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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Bevington, J. C. and Hunt, B. J.(2005) 'Effects of Nitroxides on Radical Polymerizations', Journal of Macromolecular Science, Part A, 42: 2, 203 – 210

To link to this Article: DOI: 10.1081/MA-200046978

URL: <http://dx.doi.org/10.1081/MA-200046978>

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Effects of Nitroxides on Radical Polymerizations

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The stabilized nitroxide known as 3-carboxy-PROXYL acts almost ideally as an inhibitor for radical polymerizations at 60°C when azobisisobutyronitrile is used as initiator, but not when benzoyl peroxide is used. During inhibition, there is production of a substance which has a profound effect in reducing the average molecular weight of poly(methyl methacrylate) formed in the subsequent polymerization; apparent reductions in the polydispersities of polymers seem to be due to losses of smaller polymer molecules during the recovery by precipitation in methanol.

Keywords radical polymerization, inhibition, nitroxides, methyl methacrylate

Introduction

Certain stabilized nitroxides viz. 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and its 4-hydroxy and 4-oxo derivatives (TEMPOL and TEMPONE, respectively) have been examined as inhibitors of the radical polymerization of methyl methacrylate (MMA) in solution at 60°C.^[1–4] Limited use has also been made of styrene (STY) and acrylonitrile (ACN) as monomers in similar experiments and of 2,2-diphenylpicrylhydrazyl (DPPH) as inhibitor. When azobisisobutyronitrile (AIBN) was used as the source of radicals, there seemed to be no abnormalities.^[1,2] Plots of inhibition period (IP) vs. [inhibitor]/[AIBN] were linear and had slopes close to 1500 min leading to a value for the rate of formation from AIBN of available radicals in agreement with those found previously by completely different methods.^[5]

Polymerizations of MMA after the IP were retarded but only slightly when a nitroxide had been used but rather more so after inhibition by DPPH. Samples of polyMMA obtained from the polymerizations after inhibition had average molecular weights well below those for “blank” polymers prepared and recovered under similar conditions but without the involvement of an inhibitor; the polymers obtained after inhibition by a nitroxide and recovery by precipitation in methanol had comparatively low polydispersities, values of DP_w/DP_n commonly being between 1.50 and 1.60 whereas those for polymers recovered similarly from “blank” experiments or those involving inhibition by DPPH exceeded 1.80.

In similar experiments in which benzoyl peroxide (BPO) or lauroyl peroxide (LPO) was the source of radicals, the results in some respects were rather different from those

Received April 2004, Accepted July 2004

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obtained when using AIBN.^[3,4] When using the peroxides, the IP's were shorter than expected on the basis of accepted rates of dissociation of the peroxides and there was a tendency for plots of IP vs. [inhibitor]/[peroxide] to be curved. The results were consistent with the belief^[6] that some of the nitroxide was consumed in direct reaction with undissociated peroxides; thus only part of the nitroxide originally present could have been involved in reactions with radicals delivered by dissociation of the peroxide. The concentration of the peroxide greatly exceeded that of the nitroxide. The polymers of MMA formed subsequent to inhibition by a nitroxide and recovered by precipitation in methanol had comparatively low average molecular weights and polydispersities, as when AIBN had been used.

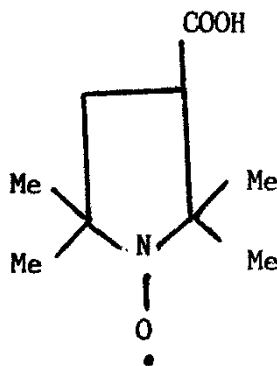
The study is being extended to other nitroxides using AIBN and BPO as sources of radicals. This report refers to 3-carboxy-2,2,5,5-tetramethyl-1-pyrrolidinyloxy (3-c-PROXYL) (Formula 1). There have also been tests in which polymers of MMA were recovered from reaction mixtures by precipitation in n.hexane; the objective was to discover whether the use of methanol as a precipitant was responsible for the low polydispersities of polymers formed after inhibition by a nitroxide.

Experimental

The procedures were those followed in the preceding similar studies.^[1-4] 3-c-PROXYL (Aldrich) was used as received. It has limited solubility in aromatic hydrocarbons; stock solutions were made in N,N-dimethylformamide (DMF) or tetrahydrofuran (THF) which were used as diluents in polymerizations. The experiments in which n.hexane was the precipitant involved MMA with AIBN and in some cases TEMPO.

