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Effects of stabilized radicals upon polymerizations initiated by benzoyl peroxide

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Abstract

A study has been made of the inhibitory effects of diphenylpicrylhydrazyl and certain nitroxides upon systems at 60 °C involving benzoyl peroxide with methyl methacrylate, styrene or acrylonitrile. The pattern of results is rather different from that found in corresponding experiments with azobisisobutyronitrile as the source of radicals. When using the peroxide, relationship between duration of inhibition and the value of [inhibitor]/[peroxide] is in some cases far from linear; there is a dependence on the polarity of the diluent used for the reaction. It appears that there are probably direct reactions between the peroxide and the nitroxides which cannot therefore be regarded as ideal inhibitors in systems involving benzoyl peroxide. Products derived from the inhibitors affect the subsequent polymerizations. When the hydrazyl is used, the polymerizations following inhibition are retarded; the retardation is very slight in systems involving a nitroxide. For both types of inhibitor, the molecular weights of the polymers are quite low; the nitroxides differ from the hydrazyl in giving rise to poly(methyl methacrylate)'s having comparatively low values of $\bar{M}_w/\bar{M}_n$.

Keywords: Radical polymerization; Inhibition; Nitroxides

1. Introduction

Stabilized radicals have been re-examined as inhibitors of radical polymerizations initiated by azobisisobutyronitrile (AIBN) at 60 °C [1,2]. The monomers were methyl methacrylate (MMA), styrene (STY) and acrylonitrile (ACN); the stabilized radicals of greatest interest were certain nitroxides, viz. 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and its 4-hydroxy- and 4-oxo- derivatives referred to as TEMPOL and TEMPONE respectively but diphenylpicryhydrazyl (DPPH) also was used. A linear relationship between the duration of inhibition and the initial value of [inhibitor]/[AIBN] was found with only slight variations with the natures of the monomer, inhibitor and diluent and with the concentrations of the individual reactants. It was deduced that the value of $k_d f$ in the expression rate of production of 'available' radicals $= 2k_d f$[AIBN] is close to 1.00×10^{-5} s^{-1}, a value consistent with that selected by Moad and Solomon [3] 'available' refers to radicals which escape geminate recombination and so can react with scavengers such as monomers and inhibitors.

When DPPH was used, polymerizations subsequent to inhibition were appreciably slower than those in the appropriate blank experiments not involving inhibitors but there were only very small effects for cases in which a nitroxide had been present. The polymers produced after inhibition had average molecular weights below those of the products from the uninhibited reactions; the effects were larger when a nitroxide had been used than when DPPH had been present. The effects on molecular weights and rates were explained by considering reactions of growing polymer radicals with products formed from the stabilized radicals during the inhibition.

The present report deals with an extension of the study, using benzoyl peroxide (BPO) as initiator; the results may be of wider significance since some of the early work on nitroxide-mediated polymerization depended upon the use of the peroxide with TEMPO to form an alkoxyamine which could dissociate at higher temperatures to radicals [4]. This

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procedure has been superseded and there has been development of special nitroxides which can dissociate at suitable temperatures to give nitroxides and reactive radicals [5].

The present study was prompted by the fact that there has been only limited examination of nitroxides as inhibitors of radical polymerization although they have been used to good effect as radical scavengers in studies of the radicals produced from various initiators [6]. Systems including BPO may show complexities not found when using AIBN because the dissociation of BPO is much more sensitive than that of AIBN to the nature of the medium and also because induced decomposition of the peroxide is quite common. Other complications arise from the possibility of the benzoyloxy radicals formed from BPO dissociating further to give phenyl radicals, the extent of the decarboxylation depending upon the nature of the environment. There is also the likelihood that the benzoyloxy radical does not combine directly with a nitroxide to give a stable product.

2. Experimental

No new experimental procedures were developed during this work; they were as described previously [1,2]. Monomers were washed appropriately to remove stabilizers and then dried and distilled. Diluents were distilled. BPO was recrystallized from methanol. Inhibitors were used as received from Aldrich. Polymerizations were performed at 60 °C under anaerobic conditions in dilatometers; consumption of monomer was restricted to 6%. Inhibition periods are quoted without allowance for the short time (about 5 min) required for the contents of dilatometers to reach the working temperature. Rates of polymerization were calculated from rates of contraction assuming that the conversion factor for a particular monomer is unaffected by change of diluent. Polymers were recovered by precipitation in methanol.

