experimental and theoretical techniques, that Gibbs free energy of hydrogen abstraction from polypropylene by methyl peroxide is strongly positive (57.2 and 29.4 kJ mol^{-1} depending on the position of the formed radical centre). Some experimental studies have even observed that the thermo-oxidative degradation of polyacrylates is inhibited (when compared with the same process under a nitrogen atmosphere) by the presence of oxygen due to the formation of stable peroxyl radicals.[18,19]

Despite these findings, BAS is almost universally applied not only to unsaturated hydrocarbons, but also to many other organic compounds[20] and polymers (polypropylene,[21] polyethylene,[22] their blends and copolymers,[23,24] polyvinyl acetate,[25] polyurethane,[26] polyvinyl chloride,[27] polyester,[28] poly(methyl methacrylate)[29]), without recognising the fact that hydrogen abstraction by the peroxyl radical should be thermodynamically unfavourable in those cases. The reason BAS is used is that it provides a convenient explanation for the kinetics and autocatalytic character of the degradation, as well as the undisputed presence of hydroperoxides among the degradation products.

This raises the questions of what is the true scope and applicability of autooxidation under relevant reaction conditions, and how do we explain experimental observations in the cases from above, where the propagation step of hydrogen abstraction, as written, can be excluded on thermodynamic grounds? Answers will enable us to establish the real mechanism of autooxidation of common polymeric materials and important biopolymers, and to identify effective solutions to the problem of their degradation. In this work we use high-level *ab initio* molecular orbital theory calculations to address these questions.

2. Theoretical methods

Standard *ab initio* molecular orbital theory and density functional theory (DFT) calculations were carried out using Gaussian 09[30] software. MOLPRO 2009.1[31] was applied for coupled cluster calculations. For all species, either full systematic conformational searches (at a resolution of 120^0) or, for more complex systems, energy-directed tree searches[32] were carried out to ensure global, and not merely local minima were located. For open-shell species, all DFT calculations were carried out using unrestricted wave functions, whereas the *ab initio* calculations used restricted open-shell wave functions to avoid the effect of spin contamination. Geometries of all species were fully optimised at the B3LYP[33,34]/6-31G(d) level of theory and frequencies were also calculated at this level and scaled by recommended scale factors.[35] Accurate

energies for all species at 298.15 K and 373.15 K were calculated using high-level composite *ab initio* G3(MP2)-RAD[35] method. It approximates CCSD(T) calculations with a large triple-ζ basis from calculations with a double-ζ basis set, *via* basis set corrections carried out at the ROMP2 level. We have recently shown that this method is capable of predicting the R–H, R–Cl, R–CH$_3$ and R–R BDEs for a broad range of carbon-centred R-groups to within chemical accuracy.[12] Entropies and thermal corrections were calculated using standard textbook[36] formulae for the statistical thermodynamics of an ideal gas under the harmonic oscillator approximation in conjunction with the optimised geometries and scaled frequencies. Reaction Gibbs free energies were computed using Gibbs fundamental equation.

Free energies of solvation were computed using the COSMO-RS (Conductor Like Screening Model for Realistic Solvents) method.[37] The COSMO-RS model uses a scaled conductor boundary condition for the calculation of the polarisation charges of a molecule in a continuum, and further performs a statistical thermodynamics post-processing of the results. The ADF[38] package was used to compute COSMO-RS solvation free energies on the gas-phase geometries at the BP/TZVP level of theory, and the rest of parameters (*e.g.*, atomic cavity radii, radius of the probing sphere, and cavity construction) were kept as default values for water. Free energies of each species in solution at 298.15 K were calculated as the sum of the corresponding gas-phase free energy and the obtained free energy of solvation. The phase change correction term $\Delta nRT(\ln V)$ for these reactions is zero as the change in the number of moles in reaction (Δn) is zero.

For a number of species, particularly for some of the hydroperoxides, the preferred gas-phase conformers contain hydrogen bonding, which is no longer present in lowest energy conformers in aqueous solution.[39] Therefore, we have performed additional full systematic conformational searches (at a resolution of 120^0) at the CPCM/B3LYP/6-31+G(d) level of theory for those species. When the geometry of solution-phase conformer was different to that in the gas-phase, we have computed new gas-phase G3(MP2)-RAD energies, COSMO-RS solvation free energies and resulting Gibbs free energies in solution for the lowest energy solution-phase conformers according to the procedure, described above.

3. Results and discussion

3.1 Kinetics *versus* thermodynamics?

In order to study the feasibility of the propagation step in standard BAS for different polymers and biopolymers, we will study the thermodynamic favourability of Reaction (4). Specifically, we will argue that, if ΔG for reaction (4) is considerably greater than 0, this reaction is not significantly contributing to the degradation process. However, first we must justify this criterion. Certainly if Reaction (4) was an isolated reaction, this approach would have been justified: irrespective of the kinetics and mechanism, if the Gibbs free energy of a chemical reaction is greater than 0, this implies that the reverse reaction dominates over the forward one. However, in reality Reaction (4) is just one step in a complicated mechanism (Scheme 1). As a result, if the formed hydroperoxide ROOH is rapidly consumed in subsequent decomposition steps (5) and (6), then according to Le Chatelier's principle this would create a driving force, perhaps strong enough to make Reaction

(4) favourable. To consider this possibility we have performed a brief evaluation of the energies of Reactions (4)–(6) for R = C_2H_5. According to the obtained results (see Fig. S3 of ESI‡ for details), not only is Reaction (4) endoergic (ΔG_{gas} = 55.4 kJ mol^{-1}), but the subsequent decomposition of the formed hydroperoxide (Reaction (5)) is also highly disfavoured (ΔG_{gas} = 134.9 kJ mol^{-1}). The alternative bimolecular decomposition pathway, Reaction (6), is very slightly exoergic (ΔG_{gas} = –4.1 kJ mol^{-1}), but this released energy falls well short of the energy requirements of Reaction (4). Moreover, even if subsequent peroxide decomposition can provide a driving force for the reaction, the kinetic significance of Reaction (4) would still depend on the exchange rate of its 'dynamic' equilibrium and, in the absence of thermodynamic driving force, the barriers for Reaction (4) are likely to be very large. For example, for the prototypical reaction $CH_4 + HOO^• \rightarrow CH_3^• + HOOH$, for which the enthalpy is approximately 70 kJ mol^{-1}, the barrier is over 100 kJ mol^{-1}.[40] For these reasons, we therefore argue that an examination of the thermodynamic feasibility of Reaction (4) should provide a good guide to its ability to propagate oxidative degradation *via* standard BAS.