Reactions at 60°C under anaerobic conditions were monitored by dilatometry and allowed to proceed until 0.7% of the monomer had been consumed. Rates of polymerization (R_p) were calculated from rates of contraction assuming that the same dilatometric factor could be applied for a particular monomer with various diluents and various concentrations of monomer.

Polymers were recovered by precipitation in methanol or n.hexane using 200 ml for a reaction mixture with volume close to 2.5 ml; the dilatometer was rinsed with 0.5 ml of the diluent used during the polymerization. Samples of polyMMA were examined by Size Exclusion Chromatography (SEC) using for reference standard polymers with narrow distributions; the equipment and procedure were as specified previously.^[3] Each of the



Formula 1.

quoted values of DP_n and DP_w/DP_n is the mean of two determinations. This report contains the results for nine samples of polyMMA; in two cases, there was a 2.5% difference between the two values of DP_n for a polymer, but in all the other cases the difference was less than 1.5%. The duplicate values of DP_w/DP_n agreed well; for one polymer the difference was 0.02, but for the others it was less than 0.01.

Results and Discussion

Figure 1 shows the dependence of IP upon the initial value of $[3\text{-c-PROXYL}]/[\text{AIBN}]$. The slope of the line as drawn in 1400 min and is close to those of corresponding plots for TEMPO, TEMPOL and TEMPONE as inhibitors. Most of the points refer to systems containing MMA with DMF as diluent but those for MMA with THF and for STY or ACN with DMF are close to the line.

According to Figure 1, the IP can be taken as 60 min when $[\text{nitroxide}]/[\text{AIBN}]$ is initially 4×10^{-2} . Evidently, during 3600 s at 60°C , a mole of AIBN in dilute solution yields radicals sufficient to deactivate 4×10^{-2} moles of the nitroxide in a 1:1 reaction. The number of radicals formed during the IP and capable of reaction with an inhibitor can also be expressed in terms of the rate constant (k_d) for the dissociation of the azonitrile and the factor (f) referring to the fraction of radicals escaping geminate

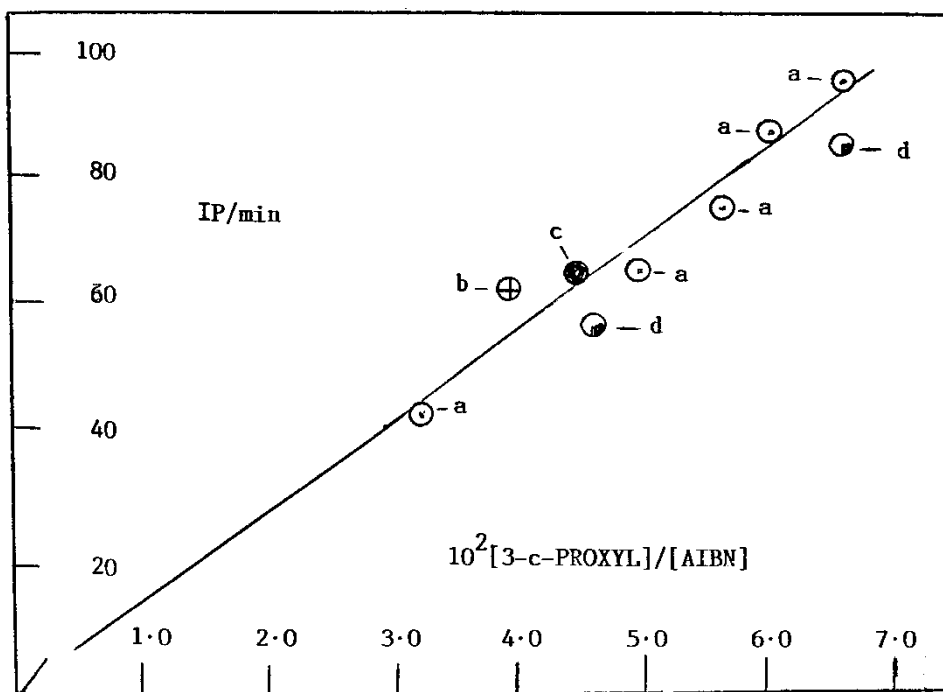


Figure 1. Dependence of inhibition period upon the ratio of the concentrations of nitroxide and AIBN. a— $[\text{MMA}] = 2.46 \text{ mol dm}^{-3}$; $[\text{AIBN}] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$; diluent = DMF. b— $[\text{STY}] = 2.28 \text{ mol dm}^{-3}$; $[\text{AIBN}] = 2.50 \times 10^{-2} \text{ mol dm}^{-3}$; diluent = DMF. c— $[\text{ACN}] = 4.15 \text{ mol dm}^{-3}$; $[\text{AIBN}] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$; diluent = DMF. d— $[\text{MMA}] = 2.46 \text{ mol dm}^{-3}$; $[\text{AIBN}] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$; diluent = THF.

