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Radical polymerizations of methyl methacrylate initiated by methyl 2-[(4-diphenylmethylene)-2,5-cyclohexadienyl]-2-methyl-propanoate: a model system for so-called 'quasi-living' polymerizations of methyl methacrylate initiated by phenylazotriphenylmethane

John R. Ebdon*, Thomas N. Huckerby, Barry J. Hunt, Stephen Rimmer, Melanie J. Shepherd and Mircea Teodorescu†
The Polymer Centre, School of Physics and Chemistry, Lancaster University, Lancaster LA1 4YA, UK

The kinetics of radical polymerizations of methyl methacrylate initiated by methyl 2-[(4-diphenylmethylene)-2,5-cyclohexadienyl]-2-methyl-propanoate, a model for the growing chain end in 'quasi-living' radical polymerizations of methyl methacrylate mediated by trityl radicals, conventionally generated from phenylazotriphenylmethane, have been investigated. It is shown that the polymerizations have many of the characteristics of living systems, including the ability for polymer chains recovered from the polymerizations to reinitiate polymerization when added to fresh monomer. However, molecular weight distributions of polymers broaden considerably with conversion, suggesting significant termination, probably via transfer to trityl radicals and/or conventional bimolecular termination. Also, the polymers recovered from reinitiation experiments have molecular weights which are too high to be consistent with simple reinitiation via regeneration of growing radicals; rather it seems probable that reinitiation occurs via breakdown of a peroxidic species introduced during work-up of the original polymer. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: methyl methacrylate; methyl 2-[(4-diphenylmethylene)-2,5-cyclohexadienyl]-2-methyl-propanoate; radical)

INTRODUCTION

Phenylazotriphenylmethane (PAT) (1) was one of the first initiators used by Otsu et al. to demonstrate the concept of what has come to be called 'quasi-living' free-radical polymerization, i.e. radical polymerization in which there is at least some reversible termination of propagating polymer chain ends[1]. They proposed that radical polymerizations, particularly of methyl methacrylate (MMA), were thermally initiated by phenyl radicals produced from PAT and reversibly terminated by trityl radicals. However, subsequent investigations showed that PAT-initiated polymerizations of methacrylic monomers are not completely living, but are accompanied by some deactivation of chain ends, the extent of which depends on polymerization conditions[2]. Nevertheless, sufficient chains appear to remain active to high conversion to allow the production of some block copolymer upon introduction of a second monomer[2,3]. Recently, a more detailed study of the kinetics of PAT-initiated polymerizations of MMA has been reported which has highlighted the effects of the very different rates of decomposition of the PAT and the reversibly terminated chain ends[4].

All the papers to date that deal with PAT-initiated radical polymerizations of MMA appear to assume that the reversibly terminated chain species is (primarily at least) one in which the triphenylmethyl radical is bound to the polymer chain end via the quaternary carbon atom (i.e. structure 2 in *Scheme 1*)[1-4].

However, taking into account steric hindrance and the known propensity for the trityl radical to react with other radicals via one of the *para*-positions on the phenyl rings, the real structure of the active chain end is much more likely to be a semibenzene (i.e. structure 3 in *Scheme 1*)[5,6]. This contention is supported by the results of a study of the thermal dissociation-recombination equilibrium of methyl 2-[(4-diphenylmethylene)-2,5-cyclohexadienyl]-2-methyl-propanoate (MDCMP) (4) which has been shown unequivocally to dissociate to give trityl and methyl isobutyryl radicals but to exist in the undissociated form only as the semibenzene structure (see *Scheme 2*)[7].
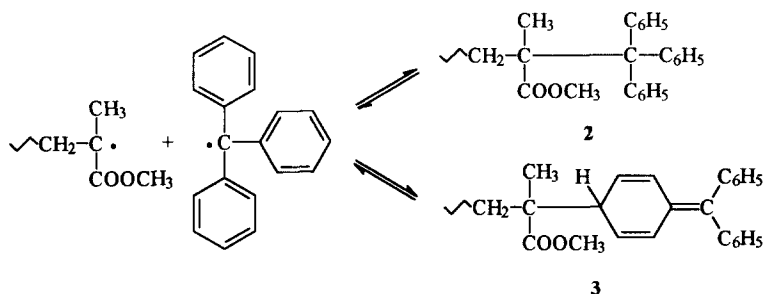
MDCMP thus is thought to represent a good model for the active chain end in PAT-initiated polymerizations of MMA
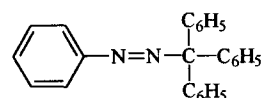
* To whom correspondence should be addressed.
† Present address: Department of Polymer Technology, Polytechnic University, 1 Gh. Polizu Street, 78126 Bucharest, Romania.