Values of $\bar{M}_n$ for polymers were obtained by size exclusion chromatography (SEC) by reference to standard samples of polyMMA having narrow distributions. The equipment consisted of a Waters pump, Gilson autosampler and Erma refractive index detector; the columns contained PL gel mixed B (Polymer Laboratories) and tetrahydrofuran was used as eluent. Data were analyzed with a Polymer Laboratories Data Station using Caliber software.

3. Results

Fig. 1 refers to experiments in which BPO and DPPH were used with MMA, STY or ACN. The relationship between the inhibition period (IP) and the initial value of [DPPH]/[BPO] is close to linear (line 'A') for systems in which benzene was used as diluent for either MMA or STY

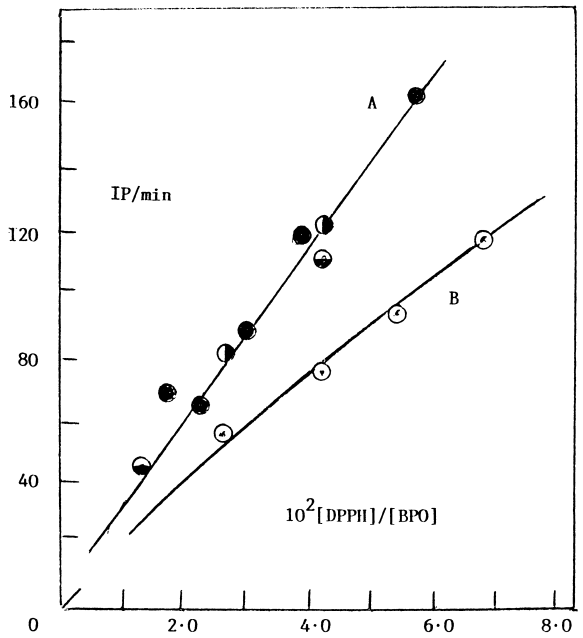


Fig. 1. Inhibition period vs [DPPH]/[BPO]: (●) [MMA] = 2.46 mol dm^{-3}, 10^2 [BPO] = 1.80 mol dm^{-3} in benzene; (◒) [STY] = 3.20 mol dm^{-3}, 10^2 [BPO] = 2.70 mol dm^{-3} in benzene; (◑) [ACN] = 4.15 mol dm^{-3}, 10^2 [BPO] = 2.50 mol dm^{-3} in benzene/DMF; (⊙) [MMA] = 2.46 mol dm^{-3}, 10^2 [BPO] = 2.50 mol dm^{-3} in DMF.

and a mixture of benzene with dimethylformamide (DMF) (1 to 2 parts by vol) for ACN. The slope of line 'A' is 2780 min. The IP's were much shorter when DMF replaced benzene as diluent for polymerizations of MMA; line 'B' refers to systems MMA/DMF and has a slope of 1620 min. Following inhibition, the rate of polymerization (R_p) was depressed as shown in Fig. 2 for MMA with either benzene or DMF as diluent.

Plot 'C' in Fig. 3 shows IP vs [TEMPO]/[BPO] for cases when MMA or STY was used with benzene as diluent. There was no apparent dependence of IP upon the nature of the monomer or its concentration. Values of R_p after

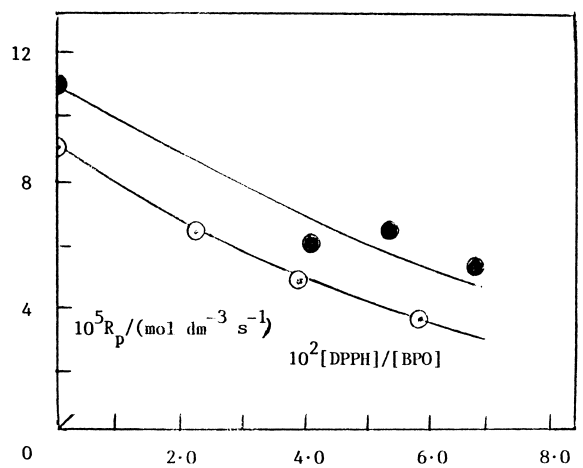


Fig. 2. Rate of polymerization of MMA at 2.46 mol dm^{-3} after inhibition by DPPH at various concentrations with BPO at 1.80×10^{-2} mol dm^{-3} (⊙) in benzene; (●) in DMF.

