Mechanistic insight into TEMPO-inhibited polymerisation: simultaneous determination of oxygen and inhibitor concentrations by EPR

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Received 25th March 2009, Accepted 12th May 2009
First published as an Advance Article on the web 26th May 2009
DOI: 10.1039/b905893a

Convolution-based fitting of EPR spectra makes it possible to simultaneously determine concentrations of TEMPO and oxygen in TEMPO-inhibited polymerisations and autoxidations; this method is useful for understanding the chemistry of inhibitor mixtures.

Polymerisation inhibitors and antioxidants play a major role in stabilising many products of the chemical industry. A number of different inhibitor types have been established.[1] For instance, stable nitroxide free radicals (such as TEMPO) react rapidly with the carbon-centred radicals thus stopping the chain propagation. Oxygen can be considered as belonging to this class of inhibitors as it reacts extremely efficiently with alkyl propagating radicals and forms peroxy radicals ($RO_2^{\bullet}$) which are much less efficient at initiating the polymerisation. Other chain-breaking inhibitors (*e.g.*, phenols) act by intercepting peroxy radicals ($RO_2^{\bullet}$). The latter compounds work best as polymerisation inhibitors in the presence of oxygen.

The efficiency of polymerisation inhibitors could be assessed by a number of tests. Most commonly the reactions are followed by monitoring consumption of oxygen in the system. An oxidative induction time test, a popular industrial method, measures the time lag before the onset of rapid oxidation/polymerisation of the sample in an oxidising atmosphere at a given temperature.[2] This is usually done using DSC.

Apart from conventional methods, the concentration of oxygen in solutions could be conveniently monitored by EPR spectroscopy by taking advantage of the broadening of EPR lines by paramagnetic oxygen. This method is particularly suitable for studying TEMPO-inhibited systems, as TEMPO produces a suitable EPR signal. The application of EPR spectroscopy to monitor oxygen consumption in TEMPO-inhibited autoxidation reactions has been explored by Pedulli *et al.*[3] The oxygen concentration was calculated from the intensity of EPR lines. This method assumed that concentration of TEMPO is unchanged during the reaction. For systems which show decay of TEMPO during autoxidation, these authors successfully replaced TEMPO with an alternative, non-reactive probe, fusinite (a paramagnetic charcoal).

We reasoned that the EPR spectra of TEMPO-inhibited systems contain information about both TEMPO and oxygen concentrations, and appropriate numerical analysis should make it possible to extract information about concentrations of both species. Indeed, the frequency of collisions of TEMPO (ω) with paramagnetic oxygen can be described by the Smoluchowski equation (1):[4]

$$\omega = 4\pi r_0 DC \quad (1)$$

Here r_0 is the collision distance, D and C are diffusion coefficient and concentration of oxygen, respectively. Collisions of TEMPO with oxygen lead to the shortening of the electron relaxation times T_1 and T_2 of the nitroxide. In particular, shortening of T_2 results in the additional Lorentzian broadening of the EPR line shape.[5] Smirnov *et al.* developed a method for extracting the linewidth of the incremental broadening from the EPR line shapes by fitting the experimental broadened spectra to the convolution of an unbroadened spectrum (*e.g.*, recorded in the absence of oxygen) with a Lorentzian function with a variable linewidth.[5,6] The linewidth thus obtained is linearly proportional to the frequency of TEMPO-oxygen collisions, and hence to the product of oxygen diffusion coefficient and oxygen concentration. Therefore, the linewidth of incremental Lorentzian broadening can be used as a measure of relative oxygen concentration in the system. This method has been successfully applied to oximetry studies in many biological systems.[4]

In this communication, we report on the application of this convolution-based fitting to simultaneously determine concentration of TEMPO and oxygen in TEMPO-inhibited monomers. A similar approach was used by Smirnov *et al.* to monitor oxygen consumption and nitroxide reduction in mammalian cells.[7] The solubility of oxygen in organic systems is much higher than in water,[8] and therefore the accuracy of the oxygen measurements is higher. The very significant reduction in the linewidth upon deoxygenation of an organic monomer is illustrated in Fig. 1.

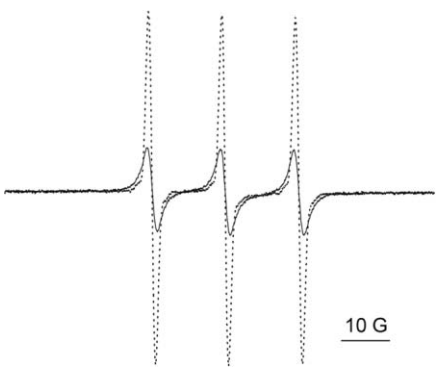

Fig. 1 X-Band EPR spectra of air-saturated (solid line) and deoxygenated (dotted line) TEMPO solutions in styrene (20 ppm) at 100 °C.