3.2 Scope of standard BAS

In order to study the applicability of BAS to different polymers and biopolymers, we need to investigate the effect of the various functional groups in them on the thermodynamics of Reaction (4). To provide a general picture of the effect of substituents we have calculated reaction enthalpies of hydrogen abstraction for a number of radicals by hydroperoxyl radical (Fig. 2). Obviously, the trends in these data simply reflect the relative values of the R–H bond dissociation energy and the associated stability of the formed R$^•$. The stability of many carbon-centred radicals has been intensively studied before (see ref. 12 and 41 for recent examples) and the trends depicted in Fig. 2 are consistent with these previous works. What is worth noting from the present results is the large extent of radical stabilisation required to make the hydrogen transfer reaction thermodynamically favourable. In the first group of radicals – hydrocarbons – only an allylic double bond is capable of stabilising R$^•$ enough to make Reaction (4) exothermic. For the benzyl radical, which will stabilise the radical centre by conjugation with the aromatic ring, the resulting reaction enthalpy is approximately 5 kJ mol^{-1}, and therefore one cannot draw an unambiguous conclusion about the applicability of BAS
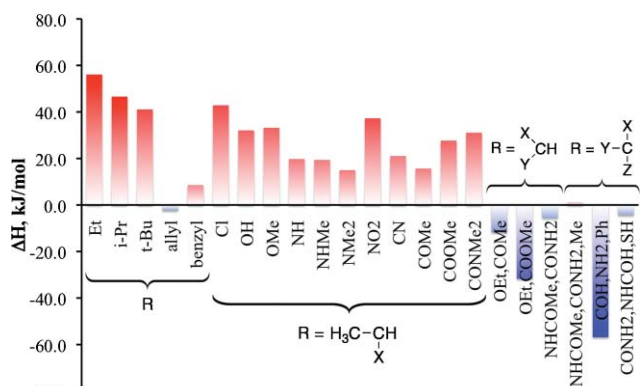
to aromatic hydrocarbon polymers. The second set of substituents consists of the groups containing heteroatoms with lone electron pairs (Cl, O, N) and unsaturated bonds with heteroatoms (C=O, C≡N, N=O). As we can see, none of these groups is able to turn the hydrogen abstraction into a thermodynamically favoured process. The third and forth sets of substituents represent the situation when the product radical centre is substituted with combinations of a π-acceptor group (such as C=O) and a lone-pair donor group (such as nitrogen or oxygen), and thus captodative stabilisation is possible. In the majority of cases here Reaction (4) is characterised with negative ΔH, thus it is now thermodynamically probable. The only exception is in the forth set and corresponds to a very slightly positive enthalpy of abstraction (1.2 kJ mol^{-1}), which falls within the uncertainty of the calculations (*ca.* 5 kJ mol^{-1}). Therefore, we can expect the propagation step of BAS to be thermodynamically probable in a limited number of cases, corresponding to the 'blue' radicals in Fig. 2.

However, Fig. 2 gives only a general overview of the reactivity of different polymers in the autoxidation propagation step. Firstly, it does not consider the nature of the attacking peroxyl radical, which would be unique in the degradation of each polymer. Secondly, values of bond dissociation energy, used to calculate the reaction enthalpies, do not reflect the entropy contribution. Finally, those BDEs correspond to standard gas-phase conditions, whereas the degradation of the polymer materials and biopolymers can be observed in very different environments. In order to estimate the influence of these additional factors for common polymers and some biopolymers, we have calculated the Gibbs free energy change for Reaction (4) from Scheme 1 (ROO$^•$ + RH $\rightarrow$ ROOH + R$^•$). For each reaction studied, calculations were carried out for the gas phase at two different temperatures – room temperature 298.15 K (25 °C) and an elevated temperature 373.15 K (100 °C) – to mimic the upper limit of conditions undergone by polymers in their usual applications. In addition, we have considered an effect of aqueous solvent (at 298.15 K), because polymers could be (at least partially) solvated during, for example, weathering, or in biological media.

The effect of temperature and solvation on the thermodynamic favourability of the propagation step is shown in Fig. 3 for our complete test set. Elevated temperature has an insubstantial effect
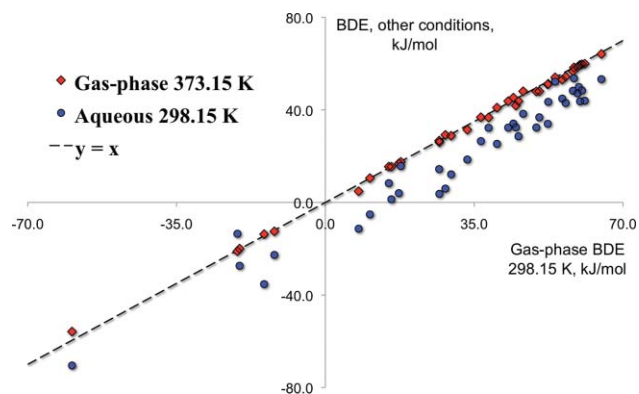
Fig. 2 Enthalpies of reaction HOO$^•$ + RH $\rightarrow$ HOOH + R$^•$ based on HOO–H and R–H BDEs calculated at the G3(MP2)-RAD level of theory.