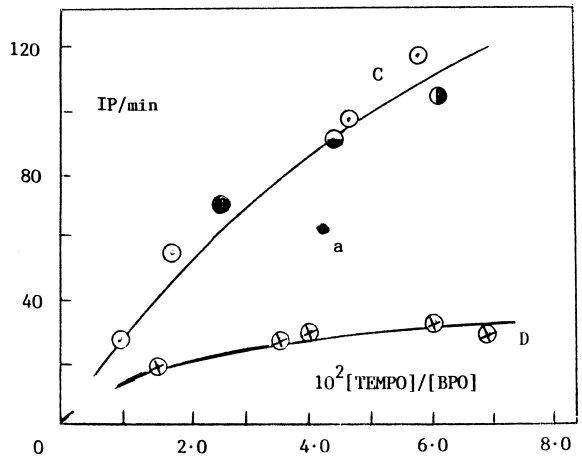


Fig. 3. Inhibition period vs [TEMPO]/[BPO]; (⊙) [MMA] = 2.46 mol dm^{-3}, 10^2 [BPO] = 1.80 mol dm^{-3} in benzene; (◑) [MMA] = 6.20 mol dm^{-3}, 10^2 [BPO] = 2.40 mol dm^{-3} in benzene; (◒) [STY] = 3.33 mol dm^{-3}, 10^2 [BPO] = 2.60 mol dm^{-3} in benzene; (●) [STY] = 5.00 mol dm^{-3}, 10^2 [BPO] = 2.60 mol dm^{-3} in benzene; (⊗) [ACN] = 4.15 mol dm^{-3}, 10^2 [BPO] = 2.85 mol dm^{-3} in DMF.

inhibition were only slightly affected by the earlier presence of TEMPO. When benzene was progressively replaced by DMF while [MMA], [BPO] and [TEMPO] were fixed, the IP became shorter. For the experiment leading to point 'a' in Fig. 3, tetrahydrofuran (57% by vol of the reaction mixture) was used with benzene (16% by vol) and MMA. Plot 'D' in Fig. 3 refers to systems containing ACN with DMF as the sole diluent. The IP's were only about 30 min with little variation over the range 1.00×10^{-2}–7.00×10^{-2} for [TEMPO]/[BPO]. Gradual replacement of DMF by benzene while [ACN], [BPO] and [TEMPO] were fixed led to lengthening of the IP. The initial presence of TEMPO had very little effect on R_p after inhibition for any of the sets of experiments.

Figs. 4 and 5 are concerned with systems containing TEMPOL or TEMPONE respectively; they show the

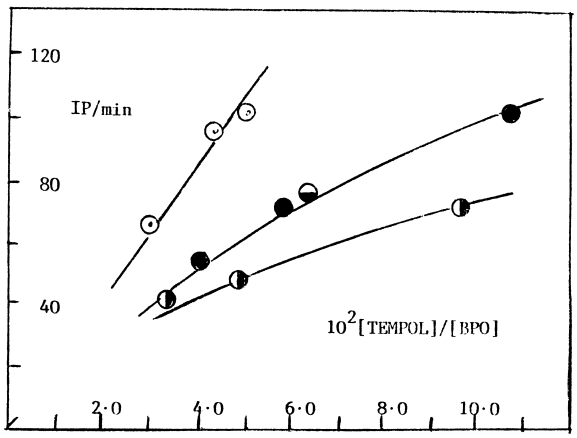


Fig. 4. Inhibition period vs [TEMPOL]/[BPO]; (⊙) [MMA] = 2.34 mol dm^{-3}, 10^2 [BPO] = 2.58 mol dm^{-3} in toluene; (●) [MMA] = 2.46 mol dm^{-3}, 10^2 [BPO] = 1.75 mol dm^{-3} in DMF; (◒) [STY] = 2.28 mol dm^{-3}, 10^2 [BPO] = 2.10 mol dm^{-3} in DMF; (◑) [ACN] = 4.15 mol dm^{-3}, 10^2 [BPO] = 1.85 mol dm^{-3} in DMF.