interaction and so becoming available for reaction with scavengers. [AIBN] does not change appreciably during the IP's dealt with here so that for a solution containing one mole of AIBN.

$$2fk_d \times 3600 = 4 \times 10^{-2}$$

and 10^6fk_d is found as 5.6 s^{-1} ; its value appears to be slightly affected by the nature of the medium.

Cases in which BPO was the source of radicals and 3-c-PROXYL was the inhibitor are referred to in Fig. 2. For the systems involving ACN and DMF, the relationship

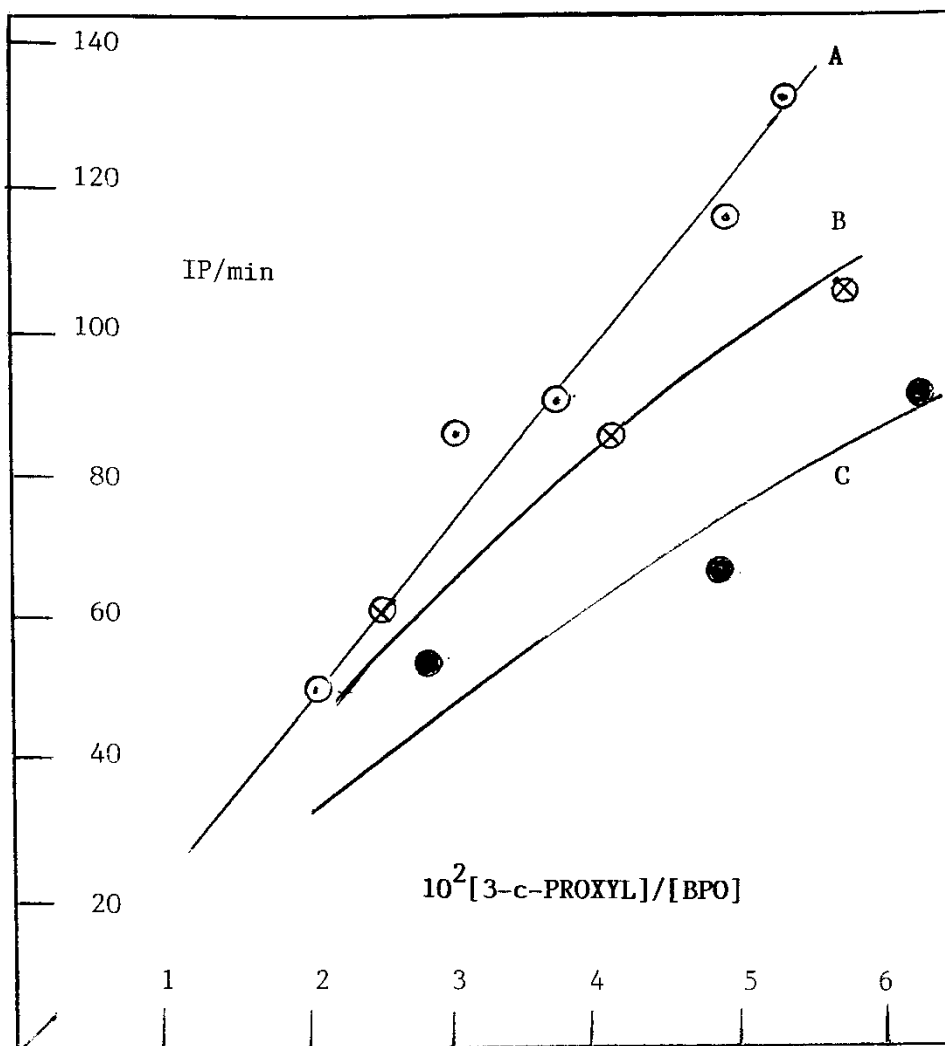


Figure 2. Dependence of inhibition period upon the ratio of the concentrations of nitroxide and BPO. A—[ACN] = 4.15 mol dm^{-3} ; [BPO] = $1.85 \times 10^{-2}\text{ mol dm}^{-3}$; diluent = DMF. B—[MMA] = 2.46 mol dm^{-3} ; [BPO] = $1.75 \times 10^{-2}\text{ mol dm}^{-3}$; diluent = THF. C—[MMA] = 2.46 mol dm^{-3} ; [BPO] = $1.75 \times 10^{-2}\text{ mol dm}^{-3}$; diluent = DMF.