Fig. 3 Reaction Gibbs free energies, calculated at the G3MP2-RAD// B3LYP-6-31G(d) level of theory, kJ mol^{-1}, in gas-phase at 373.15 K (red diamonds) and in water solution (COSMO-RS/BP/TZVP level of theory used to calculate Gibbs free energies of solvation) at 298.15 K (blue circles) plotted against the corresponding values in gas-phase at 298.15 K.

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on the reaction Gibbs free energy, varying from −3 to 1 kJ mol⁻¹. The addition of the aqueous solvent generally increases the favourability of the reaction by approximately 10–20 kJ mol⁻¹ as the products (hydroperoxides and polymer radicals) are stabilised to a greater extent by the polar solvent than the reactants (peroxyl radicals and polymer chains). The only exception to this is hydrogen abstraction from an alanine-based peptide, where the conformational changes between the gas- and solution-phases lead to a small increase in ΔG in aqueous solution. With this minor exception, solution-phase results represent the 'worst' conditions for the polymers in a practical setting; therefore they will be given therein (gas-phase reaction Gibbs free energies at 298.15 K and 373.15 K are available in Table S2 of the ESI‡). However, we will comment explicitly on any cases where the presence of water results in a change from a positive to a negative value of the reaction Gibbs free energy.

The first group of the polymers are those that contain unsaturated fragments, specifically lipids and rubbers, for which BAS was initially proposed, and also polystyrene and polyacrylonitrile. Structures of the polymers and compounds (in the form of R˙) used to model their degradation are collected in Fig. 4; these were chosen to represent the principal types of radical that could be formed by hydrogen abstraction or chain scission of the main structural units. In designing these small model radicals we included all alpha, beta and gamma substituents; except where conjugation extends along the polymer backbone, remote substituents are unlikely to have a significant effect on the reaction free energy. For each of these model radicals, the Gibbs free energy of Reaction (4) was calculated in aqueous solution at 298.15 K and the results are included in Fig. 4. An example of the studied reaction for the case of n-octa-2,6-diene (PBD in Fig. 4), used to model lipids and rubbers, is shown in Scheme 3.
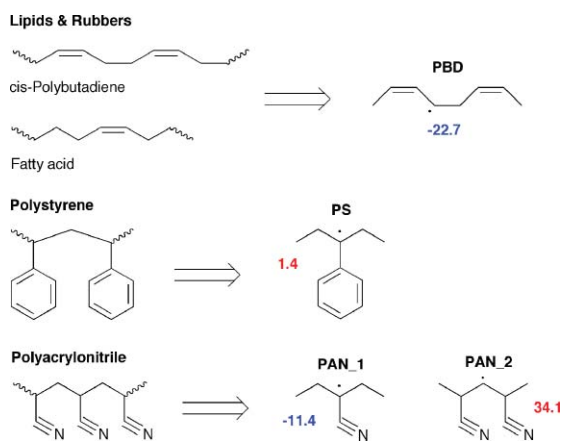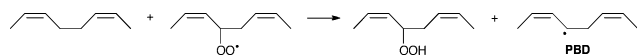

Fig. 4 Model radicals (R˙) formed during the degradation of polymers with unsaturated fragments and the corresponding calculated Gibbs free energies (kJ mol⁻¹, aqueous solution, 298.15 K) of Reaction (4). Here and hereinafter these values are marked in blue when negative, and in red when positive.

Scheme 3 Model reaction of hydrogen abstraction from a lipid or rubber fragment by the corresponding peroxyl radical.

The obtained results for the autooxidation of lipids and rubbers are in a good agreement with the experimental data for the corresponding BDEs and confirm Bolland and Gee's initial research. The reaction of a model compound PBD with a corresponding peroxyl radical is largely exoergic, and thus rubbers, lipids and other polymers with allylic fragments in their chains undoubtedly degrade according to BAS. However, the same conclusion could not be applied to the oxidative damage of polystyrene, as the Gibbs free energy of the propagation reaction for the model compound PS is positive. Though ΔG for this abstraction reaction, where the formed radical centre is in an α-position to the aromatic ring, is comparatively small in water solution, it is still large enough (15.5 kJ mol⁻¹) in the gas phase. Therefore BAS should not be strictly applied to any aromatic hydrocarbon polymer without careful investigation of its reactivity with peroxyl radicals. As for the acrylonitrile, hydrogen abstraction from the position α to the cyano group is favoured in solution, and it is one of the cases, mentioned above, where aqueous and gas-phase reaction Gibbs free energies have different signs. Thus, the oxidative damage of polyacrylonitrile is promoted by the presence of water.

The next group consists of those polymers with saturated hydrocarbon chains, as prepared by catalytic, anionic and/or radical polymerisation, namely polyethylene, polypropylene, polyvinyl chloride, poly(methyl methacrylate), polyvinyl acetate and poly(methyl vinyl carbonate) (Fig. 5). In addition to intermolecular hydrogen abstraction, for polyethylene we have also considered a case of intramolecular reaction through a six-member cycle as shown in Scheme 4. It is easy to see that all calculated Gibbs free energies of propagation reaction for the second set of polymers are highly positive, and thus for none of them is Reaction (4) thermodynamically favoured. The effect of carbon centre hybridisation could be estimated through a comparison of the data for polypropylene fragments PP_1 and PP_2: the stabilisation effect of branching is only about 3 kJ mol⁻¹. Abstraction from a primary carbon in PP_3 is actually characterised with the lowest ΔG of this set as a result of the reduced steric hindrance. Inclusion of a chlorine atom (as in PVC) lowers the reaction's Gibbs free energy by approximately 10 kJ mol⁻¹ because of the stabilising effect of conjugation between chlorine lone pairs and the formed radical centre. Nonetheless, even here the reaction still remains strongly disfavoured. For the PMMA set, the results are of a similar magnitude to PP in cases where the immediate substituents are alkyl groups (PMMA_1 and PMMA_2), and of a similar magnitude to PVC in cases where the product radical can be stabilised by the lone pair of a donor oxygen group (PMMA_3). Results for PVA and PMVC are similar to those for PMMA. In general, all considered polymers in the second group are unlikely to degrade via the classic propagation step of BAS.
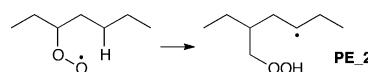
Scheme 4 Intramolecular hydrogen abstraction in polyethylene.