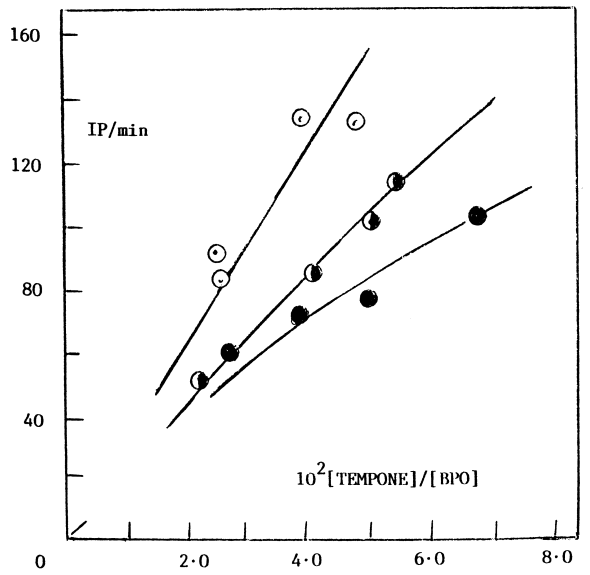


Fig. 5. Inhibition period vs [TEMPONE]/[BPO]; (⊙) [MMA] = 2.46 mol dm^{-3}, 10^2 [BPO] = 1.80 mol dm^{-3} in benzene;(●) [MMA] = 2.46 mol dm^{-3}, 10^2 [BPO] = 1.80 mol dm^{-3} in DMF; (◑) [ACN] = 4.15 mol dm^{-3}, 10^2 [BPO] = 1.80 mol dm^{-3} in DMF.

dependence of IP on the initial value of [nitroxide]/[BPO]. In all cases, the presence of a nitroxide in the original mixture had only a small effect on the subsequent value of R_p.

Values of $\overline{M}_n$ for polymers of MMA formed after inhibition were much less than those for polymers produced in corresponding experiments without inhibitor; the effects were found for each of the four stabilized radicals (see Table 1). It was also found that, for cases in which [MMA] and [BPO] were fixed, $\overline{M}_w/\overline{M}_n$ of the polymer decreased with increasing initial concentration of a nitroxide but increased slightly if the initial value of [DPPH] was raised. Each of the

Table 1
Average molecular weights of polymers of methyl methacrylate, formed after inhibition

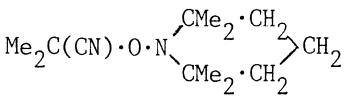
Inhibitor	10^2 [inhibitor]/[BPO]	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
–[a]	0	109,800	1.81
DPPH[a]	2.70	41,600	1.98
DPPH[a]	4.97	32,300	1.99
TEMPO[a]	1.02	78,400	1.72
TEMPO[a]	2.20	55,600	1.50
TEMPO[a]	4.50	41,600	1.46
TEMPONE[a]	3.96	40,900	1.47
TEMPONE[a]	4.91	38,900	1.44
–[b]	0	83,300	1.90
TEMPOL[b]	3.26	50,000	1.73
TEMPOL[b]	4.62	34,200	1.64
TEMPOL[b]	5.29	36,900	1.59
–[c]	0	93,400	1.95
TEMPOL[c]	4.11	46,100	1.63
TEMPOL[c]	5.60	39,000	1.59

[a] 10^2 [BPO] = 1.80 mol dm^{-3}; [MMA] = 2.46 mol dm^{-3}; benzene.
[b] 10^2 [BPO] = 2.60 mol dm^{-3}; [MMA] = 2.34 mol dm^{-3}; toluene.
[c] 10^2 [BPO] = 1.80 mol dm^{-3}; [MMA] = 2.46 mol dm^{-3}; DMF.