between IP and $[3\text{-c-PROXYL}]/[\text{BPO}]$ is linear or nearly so; an initial value of 3×10^{-2} for the ratio of concentrations corresponds to an IP of 72 min. The rate of production of radicals is expressed as $2k_d[\text{BPO}]$ and the relationship:

$$2k_d \times 4320 = 3 \times 10^{-2}$$

gives $10^6 k_d$ as 3.5 s^{-1} ; values between 1.5 and 2.0 s^{-1} have been given for BPO at 60°C using methods regarded as reliable.^[7,8] The factor “f” used in connection with AIBN is omitted during consideration of BPO for the reason which follows. Geminate recombination of the benzyloxy radicals first formed by thermal dissociation of BPO regenerates a molecule of the peroxide whereas the process with 2-cyano-2-propyl radicals gives a product or products different from the original azonitrile. Reasonable estimates of k_d cannot be made for the other systems referred to in Fig. 2, the plots being non-linear presumably because the conditions favor direct reaction between the nitroxide and the peroxide. The scatter of points in Fig. 2, particularly noticeable for line C, might be attributed to different times elapsing in the various cases between making a dilatometer ready and placing it at 60°C so that there could have been variations in the extent of any direct reaction between inhibitor and peroxide. The present results confirm that serious complications may arise when using nitroxides in the presence of peroxides.

Table 1 refers to systems involving 3-c-PROXYL with MMA and AIBN. After inhibition, the polymerizations proceeded at steady rates up to at least 7% conversion of monomer with no indication of appreciable retardation. Values of DP_n and DP_w/DP_n for the polymers of MMA recovered by precipitation in methanol were less than those for polymers formed in “blank” experiments.

In all cases, $[\text{MMA}] = .46 \text{ mol dm}^{-3}$, $[\text{AIBN}] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$ and DMF used as diluent. Polymers recovered by precipitation in methanol.

It is supposed that, during the inhibition, a nitroxide represented as O'NX is converted to an alkoxyamine R'O'NX where R- is derived from the initiator; there may also be minor amounts of products having a small number of MMA units between R- and -O'NX. The substances derived from the nitroxide must be responsible for the low values of DP_n and they might be regarded as transfer agents in the polymerizations. On this basis, transfer constants could be found from plots of $1/\text{DP}_n$ vs. $[\text{nitroxide}]/[\text{MMA}]$. When MMA and AIBN were used with TEMPO, TEMPOL or TEMPONE, there was a scatter of the points but the apparent transfer constants were about 3.0. The slope of the line in Fig. 3 gives a constant for the alkoxyamine derived from 3-c-PROXYL as about 1.3. There is no good reason for believing that the alkoxyamines would be very reactive in

Table 1
Experiments with MMA, 3-c-PROXYL and AIBN

Ref.	$10^4 [3\text{-c-PROXYL}]/$ mol dm^{-3}	IP/min	$10^5 R_p/$ $\text{mol dm}^{-3} \text{ s}^{-1}$	DP_n	DP_w/DP_n
[1]	0	0	9.85	1,025	2.10
[2]	3.33	42	10.41	873	2.00
[3]	5.00	63	10.32	861	2.00
[4]	5.93	88	10.13	792	1.91