Condensation polymers like polyesters (polycaprolactone, polyglycolide, polylactide and polyethylene terephthalate), polyurethanes and polyamides, form the third group of model species (Fig. 6). For all considered cases, except one (PES_3), the
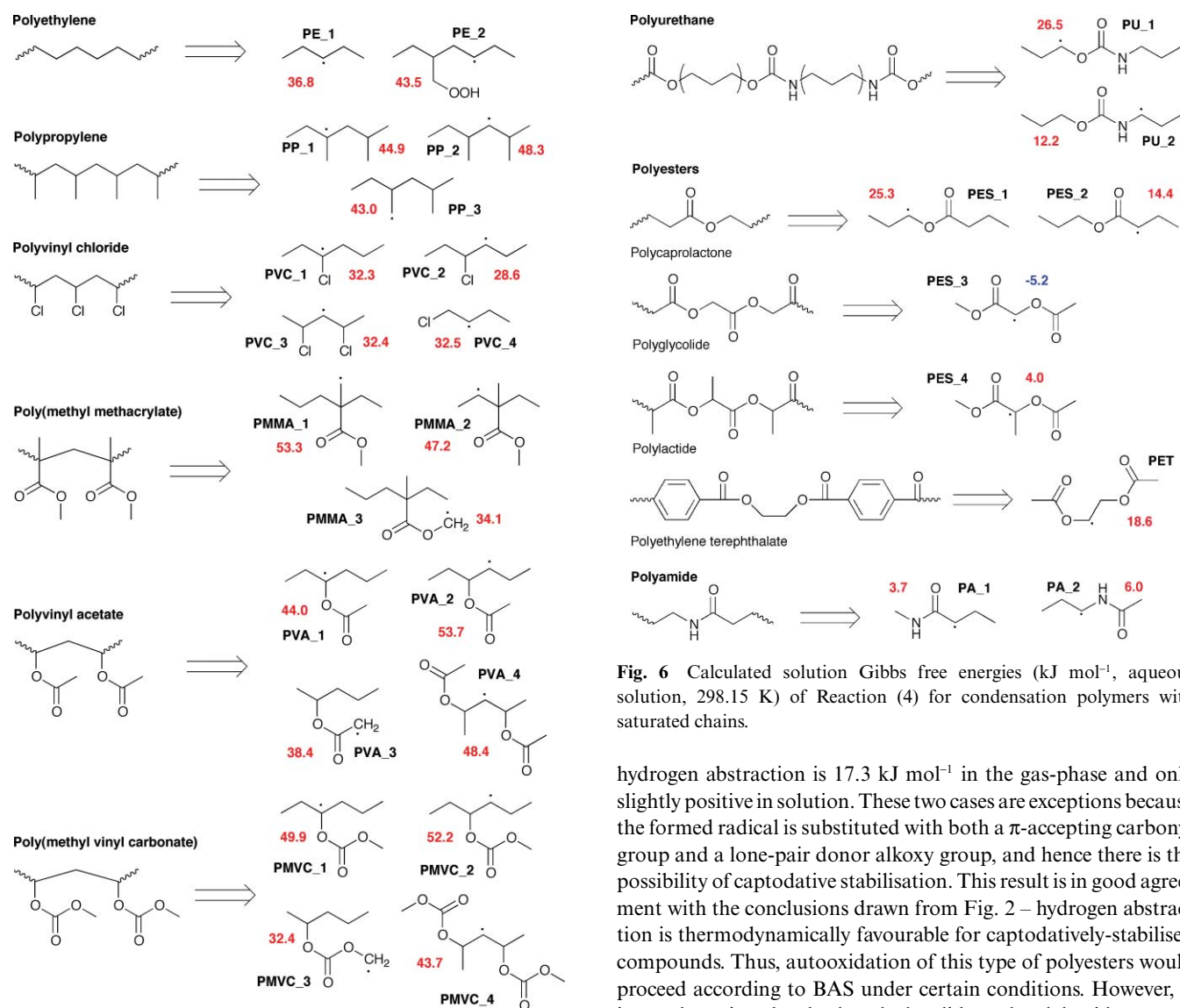
Fig. 5 Calculated solution Gibbs free energies (kJ mol⁻¹, aqueous solution, 298.15 K) of Reaction (4) for polymers with unsaturated chains, prepared by anionic and/or radical polymerisation.

Fig. 6 Calculated solution Gibbs free energies (kJ mol⁻¹, aqueous solution, 298.15 K) of Reaction (4) for condensation polymers with saturated chains.