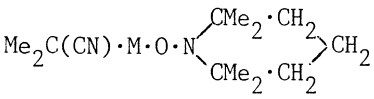
chromatograms had a single peak; most of them showed no unusual features but, in a few cases, there was slight distortion of the trace on the side of the peak corresponding to low molecular weights.

4. Discussion

The 2-cyano-2-propyl radical formed from AIBN probably adds to DPPH to give the substituted hydrazine *p*-$Me_2C(CN)-C_6H_4-NPh-NH-C_6H_2(NO_2)_3$ and to nitroxides to give alkoxyamines such as (I). If a monomer (M) is present, some of the appropriate alkoxyamine (II) also may be produced with related products containing more than one monomeric unit.



(I)



(II)

There are complications when BPO is the source of radicals, the first being that the peroxide can give rise to radicals of two types, viz. Ph–CO–O$^{\cdot}$ and Ph$^{\cdot}$

When very dilute solutions of BPO in a solvent such as benzene are kept at 60 °C, almost all the resulting benzoyloxy radicals undergo decarboxylation to give phenyl radicals. The yield of carbon dioxide is reduced if radical scavengers such as DPPH are present in the solution [7]. The hydrazyl can react directly with the benzoyloxy radical, probably to give the substituted hydrazine *p*-Ph–CO–O–C_6H_4–NPh–NH–$C_6H_2(NO_2)_3$ although there may be some of a similar product with Ph– replacing Ph–CO–O$^{\cdot}$–.

A stable product is unlikely to result from combination of a nitroxide with an oxygen-centred radical such as benzoyloxy. In a system containing monomer, BPO and a nitroxide, there are several possibilities. The inhibitor may combine with the radical Ph–CO–O–M$^{\cdot}$ formed by addition of the benzoyloxy radical to the monomer, with the phenyl radical produced from a benzoyloxy radical or with the radical Ph–M$^{\cdot}$. For MMA at 2–5 mol dm^{-3} in benzene or toluene at 60 °C, about 60% of the benzoyloxy radicals are expected to dissociate [8] so that the alkoxyamines containing the benzoate group and those containing the derived phenyl group are expected to be in the approximate proportions 2:3. STY is considerably more reactive than MMA towards Ph–CO–O$^{\cdot}$ so that the decarboxylation is less important when using STY at the same concentration as MMA; the products analogous with those considered for MMA are expected in the proportions of about 6:1. ACN is much less reactive than MMA towards Ph–CO–O$^{\cdot}$ so that the decarboxylation of that radical is not greatly suppressed and the dominant alkoxyamines are likely to be Ph–CH_2–CH(CN)–O–NQ and Ph–O–NQ where the nitroxide is represented as $^{\cdot}$O–NQ.

The plots of IP vs [DPPH]/[BPO] were close to linear when MMA was used with benzene or with DMF as diluent but the IP's were shorter for the latter (see Fig. 1). The rate constant for the dissociation of BPO can be found by a simple procedure using a linear plot of IP vs [inhibitor]/[BPO] for results which refer to a range of times over which the extent of decomposition of BPO is quite small, as in the cases being considered. It is supposed that dissociation of a molecule of BPO gives two radicals each of which directly or indirectly deactivates one molecule of inhibitor. Line 'A' in Fig. 1 indicates an IP of 100 min for an initial value of 3.4×10^{-2} for [DPPH]/[BPO] in benzene; thus, over a period of 100 min, 1 mol of BPO gives radicals sufficient to deactivate 3.4×10^{-2} mol of DPPH. The derived value of 2.8 s^{-1} for $10^6 k_d$ differs from those in the range 1.5–2.0 s^{-1} obtained by other methods thought to be sound. [7,9] Line 'B' in Fig. 1 refers to systems involving DMF; an initial value of [DPPH]/[BPO] of 5.8×10^{-2} corresponds to an IP of 100 min so that $10^6 k_d$ would be 4.8 s^{-1}, i.e. appreciably greater than when benzene was used as diluent.