$$\text{(phenyl ring)}-N{=}N-\underset{\underset{C_6H_5}{|}}{\overset{\overset{C_6H_5}{|}}{C}}-C_6H_5$$

1

Scheme 1

and for this reason was chosen as the initiator in the studies reported here. These studies mirror those first carried out by Rizzardo *et al.* with alkoxyamines, i.e. models for the active chain ends thought to be involved in nitroxide-mediated quasi-living radical polymerizations[8].

EXPERIMENTAL

MDCMP was synthesized from dimethylketene dimethyla-cetal and trityl bromide following the procedure of McElvain and Aldridge[9]. Methyl methacrylate (Aldrich) and ethyl methacrylate (Koch Light) were washed with 2% aqueous NaOH solution (three times) to remove phenolic inhibitors and then with water until the washings were neutral. They were then dried by standing for several hours over calcium chloride and finally were distilled under vacuum. Azoisobutyronitrile (AIBN) was purified by recrystallization from warm ethanol.

All polymerizations were performed with bulk MMA at either 60, 80 or 100°C and the MDCMP concentration was always 0.1 mol.% based on MMA. Polymerizations were carried out in ampoules sealed under vacuum after four freeze–pump–thaw cycles. A conversion *versus* time experiment was run in five ampoules each containing 4 ml of a mother solution of MDCMP in MMA. After appropriate time intervals, ampoules were taken out of the heating bath, cooled down in an ice–water mixture and opened. The reaction mixtures were then diluted with benzene (liquid samples) or dissolved in methylene chloride (solid samples) and added dropwise with stirring to large excesses of hexane. The polymer precipitates were collected and dried first under air and then under vacuum at room temperature, until constant weights were obtained. Conversions were determined gravimetrically.

Average molecular weights (M_w and M_n) and polydispersities (M_w/M_n) of polymers were determined by size exclusion chromatography (s.e.c.) in THF at a flow rate of 1 ml min^{-1} using an instrument comprised of a Waters Model 510 pump unit, a Gilson 234 autoinjector, 3 × 30 cm (3/8″ dia.) steel columns filled with Polymer Laboratories Plgel® MIXED B gel beads, and an Erma ERC-7512 refractive index detector. The columns were calibrated with Polymer Laboratories narrow polydispersity poly(-MMA) standards.
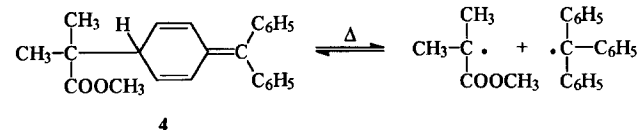
RESULTS AND DISCUSSION

The structure and purity of MDCMP was confirmed by ^{1}H and ^{13}C n.m.r. spectroscopy. The ^{1}H n.m.r. spectrum is shown in *Figure 1* together with a structural formula indicating the assignments.

At 60°C, polymerization of bulk MMA initiated by MDCMP was slow (12.5% conversion after 69 h), much slower than in the case of AIBN-initiated polymerization carried out under identical conditions (96% conversion after 16 h). For this reason, only a single experiment was carried out at this temperature. Also, as will be discussed later, there is some evidence from this single experiment that the rate of dissociation of the initiator, and by implication of the chain end derived from it, is relatively low. For these reasons, polymerizations have been carried out primarily at the higher temperatures of 80 and 100°C.