The experiments were carried out by heating an air-saturated, sealed TEMPO solution in neat monomer (styrene) or with other

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additives in an X-band EPR cavity at a constant temperature.‡ The concentration of TEMPO was maintained at 20 ppm. The set of EPR spectra recorded at regular intervals was then analysed using the EWVoigt program developed by Smirnov.[9] The Lorentzian broadening was obtained by fitting the spectra against the unbroadened spectrum (which was either recorded at the same temperature by deoxygenation of TEMPO solution in the same monomer, or obtained by natural deoxygenation of the system upon heating). For systems with small broadening (*e.g.*, at low oxygen concentration), this approach fails due to software limitations; in these cases, the broadening was obtained by fitting the spectrum of an air-saturated mixture against every spectrum in the series convoluted with a variable linewidth Lorentzian function. An additional advantage of the convolution-based fitting as compared to measuring the line heights is the increased accuracy: the convolution-based fitting utilises all data points in the spectrum, while the line height measurements usually rely on just two points (maximum and minimum).

Formation of oligomers/polymers in the inhibited polymerisation mixture could increase the viscosity of solutions. This could affect the EPR line shape and hence render our method invalid. To investigate the potential viscosity increase, we have recorded the spectra of deoxygenated TEMPO solutions in styrene before and after thermal treatment. The identical line shape of these spectra confirmed that the viscosity increase was negligible (if any) during the time of these experiments (*e.g.*, until complete disappearance of the TEMPO signal). Fig. 2 shows the time dependence of the oxygen and TEMPO concentration for AIBN-initiated styrene polymerisation.

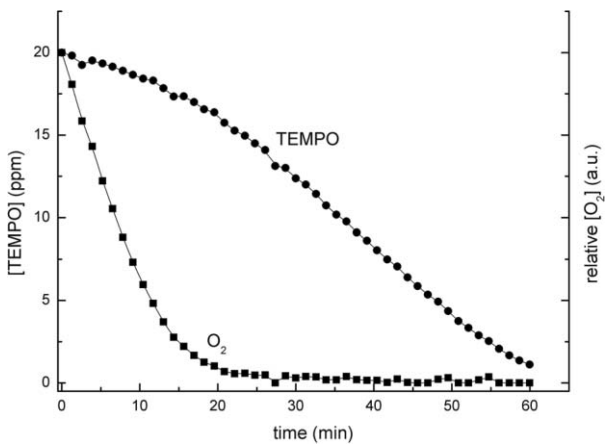
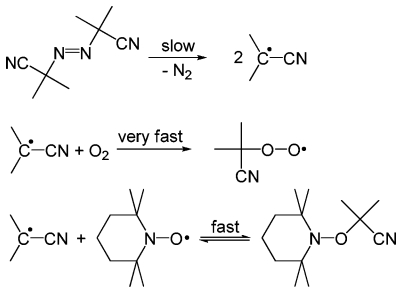


Fig. 2 Time-dependent decay of TEMPO (●) and oxygen (■) during AIBN (100 ppm) initiated styrene polymerisation at 70 °C.

One can see that in the initial stages of the reaction, the oxygen concentration decreases nearly linearly with time. This is consistent with the fast reaction of oxygen with radicals produced at a constant rate by the AIBN decomposition (Scheme 1).

The concentration of TEMPO is decaying slowly even in the early stages of the reaction. This is probably due to the capture of some 2-cyanopropyl radicals by TEMPO (Scheme 1). Nitroxides show poor affinity for the oxygen-centered radicals, and therefore are unlikely to trap peroxy radicals efficiently.[10] After the depletion of oxygen, the 2-cyanopropyl radicals are scavenged by TEMPO,



Scheme 1 Formation and quenching of 2-cyanopropyl radicals by oxygen and TEMPO.

and the concentration of TEMPO consequently decays almost linearly with time.

If another inhibitor, *p*-methoxyphenol, is added to the styrene solution of TEMPO, the decay of oxygen is significantly slowed down (Fig. 3). The rate of oxygen consumption decreases steadily with the increased *p*-methoxyphenol concentration. This is consistent with the high antioxidant efficiency of phenols which slows down autoxidation reactions *via* a chain-terminating mechanism.[3,11] Peroxy radicals formed during autoxidation (Scheme 1) are quenched by abstracting a hydrogen atom from the phenol. The resultant phenoxy radical then recombines with a monomer radical. Interestingly, TEMPO decay (which is observed after consumption of oxygen) is less affected by the presence of *p*-methoxyphenol. Presumably, while very reactive with oxygen-centered radicals, phenols cannot compete efficiently with TEMPO for carbon-centered radicals which dominate the reaction in the absence of oxygen.

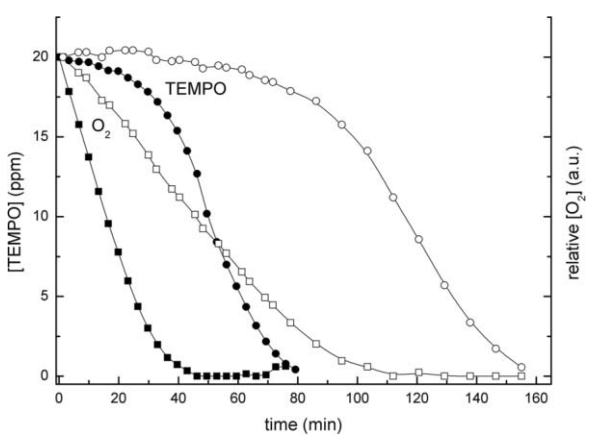


Fig. 3 Time-dependent decay of TEMPO (circles) and oxygen (squares) during AIBN (100 ppm) initiated styrene polymerisation in the presence of *p*-methoxyphenol at 70 °C. Filled and open symbols correspond to the 40 and 80 ppm *p*-methoxyphenol concentration, respectively.