Bamford and White [10] showed that there is a rapid decomposition of BPO in DMF in the absence of scavengers, explaining it in terms of a chain reaction having the propagation steps

$$\text{Ph–CO–O}^{\cdot} + \text{H–CO–NMe}_2 \rightarrow \text{Ph–CO–OH} + \text{H–CO–NMe–CH}_2^{\cdot}$$

$$\text{H–CO–NMe–CH}_2^{\cdot} + (\text{Ph–CO–O})_2 \rightarrow \text{H–CO–NMe–CH}_2\text{–O–CO–Ph} + \text{Ph–CO–O}^{\cdot}$$

The suppression of the rapid decomposition when scavengers are present indicates that the induced decomposition cannot be the cause of the difference between the cases of benzene and DMF as diluents in the systems considered here.

The rate of dissociation of any initiator into radicals must be affected to some extent by the nature of the medium. The change from reactant to transition state is associated with activation parameters which are dependent in magnitude upon the nature of the medium because of solvation effects; the consequent variations in rate of production of radicals are unlikely however to be sufficient to account for the differences in IP so evident for the systems under consideration. The results are consistent with the view that DPPH, even at low concentrations, may induce the dissociation of BPO into radicals and that the process may be favoured in a polar solvent such as DMF.

Some of the plots of IP vs [nitroxide]/[BPO] show marked curvature and comparatively short IP's; the plots cannot be used in the simple procedure for determining k_d

for the peroxide. For each of the three nitroxides used here with MMA and BPO, replacement of benzene or toluene by the polar DMF resulted in substantial reduction in IP; some reduction was caused when a solvent of intermediate polarity viz. tetrahydrofuran was present. IP's were particularly short when ACN was used with TEMPO; the shortening was less evident for ACN/TEMPOL and almost absent for ACN/TEMPONE. The effects on IP might be explained by supposing that the nitroxides could promote the dissociation of BPO, especially in polar media, to an extent depending upon the precise nature of the nitroxide and its concentration. Another explanation might be based upon the possibility that the nitroxides could be consumed by direct reactions with BPO as well as by reactions with small radicals formed as a result of the dissociation of the peroxide.

Rozantsev et al. [11] discussed the many complexities found when BPO is used with nitroxides. They proposed the formation of donor–acceptor complexes

$$\dot{O}\text{–NQ} + \text{BPO} \rightleftharpoons \text{complex} \rightarrow \dot{O}\text{–NQ} + 2\ \text{Ph–CO–O}^{\cdot}$$

where $\dot{O}$–NQ represents a nitroxide. They suggested that dissociations of such complexes to benzoyloxy radicals might be much faster than that of BPO itself. The precise nature of the nitroxide and the polarity of the medium could be expected to affect the behaviour. The scheme proposed by the Russian authors seems to satisfy the conditions since it shows the nitroxide as being regenerated and therefore available to function as an inhibitor by trapping radicals which would otherwise initiate polymerization.

An alternative scheme for an induced decomposition of BPO can be represented thus

$$\text{nitroxide} + (\text{Ph–CO–O})_2 \rightarrow (\text{nitroxide})^{+} + \text{Ph–CO–O}^{-} + \text{Ph–CO–O}^{\cdot} \quad \text{(III)}$$

It resembles a reaction believed to occur between *N*-vinylcarbazole and BPO and for which there is convincing evidence [12,13]. The process would involve separation of charge and so would be favoured in a polar medium. The benzoyloxy radical formed in (III) or a radical derived from it could react with another molecule of the nitroxide during the inhibition; the original molecule of BPO would therefore cause in total the deactivation of two molecules of the nitroxide.

Nitroxides certainly function as inhibitors of radical polymerizations initiated by BPO but the systems show many complexities. It is clear that the nitroxides cannot be used for reliable determination of the rates at which BPO can initiate polymerizations. This limitation is likely to apply to other initiators which yield oxygen-centred radicals.

After inhibition by a nitroxide or by DPPH, R_p and $\overline{M}_n$ of the resulting polymer were affected in ways which are generally similar for cases involving BPO as for those with AIBN [2]. The interpretation of the results is essentially the same for the two sources of radicals. It is supposed that the effects were due to involvement of substances produced during the inhibition as a result of reactions between the inhibitor and radicals derived directly or indirectly from the initiator.