Figure 2 shows the dependence of conversion and $\ln[M]_0/[M]$ (in which $[M]_0$ is the initial monomer concentration and $[M]$ that at later times) on time for experiments carried out at 80 and 100°C up to conversions of just over 60%. The logarithmic conversion data obtained at 80°C plotted against time fits a straight line passing through the origin which seems to indicate a constant concentration of growing radicals during polymerization, in contrast with the downward curvature observed in the data at 100°C, which is consistent with a significant decrease in the concentration of active centres with time.

The number-average molecular weights, M_n, of the poly(MMA)s formed are close to the theoretical ones, $M_{n,th}$, calculated assuming that each molecule of MDCMP produces one initiating radical (methylisobutyryl) and one capping radical (trityl) and that no chains become permanently deactivated, i.e. calculated using the equation

$$M_{n,th} = [MMA]_0/[MDCMP]_0 \times M_{MMA} \times \%conversion$$

in which $[MMA]_0$ and $[MDCMP]_0$ represent the initial concentrations of MMA and MDCMP, respectively, and M_{MMA} is the molecular weight of MMA (see *Figure 3*).

However, at the lowest conversion (*ca.* 10%), the measured M_n values are significantly greater than $M_{n,th}$
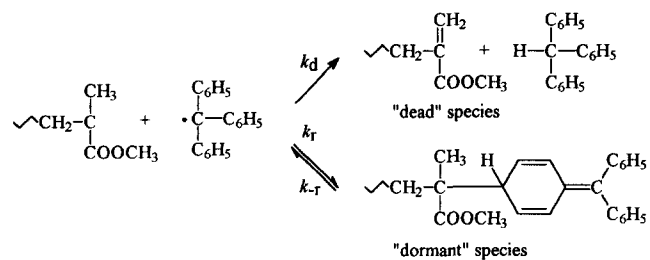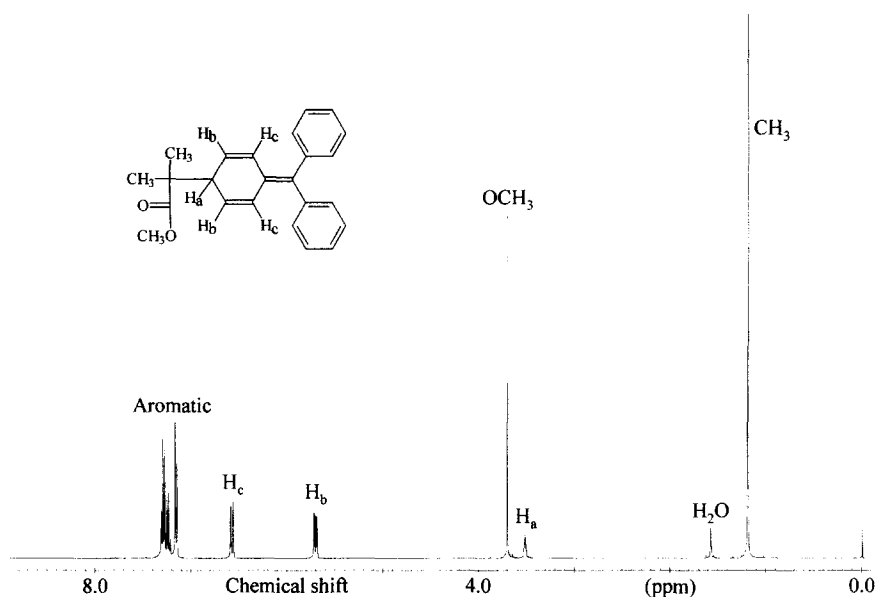

Scheme 2

Scheme 3

Figure 1 ^{1}H n.m.r. spectrum of MDCMP

(especially for the experiments at 60 and 80°C), whereas at higher conversions (above *ca.* 40%) the measured M_n values are significantly less than $M_{n,th}$, especially for the experiments at 100°C.

