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# STABILIZED RADICALS AS INHIBITORS OF POLYMERIZATION—REACTIONS OF ALKOXYAMINES WITH GROWING POLYMER RADICALS

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## ABSTRACT

Stabilized nitroxide radicals (TEMPO and its 4-hydroxy- and 4-oxo-derivatives) have been examined as inhibitors of the radical polymerization at 60°C of methyl methacrylate using azobisisobutyronitrile as initiator. Inhibition periods have been recorded and also the rates of the subsequent polymerizations and the molecular weights of the resulting polymers. It is concluded that alkoxyamines, formed during the inhibition, affect the polymerizations and lead to lowering of the molecular weights of the resulting polymers. The effect is attributed to a radical-displacement process involving the alkoxyamine and a growing polymer radical.

*Key Words*: Methyl methacrylate; Azonitrile; Nitroxides; Alkoxyamines

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## INTRODUCTION

An account has been given[1] of a systematic examination of the stabilized radicals 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and 2,2-diphenyl-1-picrylhydrazyl (DPPH) as inhibitors of polymerizations at 60°C of methyl methacrylate (MMA), styrene (STY) and acrylonitrile (ACN) using azobisisobutyronitrile (AIBN) as initiator. The study is now extended to include MMA with other nitroxides viz. the 4-hydroxy- and 4-oxo- derivatives of TEMPO (referred to as TEMPOL and TEMPONE respectively). These substances could be useful in several connections including determination of the rates of production of radicals in various systems. Nitroxides have been used successfully as radical-traps in studies of the precise natures of the initiating processes in radical polymerizations.[2] There is great interest in the alkoxyamines formed by the combination of nitroxides with carbon-centred radicals including those produced by dissociation of typical initiators such as AIBN; these products are significant in connection with nitroxide-mediated living free radical polymerization, a subject which has been comprehensively reviewed by Hawker, Bosman and Harth.[3] Any study of the involvement of nitroxides in radical polymerizations is likely to be relevant to the full understanding of these mediated polymerizations which form a very important development in the control of polymerizations proceeding by radical mechanisms. It appears that nitroxides are not particularly effective for controlling the polymerization of MMA but that monomer has been used in the present work because it is especially suitable for study of inhibition in radical polymerizations.

When using TEMPO or DPPH at low concentrations with AIBN at a fixed concentration, inhibition of polymerization lasted for a time proportional to the initial value of [inhibitor] for systems involving MMA, STY or ACN. The results were consistent with the belief that each ‘‘available’’ radical derived from the azonitrile reacts with one molecule of the inhibitor. The polymerizations subsequent to inhibition were slightly retarded when either TEMPO or DPPH was used. The polymers had molecular weights appreciably below those of polymers formed in appropriate blank experiments in which inhibitors had not been present; the effects were particularly evident when using TEMPO.

Replacement of AIBN by benzoyl peroxide (BPO) as initiator led to complications. They were expected in view of the fact that nitroxides do not react directly with oxygen-centred radicals, such as benzoyloxy, and the discovery that nitroxides can induce the decomposition of BPO.[4] It has been found that the duration of inhibition for systems involving BPO and nitroxides depends markedly on the nature of the diluent used in the polymerization; this work will be described in a separate publication.

TEMPONE undergoes changes if kept in benzene solution at 80°C for several hours.[5] Tests have been performed to discover whether the reactions are appreciable at 60°C and have serious implications in connection with the use of TEMPONE as an inhibitor at that temperature.

Benzene formed about 75% by volume of the systems involving AIBN with TEMPO or DPPH and with MMA or STY; when ACN was used, dimethylformamide (DMF) was the principal diluent (about 75% by volume) although a small amount of benzene (about 5% by volume) was also present.[1] In most of the subsequent experiments, benzene has been replaced by toluene. Consideration has been given to the possibility that change of diluent might affect the results when using AIBN with nitroxides.

## EXPERIMENTAL

Monomeric MMA, solvents and AIBN were purified by standard procedures. TEMPO was used as previously.[1] TEMPOL and TEMPONE (Aldrich) were used as received; the latter was examined by TLC using ethyl acetate as solvent and a 2:1 mixture of hexane with ethyl acetate as eluent; no impurities were detected. Stock solutions of TEMPOL and TEMPONE had concentrations in the region of $1\,\mathrm{g\,dm^{-3}}$ and normally were stored at $-10$°C.

Polymerizations and recovery of polymers were performed as already described[1] as were the examinations of polymers by Size Exclusion Chromatography. Inhibition periods were recorded as the points of intersection with the time axis of the linear plots of contraction vs. time for the subsequent polymerizations.