Gibbs free energy of hydrogen abstraction by peroxyl radical is still positive. These values are noticeably lower, than in the second set of polymers due to a strong positive mesomeric stabilising effect of ester, amino ester and especially amide functional groups. Moreover, comparing the data for polyvinyl chloride, polyesters and polyurethane species, we can arrange corresponding heteroatoms according to their stabilisation strength: chlorine (ΔG for Reaction (4) ≈ 30 kJ mol⁻¹) < oxygen (ΔG ≈ 25 kJ mol⁻¹) < nitrogen (ΔG ≈ 10 kJ mol⁻¹); this observation is in agreement with Mendeleev's periodic law. It is also clear, that proximity of the π accepting C=O double bond has substantial stabilisation effect on the radical centre (PES_2, PA_1) too. However, two species in this set are characterised with much lower values of free energies of reaction (4) – namely, polyglycolide (PES_3) and polylactide (PES_4). For polyglycolide the propagation reaction is slightly exergic in solution (but still endoergic in the gas-phase: ΔG_{gas} = 10.5 kJ mol⁻¹), and for polylactide the Gibbs free energy of

hydrogen abstraction is 17.3 kJ mol⁻¹ in the gas-phase and only slightly positive in solution. These two cases are exceptions because the formed radical is substituted with both a π-accepting carbonyl group and a lone-pair donor alkoxy group, and hence there is the possibility of captodative stabilisation. This result is in good agreement with the conclusions drawn from Fig. 2 – hydrogen abstraction is thermodynamically favourable for captodatively-stabilised compounds. Thus, autooxidation of this type of polyesters would proceed according to BAS under certain conditions. However, it is worth noting that both polyglycolide and polylactide, as well as their copolymers, are not usually used in elevated temperature applications (*e.g.* surface coatings, engineering plastics) where BAS is assumed to be significant, but rather as biodegradable materials in applications (*e.g.* dissolving sutures) where they can degrade *via* acid or base catalysed hydrolysis. For the other polyesters, in applications for which BAS has been proposed,[28] the propagation step is not thermodynamically favoured.

The last group corresponds to biopolymers, represented in this study by peptides consisting of the following amino acids: glycine, alanine, phenylalanine and cysteine (Fig. 7). As expected, the possibility of captodative stabilisation of the resulting product radical ensures the thermodynamic favourability of the hydrogen abstraction reaction. In all such cases (namely, GLY, ALA, PHE_1 and CYS_1) Reaction (4) is highly exoergic, and the propagation step is therefore thermodynamically favourable for the oxidative degradation of natural peptides. The obtained results are in a good agreement with earlier works of Rauk *et al.* and Davies *et al.*[30–35] The calculations also further confirm that the proximity of only one functional group, capable of conjugation with the radical centre (aromatic ring in PHE_2 and sulfur's lone pairs in CYS_2), is not enough to make the propagation step probable on
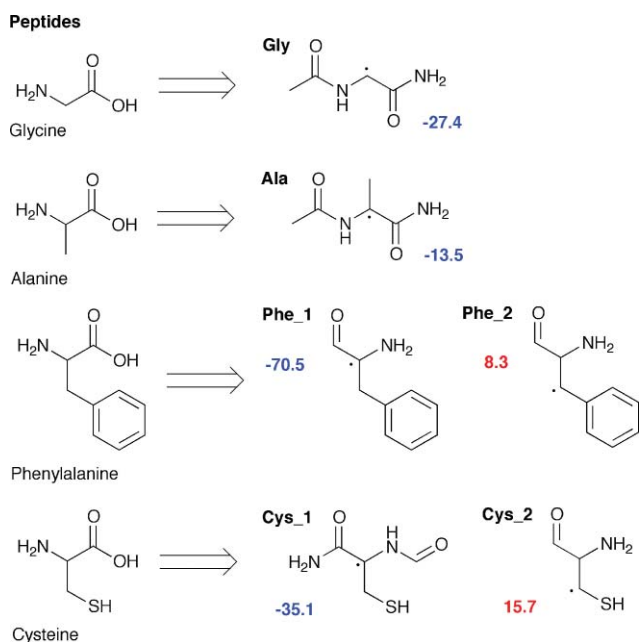
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Fig. 7 Calculated solution Gibbs free energies (kJ mol^{-1}, aqueous solution, 298.15 K) of Reaction (4) for peptides.

thermodynamic grounds. In other words, from a thermodynamic perspective oxidative damage is unlikely to be *propagated* through the side chains, though such radicals may of course be generated during other steps of the degradation process. As noted earlier, this latter finding is interesting, given that experimental studies of free amino acids have shown that peroxides are formed exclusively on the side chains, rather than the backbone atoms.[42] In the light of our results, alternative pathways for the formation of side chain peroxides may need to be considered. For example, it is well known that side chain radicals may be formed *via* hydrogen abstraction by more reactive radicals (such as HO$^{\bullet}$),[43] once formed these may then convert to the peroxyl radical by reaction with oxygen in the normal manner. The resulting peroxyl radicals may then pick up a hydrogen from the backbone, thereby propagating the damage, (albeit through the main chain not the side chain) or may perhaps convert directly to the corresponding peroxides *via* an electrochemical route, depending on the reaction conditions.

3.3 Alternatives to BAS

Based on the results from above, we can conclude that for most (but not all) of the considered polymers, the propagation stage in BAS is thermodynamically disfavoured. It is therefore clear that some alternative processes must be responsible for the unquestionable autocatalytic nature of polymer degradation and the concurrent formation of hydroperoxides. It is well known, that in addition to the main structural units of the polymers, one can also observe the presence of various structural defects in their chains. This is particularly true for radical polymerisation where a broad range of side reactions are possible, but even in anionic or transition metal catalysed living polymerisation the chemical structures of the end groups can differ substantially from the repeat unit of the polymer. Moreover, many studies confirm that there is a correlation between the concentration of defect units in the polymer and its stability.[18,44–47] It is therefore possible

that the structural defects in a polymer might be responsible for the propagation of the autooxidative damage in many polymer materials. In order to verify this suggestion, we have chosen polymers for which the propagation step of BAS was shown to be endoergic above, and have calculated the Gibbs free energy of hydrogen abstraction by peroxyl radical (ROO$^{\bullet}$ + RH → ROOH + R$^{\bullet}$) at G3(MP2)-RAD//B3LYP/6-31G(d) level of theory in gas-phase at 298.15 K for a number of their reported defect structures. According to the previously established effect of polar solvent to decrease the ΔG of reaction by approximately 10–20 kJ mol^{-1}, in this Section we report only the gas-phase energies – obviously, if the reaction is exoergic in the gas phase, it would be even more favoured in solution.