A rather different set of results was obtained for the uninitiated polymerisation of styrene (Fig. 4). Surprisingly, the rates of oxygen/TEMPO decay were accelerated in the presence of *p*-methoxyphenol. Additionally, some noticeable TEMPO decay was observed in the mixtures containing *p*-methoxyphenol before the consumption of oxygen was complete.

To explain the very different behaviour of inhibitors in initiated and spontaneous styrene polymerisation/autoxidation, one needs to consider the mechanism for self-initiation proposed by Mayo.[12]

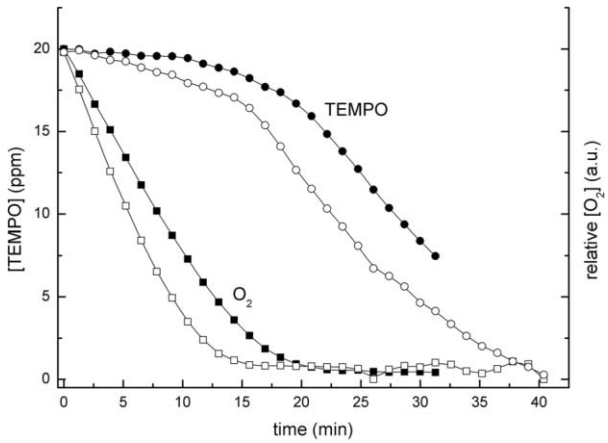
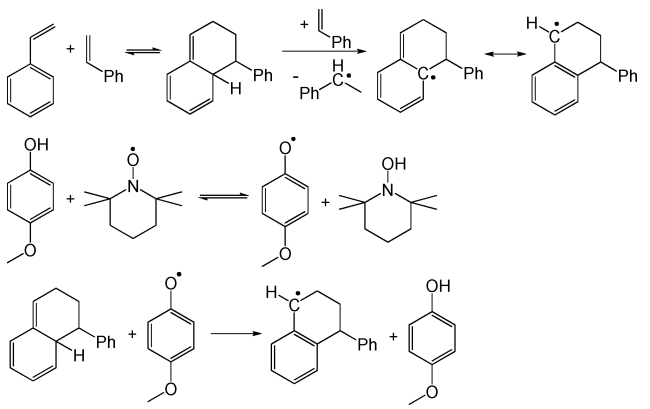


Fig. 4 Time-dependent decay of TEMPO (circles) and oxygen (squares) during uninitiated styrene polymerisation in the presence (open symbols) and absence (filled symbols) of *p*-methoxyphenol (20 ppm) at 100 °C.

In this mechanism, Diels–Alder reaction of styrene leads to the formation of an adduct with a labile hydrogen atom. Abstraction of this hydrogen by another styrene molecule leads to initiation (Scheme 2). In the presence of TEMPO, however, hydrogen could be abstracted by the nitroxide to form a hydroxylamine[13] (which forms TEMPO again upon reaction with a peroxy radical or oxygen). We speculate that the increased rate of oxygen decay in the presence of *p*-methoxyphenol is due to the equilibrium hydrogen transfer reaction between TEMPO and the phenol which produces phenoxy radicals (Scheme 2).[1] Abstraction of phenolic hydrogen by the nitroxide is commonly used to explain the synergistic antioxidant activity of the phenol/TEMPO mixtures.[1]



Scheme 2 Mayo mechanism for styrene self-initiation, and the mechanism of synergistic antioxidant action of TEMPO and *p*- methoxyphenol.

The phenoxy radical formed is likely to be more reactive towards the Mayo adduct than TEMPO, thus explaining faster initiation and oxygen consumption in the presence of both inhibitors. This reaction could also explain the noticeable decay of TEMPO before oxygen consumption is complete.

In conclusion, we have shown that the convolution-based fitting of EPR spectra of TEMPO-inhibited autoxidation mixtures makes it possible to simultaneously determine the concentrations of oxygen and TEMPO in the system. This information can be useful in mechanistic studies of autoxidation activity.

Acknowledgements

The authors acknowledge funding from Nufarm Ltd. YM would like to thank Wild Fund (University of York) for funding. Prof. A. I. Smirnov is thanked for helpful discussions.

Notes and references

‡ Oximetry measurements were carried out using a JEOL JES-RE1X ESR spectrometer. Typical instrumental parameters for the acquisition of the X-band EPR spectra were: frequency 8.97 GHz, power 5 mW, sweep width 100 G, centre field 3186 G, sweep time 60 s, time constant 30 ms, modulation frequency 100 kHz, modulation width 1 G. The samples (50 μL) were prepared in glass capillaries which were flame-sealed leaving a head space of *ca.* 20% of the total capillary volume.

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