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# Absolute rate constants for radical-monomer reactions

## The nitroxide method

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### Summary

A method is described for determining the absolute rate constants for the first few propagation steps in radical polymerization. The procedure involves a product analysis of the oligomeric alkoxyamines formed when an initiator is decomposed in monomer containing a very low concentration of a nitroxide radical scavenger. The method is illustrated with analysis of data for methyl acrylate. The rate constants for the first two propagation steps for polymerization of this monomer, $k_p(1)$ and $k_p(2)$, are at least an order of magnitude greater than $k_p$(average). Values of the absolute rate constants for reactions of phenyl and primary alkyl radicals with methyl acrylate are also estimated.

### Introduction

In modelling polymerization kinetics, it is usually assumed that the propagation rate constants $k_p$ are independent of chain length and, for long chains (length >20), there is good experimental evidence to support this assumption.(1,2) On the other hand, there is a growing body of evidence to suggest that the first few propagation steps of radical polymerization should have rate constants, $k_p(1)$, $k_p(2)$, etc., that are substantially greater than $k_p$(overall). This evidence comes from a number of sources, for example: (a) the absolute rate constants for the reaction of small model radicals with monomers are typically several orders of magnitude greater than the corresponding values of $k_p$,(3) (b) chain transfer constants ($k_p/k_{transfer}$) often show a marked chain length dependence for very short chain lengths,(4) (c) aspects of the kinetics of emulsion polymerization(5) and molecular weight distributions of polymers formed in pulsed laser photolysis experiments(6) can best be explained by invoking chain length dependence of $k_p$. (d) To date there are few direct measurements of these important kinetic parameters.(7)

Much work has been carried out in these laboratories aimed at defining the reactions of initiator derived radicals with polymerizable monomers.(8,9) One of the most effective methods for this has been the nitroxide trapping technique

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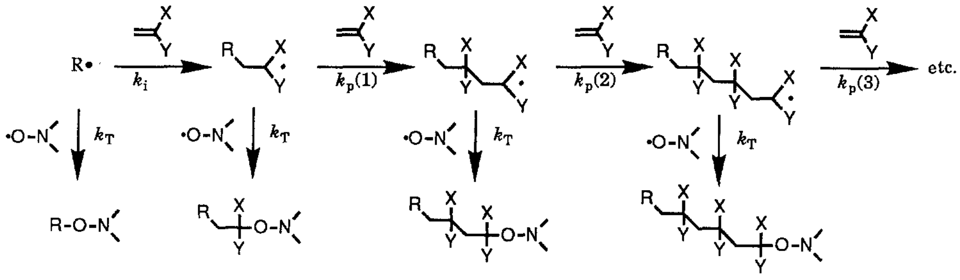
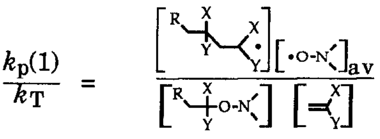
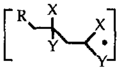
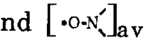
developed by Rizzardo and Solomon.(10) The method involves a product study of the stable alkoxyamines formed when a nitroxide is used to scavenge the radicals formed by reaction of initiator-derived radicals with a monomer (see Scheme 1). The technique has been successfully used to study the reactions of a variety of heteroatom-centred and more reactive carbon-centred radicals with monomers.



**Scheme 1**

In these experiments, if the rate constant for trapping of radicals by the nitroxide ($k_T$) is known (and is assumed to be independent of chain length), then the relative yields of oligomeric products can be used to calculate values of $k_i$, $k_p(1)$, $k_p(2)$, etc. (refer Scheme 1). For example, $k_p(1)$ can be calculated using the following relationship:



where  is taken as the concentration of all products derived from this species (*ie.* the trapped product plus higher oligomers) and  is the average of the initial and final nitroxide concentrations.

This possibility, of using the nitroxide trapping reaction as a method for determining rate constants for radical-monomer reactions, led us to initiate a study aimed at better defining the absolute rate constants for reactions of nitroxides with carbon-centred radicals.(11,12) Other laboratories have also been active in this area.(13-15) These studies have in turn led to the nitroxide-radical reaction being used as a clock process to measure absolute rate constants for a variety of radical reactions.(16-19)

The nitroxide trapping experiments carried out to date were designed to give information on the specificity of the initiation process and on relative rates for the various initiation pathways. Relatively high nitroxide concentrations were employed in these studies so as to keep the reaction mixtures simple by preventing propagation from the initial adducts. Thus, only with the more reactive vinyl monomers [*eg.* methyl acrylate (MA)] were significant yields of oligomeric products obtained. In this paper we have reanalysed data on initiation of MA polymerization by benzoyloxy(20) and t-butoxy(21) radical sources to obtain absolute rate constants for the reactions of various radicals with MA.