The most common defect structures in polyalkenes are the unsaturated end groups, formed *via* the chain termination reactions (*e.g.* disproportionation in free-radical polymerisation; different types of chain termination through β-H or β-CH$_3$ transfer in polypropylene anionic polymerisation with Ziegler–Natta or metallocene catalysts). In free-radical polymerisation, internal double bonds can also result from β-scission of the mid-chain propagating radical formed after inter- or intramolecular chain transfer to polymer, or by elimination of labile groups, *e.g.* dechlorination of PVC. Thus for example, radical suspension polymerisation of PVC leads to the formation of internal double bonds, chloroallylic and vinylidene end groups, in addition to chain branches formed from propagation after chain transfer (Fig. 8).[47,48]
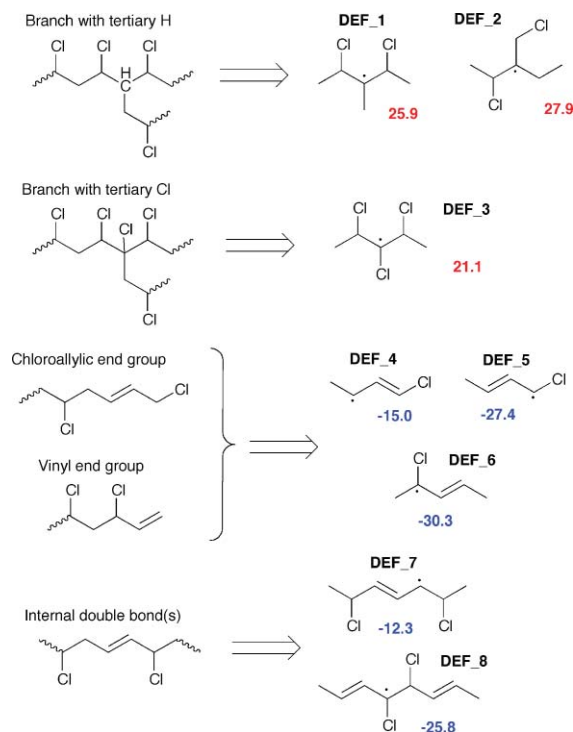

Fig. 8 Calculated Gibbs free energies (kJ mol^{-1}, gas phase, 298.15 K) of Reaction (4) for structural defects in polyvinyl chloride.

From Fig. 8, it is seen that abstraction of hydrogen from a tertiary carbon, even in the presence of several adjacent chlorine atoms, is still thermodynamically disfavoured (DEF_1–3). However, the situation is completely different for the species
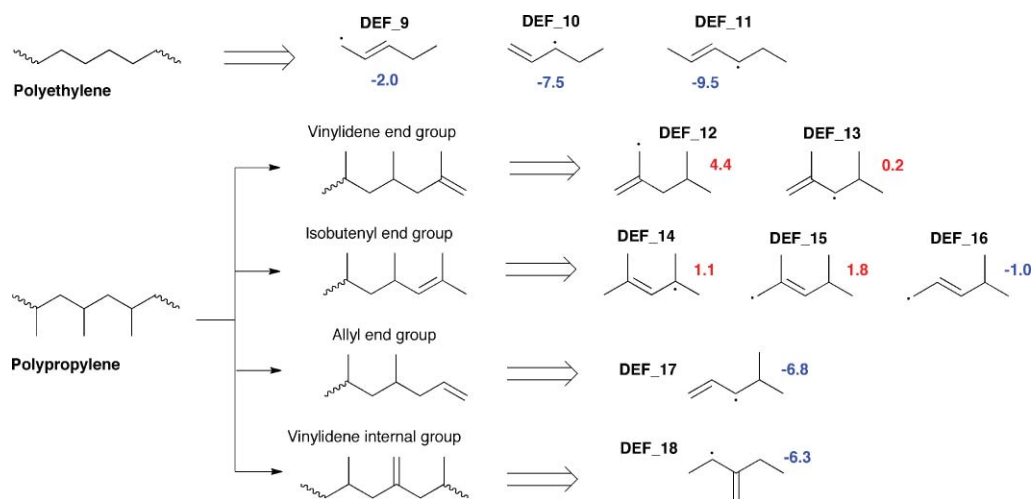
Fig. 9 Calculated Gibbs free energies (kJ mol^{-1}, gas phase, 298.15 K) of Reaction (4) for structural defects, formed in the synthesis of low-density polyethylene and polypropylene.

containing end or internal double bonds. For all 5 cases, ΔG of the propagation reaction is largely negative, especially when chlorine atoms, a radical centre and a double bond form a chain of conjugation (DEF_5,6,8). The ability of these defect structures to propagate autooxidation therefore explains the experimental observation that these defect structures lead to reduced thermal and photostability,[49] and our results suggest that it is unsaturated groups, rather than the branch points, that are crucial in this respect, though the latter will almost certainly play a role in initiation.