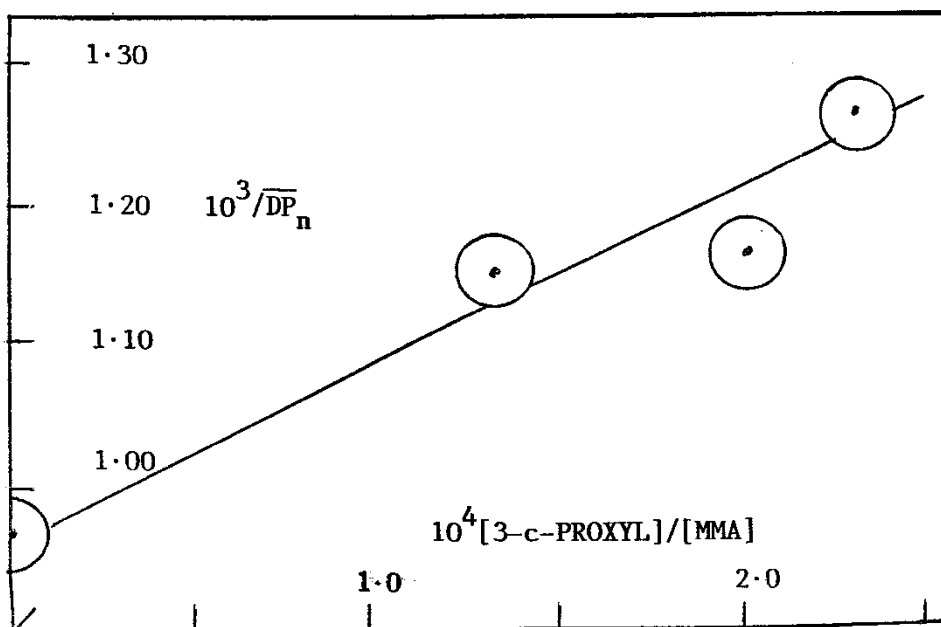
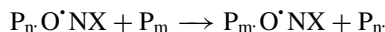


Figure 3. Plot of (reciprocal of number-average degree of polymerization) vs. (ratio of concentrations of nitroxide and monomer) for systems in which $[\text{MMA}]$ was 2.46 mol dm^{-3} , $[\text{AIBN}]$ was close to $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ and the diluent was DMF.

conventional transfer by hydrogen abstraction; a radical displacement (Reaction 1) was proposed:^[2]



where $\text{P}_n\cdot$ represents a growing polymer radical. The radical R' formed in Reaction 1 would react readily with monomer so that re-initiation would be efficient and there would be no appreciable retardation. Reaction 1 could be followed by a similar process:



Reactions of this type have been postulated as important in the nitroxyl-mediated polymerization of STY, contributing to the formation of polymer with narrow distribution of molecular sizes.^[9] It appears that Reaction 1 occurs less readily for the alkoxyamine derived from 3-c-PROXYL than for those formed from TEMPO and its close derivatives. It is quite reasonable to suppose that the rate constant for Reaction 1 should depend on the nature of the nitroxide from which the alkoxyamine was derived i.e. upon the structure of the grouping represented by X.

The products formed during inhibition by TEMPO and similar compounds seemed to have another effect on the polymerization of MMA at 60°C viz. to cause the polymers to have comparatively low polydispersities. Values of DP_w/DP_n were as low as 1.52 for polymers recovered from systems in which TEMPO and AIBN had been used; a typical value for a "blank" polymer was 1.79.^[1] Similar effects were found when TEMPO was replaced by TEMPOL or TEMPONE and AIBN by BPO or LPO; for example, a system containing LPO with TEMPOL in toluene yielded polymer for which DP_w/DP_n was 1.59, whereas the "blank" value was 1.87.^[4] For MMA with AIBN in DMF, as

considered in Fig. 3, the “blank” value of DP_w/DP_n was 2.10 and those for polymers produced after inhibition by 3-c-PROXYL were lower viz. 2.00, 2.00 and 1.91.

Comparatively low polydispersities might not result from special effects during the polymerizations but might be connected with the use of methanol as precipitant for the recovery of polymers of MMA. It has been shown^[10] that some of the smaller molecules in samples of polyMMA remain in solution in methanol so that DP_n for the precipitated polymer is greater than that for the whole polymer; DP_w is less affected by the losses so that DP_w/DP_n for the recovered polymer is below the true value. It was shown that n.hexane is better than methanol as a precipitant for polyMMA and that its use leads to higher values for the polydispersity.

Table 2 refers to polymers of MMA made at 60°C using AIBN and in some cases, TEMPO. It is apparent that polymers B and D, produced after inhibition and then recovery in n.hexane, do not have low polydispersities. DP_n for polymer E is higher than expected by comparison with that for polymer C and the polydispersity for the former is well below that for the latter; these differences are consistent with the belief that there is appreciable loss of small polymer molecules when polyMMA is recovered by precipitation in methanol. It seems clear that the comparatively low polydispersities of samples of polyMMA formed subsequent to inhibition by a nitroxide are not the result of special processes occurring during the polymerizations.