When DPPH was used with BPO, the products formed during inhibition are believed to be the substituted hydrazines already mentioned; both of them contain a labile hydrogen atom, so resembling diphenylpicrylhydrazine which is known to be a powerful transfer agent and retarder [14]. It would be expected therefore that the substituted hydrazines now considered would be effective transfer agents so that $\overline{M}_n$'s of the polymers would be much below that of polymer made in the appropriate blank experiment without inhibitor. Abstraction of the labile hydrogen would lead to the stabilized radicals *p*-Ph–CO–O–C_6H_4–NPh–$\dot{N}$–$C_6H_2(NO_2)_3$ and *p*-Ph–C_6H_4–NPh–$\dot{N}$–$C_6H_2(NO_2)_3$ which would be inefficient initiators of polymerization so that the transfer would be accompanied by retardation, as was observed (see Fig. 2). The plot in Fig. 6 leads to a transfer constant of 6.6 for the products formed in the system MMA/BPO/DPPH but no allowance has been made for the degradative nature of the transfer. The data in Table 1 show that $\overline{M}_w/\overline{M}_n$ for the polymer increased towards 2.0 as the initial value of [DPPH]/[BPO] was raised; this trend is as expected for systems in which disproportionation dominates over combination and in which transfer becomes increasingly important.

During inhibition by the nitroxides, there is thought to have been formation of alkoxyamines which had little effect on the subsequent R_p's but caused reduction in $\overline{M}_n$ of the polymers. It is supposed first that one molecule of inhibitor gave rise to one molecule of alkoxyamine which is regarded

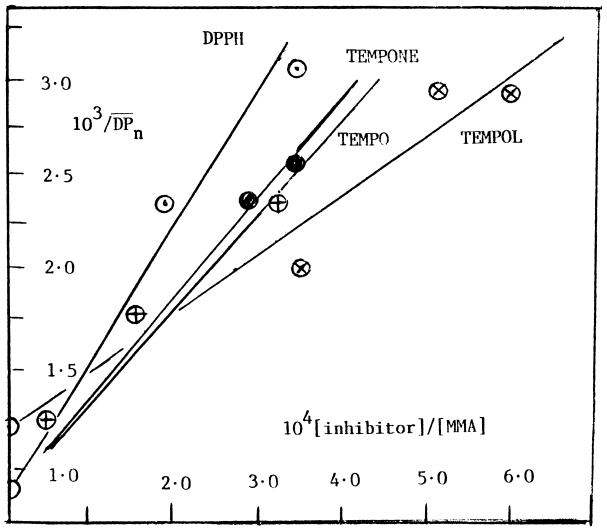


Fig. 6. Effects of initial value of [inhibitor] on $\overline{M}_n$ of polyMMA formed subsequent to inhibition.; (⊙) DPPH; [MMA] = 2.46 mol dm^{-3}, 10^2 [BPO] = 1.80: benzene; (●) TEMPONE; [MMA] = 2.46 mol dm^{-3}, 10^2[BPO] = 1.80: benzene; (⊗) TEMPOL; [MMA] = 2.34 mol dm^{-3}, 10^2[BPO] = 2.58: toluene; (⊕) TEMPO; [MMA] = 2.46 mol dm^{-3}, 10^2[BPO] = 1.80: benzene.

as a transfer agent in the polymerization of MMA; it will be shown however that this assumption and description may be inexact. The plots in Fig. 6 lead to transfer constants of 4.8, 2.9 and 5.0 for the products from TEMPO, TEMPOL and TEMPONE respectively. The set of experimental results is not comprehensive and so the derived transfer constants must be regarded as approximate; the values may be less than the true values for another reason. As explained already, there could have been some consumption of nitroxide by direct reaction with BPO; the amounts of alkoxyamines produced may therefore have been less than those assumed in the calculations.

The alkoxyamines formed in a system containing nitroxide ($^{\cdot}$O–NQ), MMA and BPO are likely to be

Ph–CO–O–CH_2–CMe(COOMe)–O–NQ (*IV*) Ph–CH_2–CMe(COOMe)–O–NQ (*V*) Ph–O–NQ (*VI*)

(IV) and (V) may be accompanied by small amounts of similar products containing more than one MMA monomeric unit; as well as (VI), there might be products such as Ph–CH_2–CMe(COOMe)–O–NQ. It is improbable that any of these substances could act as reactive transfer agents by the usual process of hydrogen-abstraction. It is very significant that the changes in $\overline{M}_w/\overline{M}_n$ (see Table I) for polymers of MMA derived from systems with increasing concentration of a nitroxide are opposite in sense to the changes when DPPH was used as the inhibitor; similar trends were found when DMF had replaced an aromatic hydrocarbon as diluent. This difference shows clearly that reactions of different natures must have occurred in the two types of system.