Based on the observed increase in polydispersity with conversion (*Figure 4*) and the change in molecular weight distribution from unimodal to bimodal during polymerization (*Figure 5*), both of which are particularly marked for the experiments at 100°C, M_n smaller than $M_{n,th}$ at higher conversion may be rationalized by the occurrence of irreversible termination reactions. This explanation is supported also by the deviation from linearity of the logarithmic conversion *versus* time plot at 100°C (*Figure 2*). At 80°C, termination would seem to occur to a lesser extent as indicated by the smaller differences between M_n and $M_{n,th}$, and by the fact that the plot of $\ln[M]_0/[M]$ *versus* time is, within experimental error, linear.

Based on the results of studies of the thermal decomposition of the model compound, MDCMP[8], the most important termination process for the growing chains is almost certainly the disproportionation between the trityl radical and the poly(MMA) macroradical which is in competition with recombination of the two radicals (*Scheme 3*), although conventional bimolecular disproportionation between pairs of polymer radicals in their 'uncapped' state cannot be excluded.

Higher temperatures would favour disproportionation between trityl radicals and polymeric radicals on entropy grounds alone, and thus it would be expected that there would be greater discrepancies between M_n and $M_{n,th}$ at 100 than at 80°C.

Evidence for polymer chains irreversibly terminated by disproportionation is contained within ^{1}H n.m.r. spectra of poly(MMA)s recovered from the polymerizations in the form of signals at 5.5 and 6.2 ppm arising from the olefinic methylene protons of unsaturated, acrylic end groups (see *Figure 6*).

As mentioned above, at low conversions M_n is larger than $M_{n,th}$, and the deviation is largest for the lowest polymerization temperature, 60°C (*Figure 3*). As the rate of decomposition of the 'dormant' chain end (governed by rate constant k_{-r} in *Scheme 3*) is almost certainly relatively low (the first-order rate constant for the decomposition of

MDCMP is only $5.93 \times 10^{-4}\,\mathrm{s}^{-1}$, in acetonitrile, even at 109.3°C)[8], one can best explain this behaviour by assuming that recombination of propagating radicals with trityl radicals (governed by rate constant k_r in *Scheme 3*) is also slow, at least compared with the rate of propagation. Slow decomposition of initiator combined with fast recombination reactions would lead, even at low conversions, to good agreement between M_n and $M_{n,th}$, because all initiator molecules would have decomposed and have added some monomer before significant conversion of monomer to
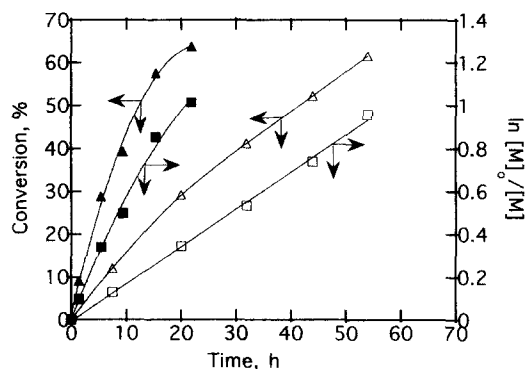

Figure 2 Dependence of conversion and $\ln[M]_0/[M]$ on time for the bulk polymerization of MMA initiated by MDCMP: $[MMA]_0 = 9.4\,M$;