## Results and Discussion

The radical trapping experiments were conducted either with benzoyl peroxide (BPO, a source of $PhCO_2\bullet$ and $Ph\bullet$) as initiator and 4-benzoyloxy-2,2,6,6-tetramethylpiperidin-N-oxyl as nitroxide(20) or with di-t-butyl peroxyoxalate (DBPOX, a source of $tBuO\bullet$ and $CH_3\bullet$) and 1,1,3,3-tetramethylisoindolin-N-oxyl (TMIO).(21) In a typical experiment,(20) a solution of the initiator and nitroxide in methyl acrylate was vacuum degassed through three freeze thaw cycles then sealed under vacuum. The mixture was placed in a constant temperature bath at 60°C for 5 h (longer reaction times lead to by-product formation) then opened and analysed directly by HPLC. Prompt analysis was essential since certain products and the residual initiator are labile. Products of chain length <3 were isolated and identified on the basis of their $^1H$ NMR spectra. HPLC response ratios were determined by analysis of mixtures of these isolated compounds. The rate constants for the reactions of radicals with MA reported in Table 1 were calculated on the basis of the product analyses reported earlier.(20,21)

Table 1. Absolute Rate Constants for Radical-MA Reactions at 60°C (bulk MA).[a]

| Radical | $k$ ($M^{-1}\ s^{-1}$) | no. experiments |
|---|---|---|
| $Ph\bullet$ | $1.9 \pm 0.2 \times 10^7$ | 4 |
| **primary alkyl radicals** | | |
| $CH_3\bullet$ | $3.0 \times 10^5$ | 1 |
| $tBuO\text{-}AM\bullet$ | $3.2 \times 10^5$ | 1 |
| $PhCO_2\text{-}AM\bullet$ | $2.2 \pm 0.2 \times 10^5$ | 4 |
| **$k_p(1)$** | | |
| $Ph\text{-}MA\bullet$ | $1.5 \pm 0.2 \times 10^4$ | 4 |
| $PhCO_2\text{-}MA\bullet$ | $3.7 \pm 0.6 \times 10^4$ | 4 |
| $tBuO\text{-}MA\bullet$ | $6.3 \times 10^4$ | 1 |
| **$k_p(2)$[b]** | | |
| $Ph\text{-}MA\text{-}MA\bullet$ | $1.4 \pm 0.2 \times 10^4$ | 2 |
| $PhCO_2\text{-}MA\text{-}MA\bullet$ | | |
| $PhCO_2\text{-}AM\text{-}MA\bullet$ | | |

[a] based on $k_T = 3 \times 10^8\ M^{-1}\ s^{-1}$ (see text).

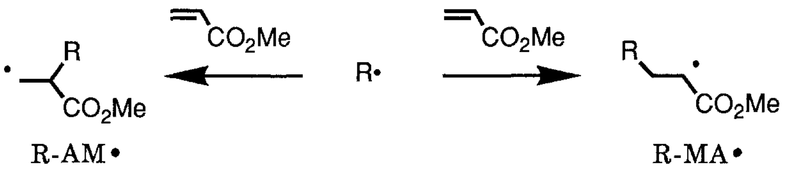
[b] The various 'trimeric products' were not individually resolved under the conditions of the HPLC analysis(20) and were determined as a group. To evaluate $k_p(2)$ it was assumed that $k_p(2)$ was independent of the initiating species.

The experiments with BPO initiator were conducted with four initial nitroxide concentrations; $[nitroxide]_o$ = 0.005, 0.01, 0.05 and 0.1M.(20) The $[nitroxide]_o$ was 2 x $[BPO]_o$. With $[nitroxide]_o \geq 0.05M$, the oligomers of length

>2 units were formed in yields too small to be reliably determined (<0.5% of total). The value of $[\text{nitroxide}]_{\text{final}}$ was ca. 0.4 x $[\text{nitroxide}]_0$. Thus, in order to calculate rate constants, $[\text{nitroxide}]_{\text{av}}$ was taken as 0.7 x $[\text{nitroxide}]_0$. In the experiment with DBPOX,(21) $[\text{nitroxide}]_0$ was 0.044 M and $[\text{DBPOX}]_0$ was 0.02 M (ca. 10% excess); $[\text{nitroxide}]_{\text{av}}$ was taken as 0.6 x $[\text{nitroxide}]_0$.