## RESULTS AND DISCUSSION

Table 1 refers to polymerizations at 60°C of MMA initiated with AIBN. The results were used with others to construct Fig. 1 which shows the linear dependence of the inhibition period upon [inhibitor]/[AIBN]. The inhibition periods caused by TEMPOL and TEMPONE match quite well those associated with TEMPO and DPPH previously reported.[1] The slope of the line drawn in Fig. 1 is 1500 min. There is no indication that the duration of inhibition depended upon which nitroxide was used. It is possible that inhibition was slightly prolonged when DMF was used as diluent during the polymerization (consider points labelled "c" and "f" in Fig. 1) but any effect was very small compared with those found when BPO was used as initiator. Any effect of the diluent upon the duration of the inhibition must have been caused by small variations in the rate of production from AIBN of "available" radicals. The inhibition period was unaffected by [MMA].

Experiment 9 was designed to test the stability of TEMPONE. The system for polymerization was made using a $7.56 \times 10^{-3}\,\mathrm{M}$ solution of the nitroxide in toluene; the solution had been kept under aerobic conditions at 60°C for 18 h, and then at about 20°C for 7 days. It is evident that the results

***Table 1.*** Experiments with Methyl Methacrylate, Azobisisobutyronitrile, and Nitroxides

| Expt. No. | Nitroxide/ Diluent | $10^2$[Nitroxide]/ [AIBN] | (Inhibition Period)/min | $10^5R_p$/ (mol dm$^{-3}$s$^{-1}$) | DP$_n$ |
|---|---|---|---|---|---|
| 1 | –/TOL | 0 | 0 | 19.77 | 1260 |
| 2 | –/TOL | 0 | 0 | 19.25 | ** |
| 3 | T1/TOL | 3.04 | 44 | 17.62 | 1055 |
| 4 | T1/TOL | 5.65 | 77 | 18.98 | 872 |
| 5 | T1/TOL | 8.69 | 125 | 18.38 | 735 |
| 6 | T1/DMF | 5.80 | 71 | 22.50 | 893 |
| 7 | T1/DMF | 7.06 | 87 | 20.18 | 716 |
| 8 | T2/TOL | 4.43 | 66 | 18.42 | 747 |
| 9* | T2/TOL | 6.06 | 84 | 18.18 | 644 |
| 10 | T2/TOL | 6.52 | 88 | 17.96 | 705 |
| 11 | T2/TOL | 7.56 | 103 | 19.25 | 614 |

[MMA] = 4.68 mol dm$^{-3}$; [AIBN] = $1.60 \times 10^{-2}$ mol dm$^{-3}$.
T1 = TEMPOL; T2 = TEMPONE.
TOL = toluene; DMF = dimethylformamide.
*TEMPONE solution pretreated at 60°C, see text.
**Polymer not recovered.

are generally in line with those obtained using a stock solution which had been stored at −10°C except for the short periods when it was being dispensed. For the purpose of the present study, there seems to be no serious problem about the stability of TEMPONE.

There are discrepancies between the rates of some of the polymerizations but plainly the rates were not greatly affected by the presence of TEMPOL or TEMPONE at the levels used in the present work. The quoted inhibition periods and the degrees of polymerization show only slight inconsistencies. The uncertainties about rates may have arisen from deficiencies in the experimental procedures.

It is clear that, after inhibition by TEMPO or one of its derivatives, polymers were formed with average molecular weights substantially below those for the products of blank experiments (see Table 1 and Table 1 in Ref. 1). A similar, but somewhat smaller, effect was apparent for polymers from systems in which DPPH had been used.[1] There must have been losses of some smaller polymer molecules during the recovery of polymers by precipitation in methanol[6] so that the quoted values of DP$_n$ are a little greater than the "true" values for the whole polymers. The differences would have been similar for all the samples in a set and they are not considered further in this discussion.

The effects on molecular weights must have been due to a substance formed during the inhibition. It is necessary to consider the possibility that a substance produced by geminate interaction of "wasted" radicals formed from AIBN may have been responsible. A test was made by performing a