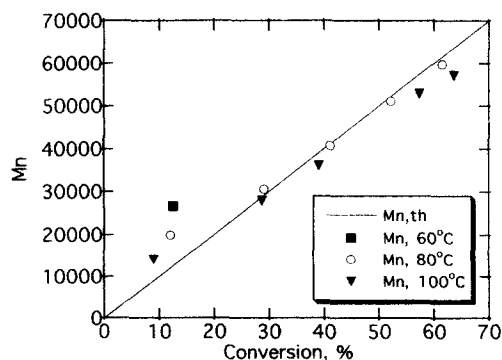**Figure 3** Dependence of M_n on conversion for the bulk polymerization of MMA initiated by MDCMP: $[MMA]_0 = 9.4\,M$; $[MDCMP]_0 = 9.4\,mM$
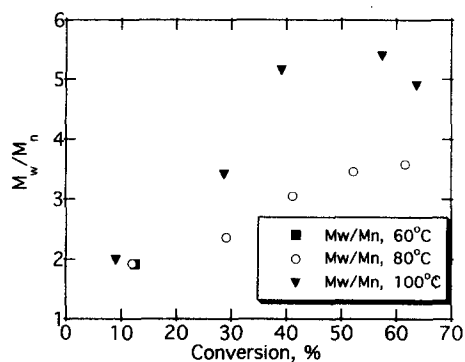
Figure 4 Dependence of M_w/M_n on conversion for the bulk polymerization of MMA initiated by MDCMP: $[MMA]_0 = 9.4$ M; $[MDCMP]_0 = 9.4$ mM

Figure 5 Molecular weight distributions of the polymers obtained in the bulk polymerization of MMA initiated by MDCMP: $[MMA]_0 = 9.4$ M; $[MDCMP]_0 = 9.4$ mM: (a) 80°C; (b) 100°C

High molecular weight polymers

Scheme 4

polymer had occurred. However, slow decomposition combined with slow recombination, i.e. slow exchange, would lead to values of M_n in excess of $M_{n,th}$ at low conversions, because only a fraction of the MDCMP molecules present would have decomposed and have contributed to the polymer-forming process. Since the activation energies increase in the order $E_{recombination} < E_{propagation} < E_{decomposition}$, higher temperatures favour initiator decomposition over propagation and recombination, and so M_n values are closer to $M_{n,th}$ even at low conversion.

As can be seen in *Figure 4*, polydispersity is high and it increases with conversion. The high values of M_w/M_n are an indication, probably, mainly of irreversible termination processes as already discussed, although two other processes may contribute as well, although to a much smaller extent. The first of these is the spontaneous thermal polymerization of MMA, which in a separate experiment without MDCMP present was found to reach 1.7% conversion in bulk MMA after 23 h at 80°C. The polymer obtained in this experiment had an M_n of 987 000, M_w/M_n of 2.14 and a peak molecular weight of 2 114 000. However, because the molecular weight distributions obtained from the s.e.c. traces for MDCMP-initiated poly(MMA)s at this temperature (*Figure 5*) show no evidence for polymer of such high molecular weight, we conclude that the spontaneous polymerization was also 'controlled' by the trityl radical. The second contributing process might be a trityl-initiated polymerization of MMA[4,10]. If such a process makes a contribution, it should only be a very minor one, given the low concentration of trityl radicals. However, there is no evidence for such a process in our data. A third process that could contribute to high polydispersities, but only at low conversions, is the slow exchange between dormant and active chain ends[11].
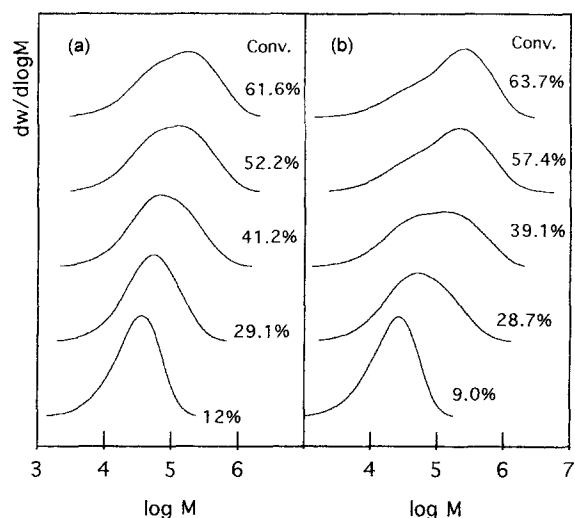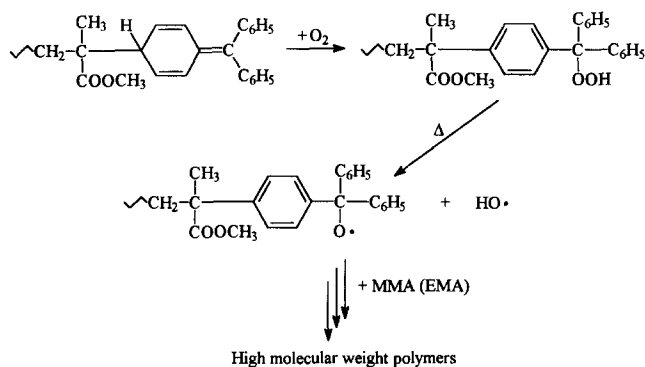
The 'livingness' of poly(MMA)s prepared with MDCMP