The main errors in evaluating $k_p$ values lie with the estimation of $[\text{nitroxide}]_{\text{final}}$ and hence $[\text{nitroxide}]_{\text{av}}$ (error ≤20%) and in the value for $k_T$. Experimental values of $k_T$ for the reactions of 2,2,6,6-tetramethylpiperidin-N-oxyl (TEMPO) and TMIO with simple alkyl radicals are ca. $1\text{x}10^9$ $M^{-1}$ $s^{-1}$ for non polar solvents(11-15) and up to ca 4-fold less in polar solvents at 80 °C.(14) In calculating $k_p$ values, the value $k_T$ has been taken as $3\text{x}10^8$ $M^{-1}$ $s^{-1}$ in methyl acrylate at 60 °C. However, there are indications that $k_T$ for sigma radicals (*eg.* phenyl, cyclopropyl)(15,22) may be significantly higher than $k_T$ for other carbon-centred radicals. Scaiano and Stewart(23) have determined the absolute rate constant for attack of phenyl on methyl methacrylate to be $1.8\text{x}10^8$ $M^{-1}$ $s^{-1}$ at 25°C in Freon 113 solvent. Relative reactivity data(20) then suggests a value for attack on MA of ca. $1\text{x}10^8$ $M^{-1}$ $s^{-1}$ at 25°C. Ignoring possible solvent effects on the addition rate constant, this suggests that $k_T$ for phenyl radical may be up to an order of magnitude greater than that for simple alkyl radicals.

The reaction scheme for the radical trapping experiment summarized in Scheme 1 illustrates the situation where initiation involves only tail addition. In practice the situation is often more complex depending on the particular radical and monomer involved.(8) Initiation of MA polymerization is complicated by a small proportion of radicals (5-15% depending on R) adding to the 'head' of the double bond to give the primary alkyl radical R-AM• (see Scheme 2).(20,21) The primary radicals R-AM• are much more reactive and add further MA substantially faster than the normal 'tail' adducts R-MA• (see Table 1).



**Scheme 2**

There have been a few previous studies on the absolute rate constants for radical reactions with MA. The values for primary alkyl attack on MA obtained in the present work appear in good agreement with these. The data of Citterio et al.(24) indicate that the absolute rate constants for 5-hexenyl radical addition to MA as 2.9 $\text{x}10^5$ $M^{-1}$ $s^{-1}$ at 25°C and 4.5 $\text{x}10^5$ $M^{-1}$ $s^{-1}$ at 69°C.(25) Baranek and Fischer(26) have examined the reactions of a simple model for an acrylate propagating species. They report that the $\bullet CH_2CO_2C(CH_3)_3$ radical adds MA with a rate constant of 2.3 x $10^5$ $M^{-1}$ $s^{-1}$ at 23°C in acetonitrile.(26)

On the other hand, the values of $k_p(1)$ and $k_p(2)$ (see Table 1) are more than an order of magnitude greater than $k_p$(overall) for MA polymerization (~$10^3$ $M^{-1}$ $s^{-1}$)(27) even allowing for experimental error. This is in accord with similar findings recently made for methacrylonitrile(7) and styrene polymerizations.(6)

The data for the various R-MA• radicals (see Table 1) show that the nature of the added radical has a substantial effect on the value of $k_p(1)$.

Nitroxides have advantages over most other trapping agents in the present context, in particular: they are extremely efficient scavengers;(20,21,28) the rate of scavenging shows no marked dependence on the radical structure or the reaction temperature;(11,14,15) they do not react directly with monomers except under forcing conditions.(29) There are, however, a number of factors which must be borne in mind when applying this technique:

(a) The initiator, nitroxide, and the reaction conditions should be selected for their compatibility. Certain initiators (*eg*. diacyl peroxides,(20,28,30) primary and secondary hyponitrites(31)) react with nitroxides to give by-products which may interfere with the product analysis.

(b) The initiating radicals should be selected for the specificity of its reaction with the monomer of interest so as to keep the product analysis as simple as possible.(8)

(c) the nitroxide concentrations required to obtain significant yields of oligomeric products are very low, especially with the less reactive monomers (*eg*. styrene(28,32)). As a consequence, the concentrations of products are also very low and this means that very sensitive analytical methods are required. Ideally the nitroxide should be used in excess to reduce errors in estimating the average nitroxide concentration.

(d) The formation of alkoxyamines is reversible at elevated temperatures (>100°C for MA with TMIO or TEMPO).(33) The importance of the reverse reaction depends on the structure of the nitroxide and the radical.(33,34) It is of particular concern when the propagating species is a tertiary radical (*eg*. methyl methacrylate(35)).

(e) While it has been demonstrated that the rate of trapping of radicals by nitroxides has no marked dependence on the radical structure,(12-14) the chain length independence of the reaction has not as yet been rigorously established.

(f) the rate constant $k_T$ is known to be solvent dependent(14) and should not be assumed to be the same for all monomers. The rate constant $k_T$ in polar solvents appears to be up to 3-fold lower than it is in nonpolar solvents.

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