It is necessary to reconsider the results on the number-average molecular weights of samples of polyMMA formed after inhibition by nitroxides and then precipitated in methanol. The losses of small polymer molecules must have become more significant as DP_n for the whole polymer became smaller. The slopes of lines such as that in Fig. 3 must therefore be less than the “true” values and the quoted “transfer” constants should be increased. There is however, no need to modify the conclusion that the alkoxyamines derived from the nitroxides are very effective in reducing the molecular weight of polyMMA formed in their presence.

If a process having some of the characteristics of a living radical system had been responsible for the low polydispersities of certain samples of polyMMA, it would be expected that DP_n of a polymer would have increased as the polymerization proceeded. Three experiments were performed with [AIBN], [TEMPO] and [MMA] fixed at 0.89×10^{-2} , 4.17×10^{-4} and 2.60 mol dm^{-3} , respectively in toluene. In each case, the IP was close to 73 min and $10^5 R_p$ to $7.20 \text{ mol dm}^{-3} \text{ s}^{-1}$; the consumptions of monomer were 4, 8, and 17%. The polymers were recovered by precipitation in methanol; the values of DP_n were 669, 686, and 670 and those of DP_w/DP_n were 1.60, 1.56, and 1.66, respectively. These results show clearly that varying the extent of

Table 2
Molecular weights and polydispersities of polymers

Ref.	[MMA]/ mol dm^{-3}	10^2 [AIBN]/ mol dm^{-3}	10^4 [TEMPO]/ mol dm^{-3}	Diluent	Precipitant	DP_n	DP_w/DP_n
A	2.05	0.98	0	Toluene	n.hexane	629	1.89
B	2.46	0.80	4.18	Toluene	n.hexane	602	1.88
C	2.05	1.09	0	Benzene	n.hexane	608	1.88
D	2.05	1.01	3.97	Benzene	n.hexane	442	1.85
E	1.64	1.14	0	Toluene	Methanol	596	1.54

conversion had no significant effect upon the average molecular weights of the polymers, confirming that the polymerizations were in no way exceptional and supporting the view that losses during recovery were responsible for the low polydispersities of certain samples of polyMMA.

Although loss of smaller polymer molecules during recovery of polyMMA provides a satisfactory explanation for low polydispersities of polymers formed after inhibition by nitroxides such as TEMPO, there are some uncertainties for systems involving DPPH. It has been shown^[1,3,4] that samples of polyMMA formed after inhibition by the hydrazyl and recovered using methanol had polydispersities of about 1.8 to 1.9 although the values of DP_n were quite low and comparable with those of polymers which had been formed subsequent to inhibition by a nitroxide and had low polydispersities. Further studies are being aimed at resolving this problem.

Conclusion

Radical polymerizations are inhibited at 60°C by 2-carboxy-2,2,5,5-tetramethyl-1-pyrrolidinyloxy. This nitroxide resembles other stabilized nitroxides used previously in showing "normal" behaviour in systems with azobisisobutyronitrile as the source of initiating radicals but not when benzoyl peroxide was used. Polymers of methyl methacrylate formed subsequent in inhibition have quite low molecular weights; their polydispersities are not abnormal provided that allowance is made for loss of smaller polymer molecules during recovery by precipitation in a non-solvent.

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. Bevington, J.C.; Warburton, J.; Hunt, B.J. Stabilized radicals as inhibitors of polymerization—reactions of alkoxyamines with growing polymer radicals. *J. Macromol. Sci. A Chem.* **2002**, *39*, 1295–1303.
3. Bevington, J.C.; Hunt, B.J.; Warburton, J. Effects of stabilized radicals upon polymerizations initiated by benzoyl peroxide. *Polymer* **2003**, *44*, 3469–3475.
4. Bevington, J.C.; Hunt, B.J. The use of stabilized radicals with monomers and lauroyl peroxide. *Eur. Polym. J.* **2004**, *40*, 103–108.
5. Moad, G.; Solomon, D.H. *The Chemistry of Free Radical Polymerization*. Pergamon: Oxford, 1955; 59.
6. Rozantsev, E.G.; 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.
7. Moad, G.; Solomon, D.H. *The Chemistry of Free Radical Polymerization*. Pergamon: Oxford, 1955; 68.
8. Barson, C.A.; Bevington, J.C. A tracer study of the benzoyloxy radical. *Tetrahedron* **1958**, *4*, 147–156.
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.; Hunt, B.J.; Barson, C.A. The polydispersities of polymers recovered by precipitation in non-solvents: Effects of beta-methylstyrene on the polymerization of methyl methacrylate. *Eur. Polym. J.* **1998**, *34*, 1387–1389.