was tested in a chain-extension experiment involving dissolution of a poly(MMA) in more MMA, followed by heating under vacuum at 80°C, and in an attempted block copolymerization experiment in which poly(MMA) was added to ethylmethacrylate (EMA) and similarly heated at 80°C. The salient results of these experiments, given in *Table 1*, would seem to indicate that both experiments have been successful: in both cases, the 'seed' polymer has apparently initiated a second polymerization giving a conversion of more than 10% (greater than could be ascribed to any spontaneous thermal process). Furthermore, M_n of the products are higher than M_n of the starting polymers.

However, s.e.c. analysis reveals bimodal distributions in both cases, indicating that only a small fraction of the starting polymer acts as an initiator for the added monomer

Table 1 Chain extension and block copolymerization experiments[a]

Exp. no.	Polymer introduced			Monomer		Polymer obtained			Conv.[b] (%)
	Wt (g)	M_n	M_w/M_n	Type	Vol. (ml)	Yield[c] (g)	M_n	M_w/M_n	
1[d]	0.305	31 000	2.36	MMA	6	1.141	137 000	10.29	14.8
2[e]	0.300	41 000	3.05	EMA	6	0.949	138 000	18.38	11.8

[a] Bulk polymerization: temperature, 80°C; reaction time, 30 h
[b] Conversion of the monomer introduced
[c] Yield including polymer introduced
[d] Polymer obtained at 29.1% conversion in the conversion *versus* time experiment carried out at 80°C (see *Figures 2–5*)
[e] Polymer obtained at 41.2% conversion in the conversion *versus* time experiment carried out at 80°C (see *Figures 2–5*)
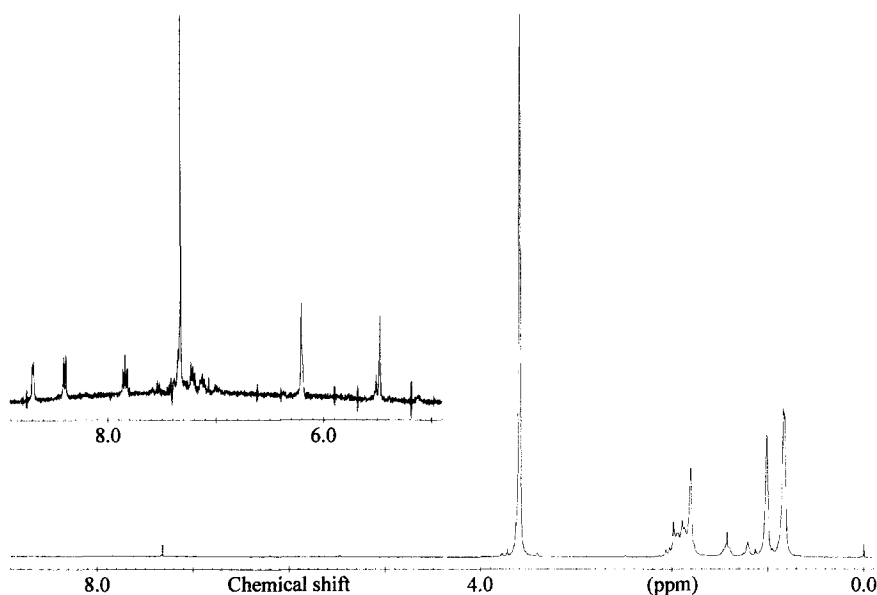
Figure 6 ¹H n.m.r. spectrum of poly(MMA) produced using MDCMP as initiator with an expansion of the region from 5.0 to 9.0 ppm