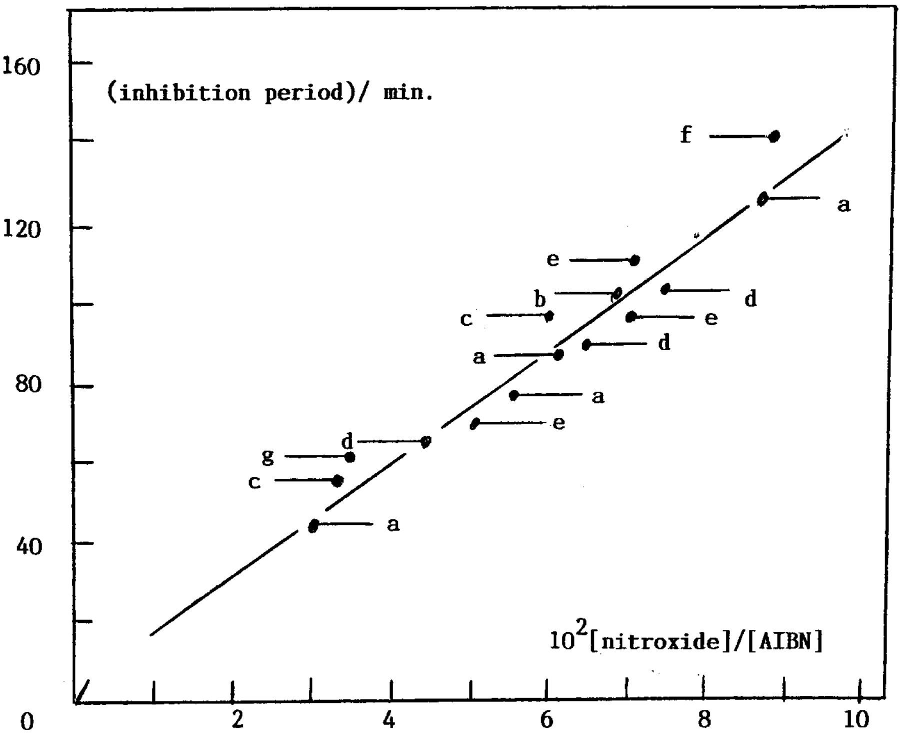

*Figure 1.* Plot of inhibition period vs. [inhibitor]/[initiator] for polymerization at 60°C of methyl methacrylate with azobisisobutyronitrile and nitroxides. Points labelled a or d–[MMA] = 4.68 mol $dm^{-3}$ and [AIBN] = $1.60 \times 10^{-2}$ mol $dm^{-3}$ labelled b, c, e, f, or g–[MMA] = 2.46 mol $dm^{-3}$ and [AIBN] = $0.90 \times 10^{-2}$ mol $dm^{-3}$ a–TEMPOL/toluene; b–TEMPOL/benzene; c–TEMPOL/DMF; d–TEMPONE/toluene; e–TEMPONE/benzene; f–TEMPONE/DMF; g–TEMPO/benzene.

polymerization using AIBN which had been kept at 60°C in an air-free solution in benzene for 2 h. The results were compared with those for a parallel experiment in which the initiator had not been subjected to prior treatment at 60°C. Various products would have been formed from AIBN during the pretreatment but only the ketenimine $Me_2C(CN){\cdot}N{:}C{:}CMe_2$ is likely to have any great effect on the system; it is known to dissociate into radicals at about the same rate as AIBN.[7]

The rate of the polymerization involving pretreated AIBN was $7.81 \times 10^{-5}$ mol $dm^{-3}s^{-1}$ and $DP_n$ for the resulting polymer was 727; for the control experiment, the corresponding quantities were $7.44 \times 10^{-5}$ mol $dm^{-3}s^{-1}$ and 769. The results show that the low values of the molecular weights for polymers formed after inhibition by nitroxides cannot be attributed to effects caused by products derived from AIBN. It must be concluded that the depressions of the molecular weights were caused by a substance formed by reaction of a radical derived from AIBN with the nitroxide during the inhibition. There might also have been small contributions from products formed in reactions of the smallest polymer radicals with the inhibitor; the discussion which follows does not include the possibility but it could readily be adapted to do so. An alkoxyamine produced by combination of a nitroxide with a 2-cyano-2-propyl radical can be represented as X·O·R where R- is the radical formed from the initiator. In those cases where DPPH had been the inhibitor, the substance causing the effect is likely to be the substituted hydrazine (1).

$$p.\mathrm{R.C_6H_4{\cdot}N(C_6H_5){\cdot}NH{\cdot}C_6H_2(NO_2)_3} \tag{1}$$

It is reasonable to suppose that the molar concentration of X·O·R produced during the inhibition was very close to that of the nitroxide originally present. If the alkoxyamine had engaged in transfer with growing polymer radicals, the transfer constant could be found by considering the degrees of polymerization of the polymers in a set produced from systems differing only in the concentration of inhibitor originally present. A plot of $1/DP_n$ vs. [inhibitor]/[monomer] would be expected to be linear and the slope of the line would give the transfer constant $k_f/k_p$.