Various unsaturated defect structures are known to result from chain termination processes in both catalytic anionic polymerisation of ethylene and propylene,[50] as well as free-radical polymerisation of ethylene. The most common defect groups are given in Fig. 9. One more type of structural abnormality – chain branches – could be found in low density and linear low density polyethylene, but this case is represented by the previous modeling of polypropylene (PP_1–3), as well as by the defect structures 12–18 below. Hydrogen abstraction from the α-position to the carbon-carbon double bond is exoergic in all cases, except for DEF_12–15 where it is very slightly positive (in the gas phase) due to steric effects that complicate the flattening of a formed π-conjugated system, thus decreasing its actual stability. Nonetheless, some of the defect structures usually present in PE and PP are thermodynamically capable of propagating their oxidative degradation.

As one further example, during the radical polymerisation of methyl methacrylate a number of abnormalities are also formed through β-elimination in the propagating radical (Fig. 10).[46,51]

These defects are end double bonds, conjugated with the nearest ester groups. Reaction (4) is exoergic in several cases, especially in DEF_21 due to the long chain of conjugation, thus causing the autocatalytic character of PMMA oxidation. More generally, in most free-radical polymerisation processes, termination *via* disproportion occurs at least to some extent and results in unsaturated end groups, which would be capable of propagating oxidative damage.

We have shown that some of the defect structures reported to form during preparation of PE, PP, PVC and PMMA, are responsible for the autooxidation of those polymers, as they represent the reactive sites in the propagation stage of the process. This leads to the suggestion that if one could minimise the occurrence of such defect structures *via* either alteration to the polymerisation process (*e.g.* using atom transfer radical polymerisation[52] in place of conventional free-radical polymerisation to reduce the relative occurrence of unsaturated end groups), or by post-reactions of the polymers themselves, one could significantly stabilise the polymer. However, in some cases, abnormalities could also occur as a result of the thermo- or photo- degradation itself, usually as a result of disproportionation of two macroradicals. In such cases, efforts to minimise defect structures during polymer synthesis may be wasted and alternative polymer stabilisation strategies would be required.

To explore this possibility, we have considered the formation of such intermediates in the degradation of poly(methyl methacrylate). Fig. 11 shows some of the possible defect structures formed during degradation of PMMA.[18,45,53,54] As one can see in Fig. 11, each corresponds to functional groups associated either with
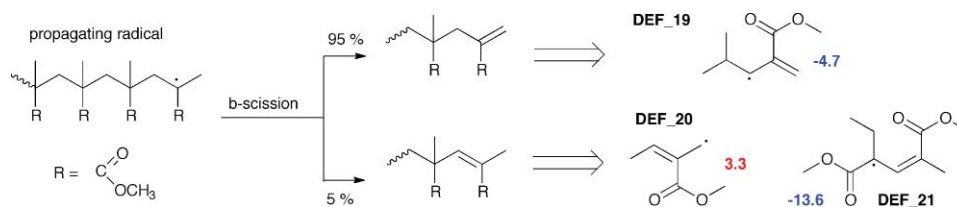

Fig. 10 Structural defects, formed in the synthesis of poly(methyl methacrylate).
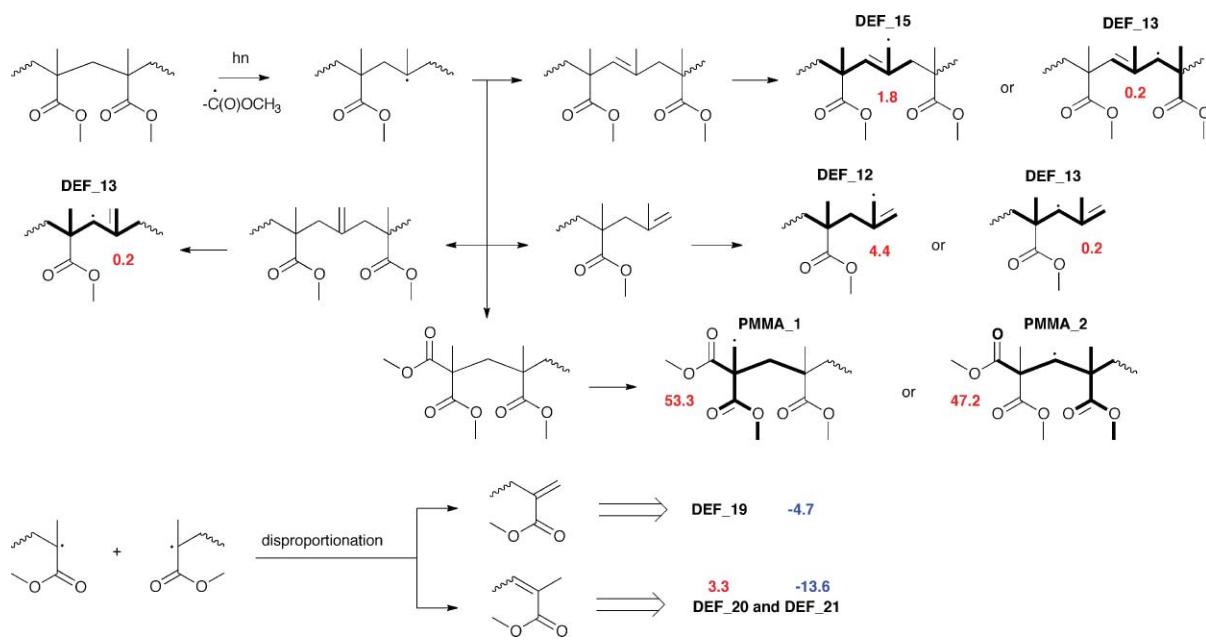
Fig. 11 Structural defects, formed during the degradation of poly(methyl methacrylate).