(Figure 7). Moreover, the very high molecular weights of the newly formed polymers denote uncontrolled polymerizations.

As the starting polymers were samples produced at intermediate conversions (29.1 and 41.2%, respectively) in the conversion *versus* time experiments carried out at 80°C, during which the 'quasi-living' character of the process was clearly demonstrated, these results are quite unexpected. The only explanation that we can provide is outlined in *Scheme 4*.

MDCMP is known readily to form a trityl hydroperoxide on exposure to atmospheric oxygen[8]. By analogy, it seems reasonable to suppose that the active chain ends of poly(MMA) initiated with MDCMP are able to react readily with oxygen also, and that they were converted to hydroperoxide during recovery of the polymers because of inevitable exposure to air. During the attempted chain extension and block copolymerization experiments, the hydroperoxide decomposes and initiates polymerization of MMA or EMA. The process is not trityl mediated and thus displays the characteristics of a conventional radical polymerization, as can be seen by comparing the molecular weight distributions (derived from s.e.c. traces) of the products obtained in these experiments with that of the polymer obtained from the AIBN-initiated polymerization of MMA *(Figure 8)*.

Aromatic hydroperoxides are known to decompose slowly even at temperatures well above 100°C. Therefore, only a small fraction of the hydroperoxide chain ends were converted into radicals and initiated chain extension or block copolymerization; most of the starting polymer remained unchanged, as shown by the molecular weight distributions *(Figure 7)*. We believe that previous attempts by Otsu and Tazaki to demonstrate the living character of poly(MMA)s made using PAT as initiator have been subject to similar effects[2]. Examination of their published molecular weight data for attempted block copolymerizations using styrene as the second monomer reveal discrepancies similar to those reported here. Moreover, in Otsu and Tazaki's experiments, considerable amounts of homopolystyrene were produced (72% of the total polymeric product in one experiment), presumably via initiation with HÖ radicals from the hydroperoxide groups, and significant quantities of
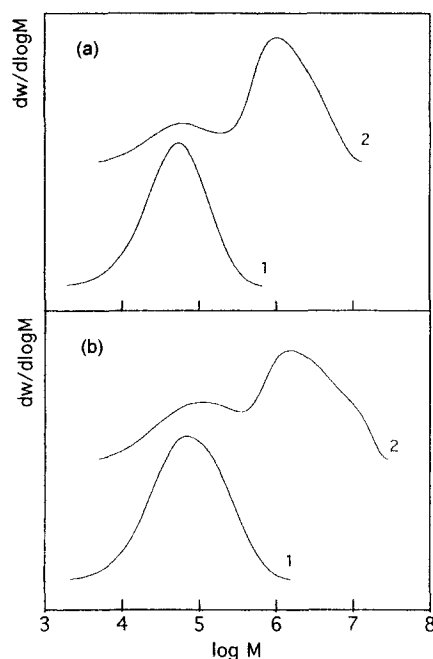

Figure 7 Molecular weight distributions of the polymers obtained in (a) attempted chain extension and (b) attempted block copolymerization experiments. Experimental conditions are identical to those displayed in *Table 1*. (1) Starting polymer; (2) polymer obtained
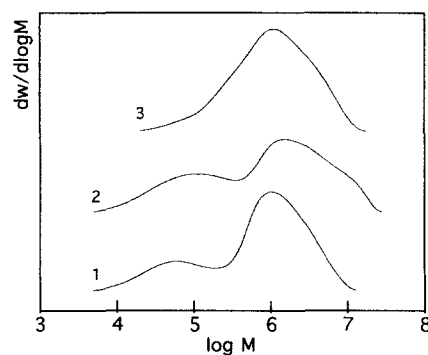