Figure 2 is based on results given either in Table 1 or previously;[1] it shows that linear plots are obtained for cases involving TEMPO, TEMPOL or DPPH and probably also for those in which TEMPONE was used. There are unusually high values for the transfer constants viz. 3.0 for TEMPO, 2.0 for TEMPOL, 3.4 for TEMPONE and 0.75 for DPPH; in each case MMA was the monomer. An attempt was previously made[8] to determine transfer constants for 2,2-diphenyl-1-picrylhydrazine (DPPH-H), a substance related to the substituted hydrazine (1) believed to be a major product of the reaction between DPPH and 2-cyano-2-propyl radicals; DPPH-H is known to have quite large effects on radical polymerizations. There was uncertainty about the results but the transfer constant may have been in the region of 0.3 for MMA. It is reasonable to suppose that (1) could readily give up a hydrogen atom to a growing polymer radical. Such a process would of course lead to a polymer of reduced molecular weight but there would also be retardation because the radical produced from (1) would be stabilized and therefore inefficient in re-initiation. It seems likely therefore that the product formed from DPPH engages in transfer involving hydrogen-abstraction, although the transfer is degradative.

It is improbable that an alkoxyamine, made by combination of 2-cyano-2-propyl radicals with TEMPO or similar substance, could engage very readily in transfer of a conventional type. It is suggested that actually it reacts with a growing polymer radical by a radical-displacement process thus:

$$\mathrm{X{\cdot}O{\cdot}CMe_2{\cdot}CN} + \mathrm{P_n}{\cdot} \rightarrow \mathrm{P_n{\cdot}O{\cdot}X} + {\cdot}\mathrm{CMe_2{\cdot}CN} \tag{2}$$

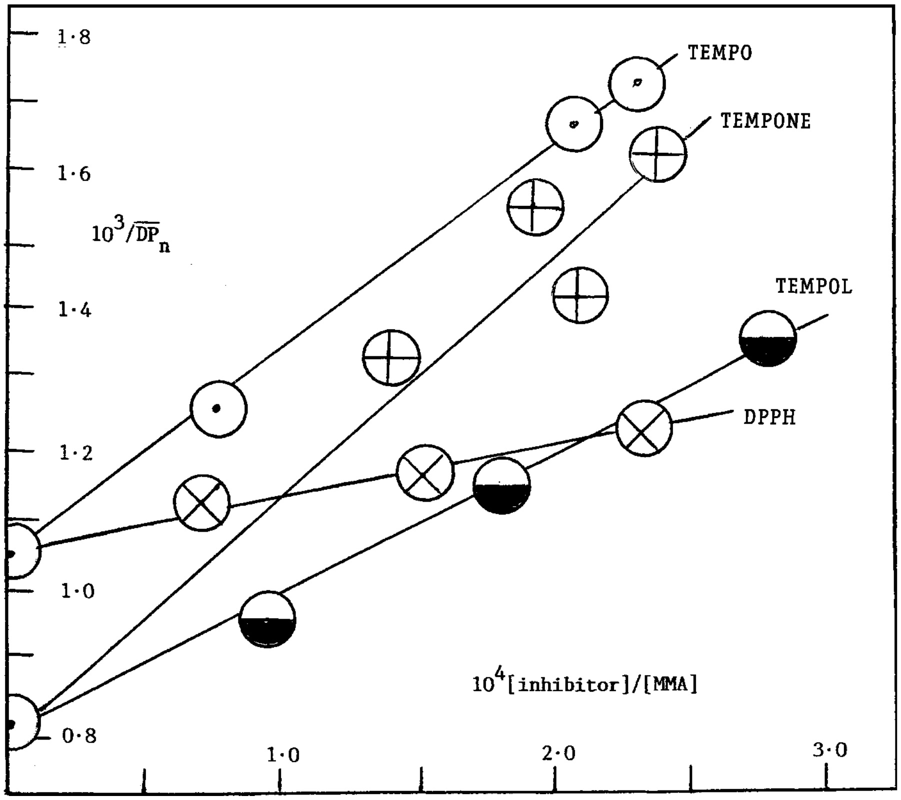

*Figure 2.* The dependence on the initial value of [inhibitor] of the molecular weight of poly(methyl methacrylate) formed after inhibition by a stabilized radicals, using azobisisobutyronitrile as initiator; plots of (degree of polymerization)$^{-1}$ vs. [inhibitor]/[monomer]. TEMPO and DPPH used in benzene with [MMA] = 2.46 mol dm$^{-3}$ and [AIBN] = 0.90 × 10$^{-2}$ mol dm$^{-3}$ TEMPOL and TEMPONE used in toluene with [MMA] = 4.68 mol dm$^{-3}$ and [AIBN] = 1.60 × 10$^{-2}$ mol dm$^{-3}$.