There are ways other than 'ordinary' transfer by which alkoxyamines, such as (IV), (V) and (VI), might influence radical polymerizations. These substances can dissociate thermally by scission of a carbon–oxygen bond to give a transient (or reactive) radical and a persistent (or stabilized) radical; this dissociation can be regarded as the starting point for the living radical polymerization of certain monomers. The formation of radicals can occur readily at moderate temperatures for the alkoxyamines derived from special nitroxides [5] but higher temperatures, say 125 °C, may be needed for the process to be significant for the alkoxyamines derived from TEMPO and its simple derivatives considered here. It is concluded therefore that thermolysis of alkoxyamines such as (IV)–(VI) could not have been responsible for any of the effects on $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ shown in Table I.

It is proposed that there is ready occurrence of a radical-displacement represented thus

$$P_n^{\cdot} + X\text{–O–NQ} \rightarrow P_nO\text{–NQ} + X^{\cdot} \quad \text{(VII)}$$

where $P_n^{\cdot}$ is a growing polymer radical and X–O–NQ is an alkoxyamine (IV), (V) or (VI) formed during the IP. The radical $X^{\cdot}$ would not be stabilized and could re-initiate readily so that the radical-displacement would not lead to retardation. Reaction (VII) could account for the lowering of $\overline{M}_n$ for the polymer but it could not by itself explain why the polymer has a fairly narrow distribution of molecular weights. Reaction (VII) resembles a process already considered [2] for polymerizations involving nitroxides and AIBN; it is similar to a reaction regarded as important during the nitroxide-mediated polymerization of STY. [16]

Reaction (VII) leads to another alkoxyamine which could react according to Eq. (VIII)

$$P_n\text{–O–NQ} + P_m^{\cdot} \rightarrow P_m\text{–O–NQ} + P_n^{\cdot} \quad \text{(VIII)}$$

so that the original radical $P_n^{\cdot}$ could resume growth. During the polymerization of MMA after the IP, there is initiation by radicals derived from BPO, termination by interaction of pairs of radicals and occasional transfer reactions; these processes by themselves would lead to polymer for which $\overline{M}_w/\overline{M}_n$ approaches 2.0, as found for polymerizations performed without any inhibitor or those occurring after inhibition by DPPH. It is now suggested that reactions such as (VII) and (VIII) lead to some of the smaller polymer molecules growing larger after their growth has apparently ceased. The interplay of this effect with the 'ordinary' polymerization could lead to a narrowing of the distribution of molecular sizes, to an extent increasing with the original concentration of nitroxide used as inhibitor and therefore the amount of alkoxyamines such as (IV)–(VI) produced during the IP.

The scheme now proposed resembles to some extent that for a living radical polymerization with the essential role of a persistent radical being played by an alkoxyamine; Fischer [15] suggested that normal molecules might in some cases function as persistent species. It is however very similar to reversible addition-fragmentation chain transfer (RAFT) polymerization [17] in which processes such as those summarized as (IX) and (X)

$$P_n^{\cdot} + S : CPh\text{–S–R} \rightarrow P_n\text{–S–CHPh} : S + R^{\cdot} \quad \text{(IX)}$$

where $R^{\cdot}$ is a reactive radical such as $Me_2C(CN)$.

$$P_m^{\cdot} + P_n\text{–S–CPh} : S \rightarrow P_m\text{–S–CPh} : S + P_n^{\cdot} \quad \text{(X)}$$

can be likened to reactions (VII) and (VIII).

There can be no doubt that the polymerizations of MMA after inhibition by the nitroxides show some special features of interest and importance. The present proposals concerning the nature of the reactions must be regarded as tentative

but further work is in progress; it includes the use of organic peroxides other than BPO and also of further nitroxides.

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