Figure 8 Comparison of the molecular weight distributions of the polymers obtained in chain extension (1) and block copolymerization (2) experiments and in AIBN-initiated polymerization of MMA (3)
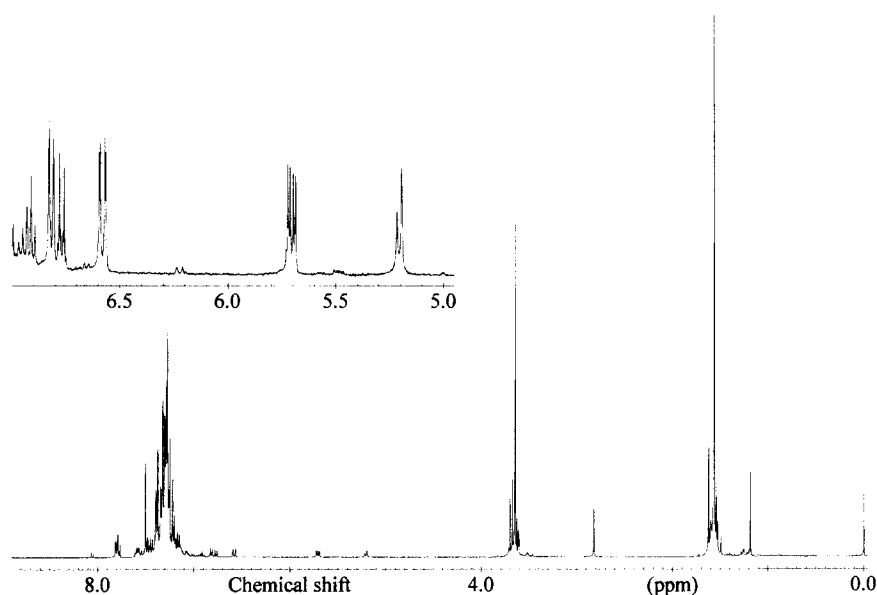
Figure 9 ^{1}H n.m.r. spectrum for 'oxidized' MDCMP with an expansion of the region from 5.0 to 7.0 ppm

poly(MMA) (45% of the total polymeric product in another experiment) were left unconverted to block copolymer.

Evidence for the facile oxidation of the dormant, diphenylmethylene cyclohexadienyl (MDCMP-like) end groups in the polyMMAs produced using MDCMP as initiator is contained within the ^{1}H n.m.r. spectra of these polymers (*Figure 6*). Comparison of the signals between 5 and 9 ppm for the polymer with those from freshly prepared MDCMP (*Figure 1*), and from MDCMP exposed to air (oxidized) for 24 h (*Figure 9*), indicates that the polymers contain none of the MDCMP-like structures, and that the oxidized MDCMP contains very few. Particularly to be noted is the complete absence in the spectrum of the polymer of characteristic MDCMP-like olefinic proton signals at 5.7 and 6.6 ppm and the much reduced intensity of these in the spectrum of oxidized MDCMP.

CONCLUSIONS

The present work shows that the radical polymerization of MMA initiated by MDCMP, a model for the supposed trityl-capped chain end in PAT-initiated polymerizations of MMA, is a 'quasi-living' process, leading to polymers, the M_n values of which are close to those expected on the basis of initial concentrations of monomer and initiator and the conversion. However, polydispersities are high and increase with conversion, probably as a consequence mainly of some termination through disproportionation between the trityl radical and the propagating chain radical. The active chain ends of the polymer are sensitive to oxidation and therefore, in order to prepare block copolymers, exposure to air during

manipulation of the seed polymer should be avoided. Our experiments in this area are continuing.

ACKNOWLEDGEMENTS

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