regular PMMA (see Fig. 5) or with defect structures formed during free-radical polymerisation (see Fig. 10). As noted above, at least some of these latter structures (DEF_19, DEF_21) are capable of propagating oxidative damage even in the gas phase, while many of the others could well become favourable in the presence of aqueous solvent (*e.g.* DEF_12, DEF_13, DEF_15 and DEF_20). Hence efforts to minimise their formation through, for example, use of anionic polymerisation would have limited value. As a second polyalkene example, we have considered possible structural defects formed during the degradation of polystyrene (Fig. 12).[19,24,55] As seen in Fig. 12, during the degradation process, terminal carbon–carbon double bonds that are conjugated with the aromatic ring may be formed *via* disproportionation, and, as shown earlier, this type of structure (DEF_22) can indeed propagate oxidative damage. Thus, once again, efforts to minimise these defect structures during the polymerisation process may have limited benefit as the same structures can also form during the degradation process itself and help to catalyse it.
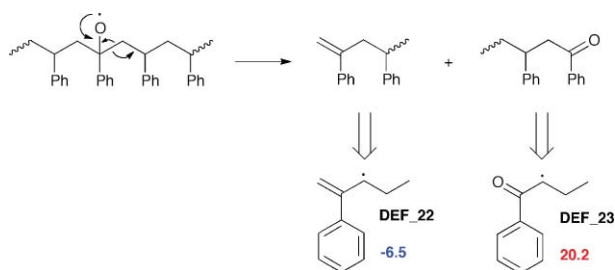

Fig. 12 Structural defects, formed during the degradation of polystyrene.

The formation of structural defects during degradation is also likely to be crucial to understanding the degradation of some condensation polymers. For example, *cis*-elimination is known to be a dominant degradation pathway in polyesters with activated C–H bonds under standard conditions.[56,57] This reaction, which

is illustrated for the case of poly(trimethylene terephthalate) in Fig. 13, results in an unsaturated end group. Depending on the length of the ester alkyl chain, the product of this reaction then features allylic hydrogens which, in the case illustrated in Fig. 13, are further stabilised by the next ester group. Not surprisingly, the propagation reaction associated with the resulting defect structure is then strongly thermodynamically favoured, in stark contrast to the corresponding reaction with the standard ester linkage for this same polymer. It is also clear that the susceptibility of the polyester to *cis*-elimination, and its consequences for the propagation of polymer autoxidation, will vary a large amount according to the structure of the polyester. Thus for example, for poly(ethylene terephthalate), the resulting *cis*-elimination product does not contain allylic hydrogens; whereas polymers with longer *n*-alkoxy chains do. Moreover, if the alkoxy group is fully branched at the beta-position, *cis* elimination would be blocked, presumably leading to greater inherent stability. Therefore, recognising the importance of *cis*-elimination (and other possible degradation reactions) in generating the catalytic sites for autoxidation is crucial to designing polymers that are more inherently stable.
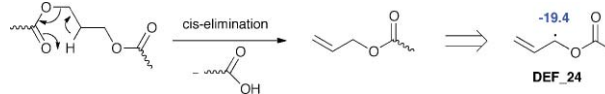

Fig. 13 Structural defects, formed during the degradation of poly(trimethylene terephthalate).

Finally, it is worth noting that in some polymers, and under some conditions, polymer autoxidation should not be limited only to Bolland's and Gee classic mechanism. Thus for example, it has been suggested that oxidative damage in polyacrylates can occur *via* non-radical processes under high-energy ultraviolet irradiation,[54,57] many polyesters can degrade *via* acid or base catalysed hydrolysis,[58] while other work has implicated the role of metal oxides, usually added to polymer coatings, in the oxidation

of polystyrene.[59] Depending on the polymer type and the reaction conditions, such alternative degradation pathways should also be considered when developing strategies for stabilising polymers.

Conclusions and implications

We have shown that the propagation step in the autooxidation of a number of popular polymers does not exactly take place according to Bolland's and Gee classic scheme, as often claimed. The reason is simple – hydrogen abstraction by peroxyl radical from the regular chain of many polymers, considered in this study (polyethylene, polypropylene, polyvinyl chloride, poly(methyl methacrylate), polyvinyl acetate, polyurethane, polyethylene terephthalate *etc.*), is strongly thermodynamically unfavourable, because the bond dissociation energy of the corresponding R–H bond is significantly higher, than that of the ROO–H bond. The reaction only becomes thermodynamically favourable when the product radical is stabilised by allylic double bonds (as in lipids and rubbers) or strong captodative effects (as in the backbone of peptides and some polyesters); any other applications should be carefully examined on a case-by-case basis. Instead, it appears that for most common polymers autooxidation is only propagated as a result of defect structures, predominantly terminal and internal double bonds, which may be formed during the original polymerisation procedure and/or the degradation process itself.

Recognition of the true nature of the propagation step(s) in polymer autooxidation is crucial to the development of better strategies for polymer stabilisation (Fig. 14). Thus, for example, when the propagation step is only possible as a result of the unsaturated end-groups formed during the polymerisation process, changes to the polymerisation conditions (*e.g.* use of ATRP[52] instead of conventional free-radical polymerisation) may result in a more stabilised polymer. If however, as is often the case, the same or similar defect structures are also formed during degradation itself, this strategy will be less effective. In those cases, an examination of the degradation reactions that give rise to the catalytic sites, and their dependence on the inherent chemical structure of the polymer, and other reaction conditions (pH, solvent, temperature, additives), will be more fruitful.

Mechanism	Polymers	Mitigation Strategies
Standard BAS	*lipids, rubbers, peptides, some polyesters*	•Antioxidants •Choice of different polymer structure
BAS via Polymer Defects	*most polyalkenes*	•Antioxidants •Changes to the polymerisation process
BAS via Degradation Products	*most polyalkenes, many condensation polymers*	•Antioxidants •Choice of different polymer structure •Changes to degradation conditions (temperature, solvent, pH, additives)
Non-BAS	Depends on polymer type and degradation conditions	

Fig. 14 Solutions to the problem of polymer stabilisation against oxidative degradation.

Acknowledgements

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