a reaction which would be close to thermo-neutral. The resulting 2-cyano-2-propyl radical would re-initiate efficiently so that the overall polymerization would not be retarded. Typical alkoxyamines can undergo thermal dissociation at slightly elevated temperatures so that the process shown in Eq. (2) is quite reasonable. A similar process, represented thus:

$$P_n{\cdot}O{\cdot}X + P_m{\cdot} \rightarrow P_m{\cdot}O{\cdot}X + P_n{\cdot}$$

has been suggested[9] as occurring during the nitroxyl-mediated polymerization of STY. An alternative to reaction (2), leading to the products $X{\cdot}O{\cdot}$ and $P_n{\cdot}O{\cdot}CMe_2{\cdot}CN$, is rejected because the radical $X{\cdot}O{\cdot}$ would fail to re-initiate so causing retardation, an effect which was not observed.

A test of the present suggestion that reaction (2) is important would require analyses for end-groups in the polymers formed subsequent to inhibition by a nitroxide. Most of the molecules should have end-groups derived directly from the nitroxide; each molecule is expected to have an end-group $Me_2C(CN)$-derived in some cases from thermal dissociation of AIBN followed by initiation of polymerization and in others from reaction (2) involving alkoxyamine produced during inhibition. The total rate of incorporation ($R_{inc}$) of initiator fragments into polymer should therefore be appreciably greater than the rate of initiation associated with the particular rate of polymerization. The measurements of $R_{inc}$ could readily be made by a well established procedure involving the use of $^{14}$C-AIBN.[10]

## CONCLUSIONS

Stabilized nitroxide radicals (TEMPO and its 4-hydroxy- and 4-oxo-derivatives) are confirmed as effective inhibitors of radical polymerizations initiated at 60°C by azobisisobutyronitrile. The rates of the subsequent polymerizations are almost unaffected by the alkoxyamines believed to be formed during the inhibition but there are considerable reductions in the molecular weights of the polymers. It appears that a radical-displacement occurs readily between a growing polymer radical and an alkoxyamine; the process resembles a reaction regarded as important during nitroxyl-mediated polymerization of styrene. When diphenylpicrylhydrazyl is used, a substituted hydrazine is formed during the inhibition and subsequently acts as a degradative transfer agent retarding the polymerization and giving polymer of quite low molecular weight.

## REFERENCES

1. Bevington, J.C.; Hunt, B.J. Examination of Some Stabilized Radicals as Inhibitors of Polymerizations. J. Polym. Mater. **2002**, *19*, 113–120.
2. Rizzardo, E.; Solomon, D.H. A New Method for Investigating the Mechanism of Initiation of Radical Polymerization. Polym. Bull. (Berlin) **1979**, *1*, 529–534.
3. Hawker, C.J.; Bosman, A.W.; Harth, E. New Polymer Synthesis by Nitroxide Mediated Living Radical Polymerization. Chem. Rev. **2001**, *101*, 3661–3688.
4. Rozantsev, E.; Gol'dfein, M.D.; Trubnikov, A.V. Stable Radicals and the Kinetics of Radical Polymerization of Vinyl Monomers. Russ. Chem. Rev. **1986**, *55*, 1070–1079.
5. Rozantsev, E.G.; Sholle, V.D. Synthesis and Reactions of Stable Nitroxyl Radicals. II. Reactions. Synthesis **1971**, 401–414.
6. Barson, C.A.; Bevington, J.C; Hunt, B.J. Efficacy of Precipitation in Non-solvents for the Recovery of Polymers from Solution. Eur. Polym. J. **1996**, *32*, 1055–1059.
7. Moad, G.; Solomon, D.H. The Chemistry of Free Radical Polymerization; Pergamon: Oxford, 1955; p. 225.

8. Barson, C.A.; Bevington, J.C.; Hunt, B.J. Application of a New Approach to the Determination of Transfer Constants for Systems showing Retardation. J. Polym. Sci., A, Polym. Chem. **1996**, *34*, 227–235.
9. Li, I.; Howell, B.A.; Matyjaszewski, K.; Shigemoto, T.; Smith, P.B.; Priddy, D.B. Kinetics of Decomposition of 2,2,6,6,-tetramethyl-1-(1-phenylethoxy)-piperidine and its Implications on Nitroxyl-mediated Styrene Polymerization. Macromolecules **1995**, *28*, 6692–6693.
10. Bevington, J.C. Initiation of Polymerization; Azo Compounds and Peroxides. Makromol. Chem., Macromol. Symp. **1987**, *10/11*, 89–107.

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