Controlled radical polymerization of methyl methacrylate in the presence of 1-*tert*-butyl-3-phenyl-1-oxytriazene

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Oxytriazenes are efficient initiators and polymer chain growth regulators in the radical polymerization of methyl methacrylate.

The development of new efficient additives for the control of polymer chain growth under mild conditions (50–70 °C) typical of the large-scale production of polymers is an urgent problem of the chemistry of polymers.[1–3]

To solve this problem, we proposed the use of 1-*tert*-butyl-3-phenyl-1-oxytriazene (BPT) as a nitroxide precursor in the controlled radical polymerization of methyl methacrylate (MMA).

With the use of diacetylperoxydicarbonate (DPC) as an initiator, the addition of an oxytriazene to a polymerizate influenced significantly the kinetics of MMA polymerization. In particular, the introduction of BPT led to a decrease of the gel effect and to a shift towards the region of higher conversions (Figure 1). At the same time, at the concentration of BPT equal to 0.05 mol% the reaction proceeded without autoacceleration. Moreover, the initial rate of polymerization decreased slightly (Table 1).

In contrast to integral kinetic curves [Figure 1(*a*)] constructed according to dilatometric data, differential kinetic curves obtained by thermography have rather complicated shapes [Figure 1(*b*)]. Probably, this is due to the simultaneous occurrence of several processes in the system: initiator decomposition, oxytriazene oxidation by the interaction with a peroxide [equations (1) and (2)], direct participation of BPT in a growth stage and gel formation.

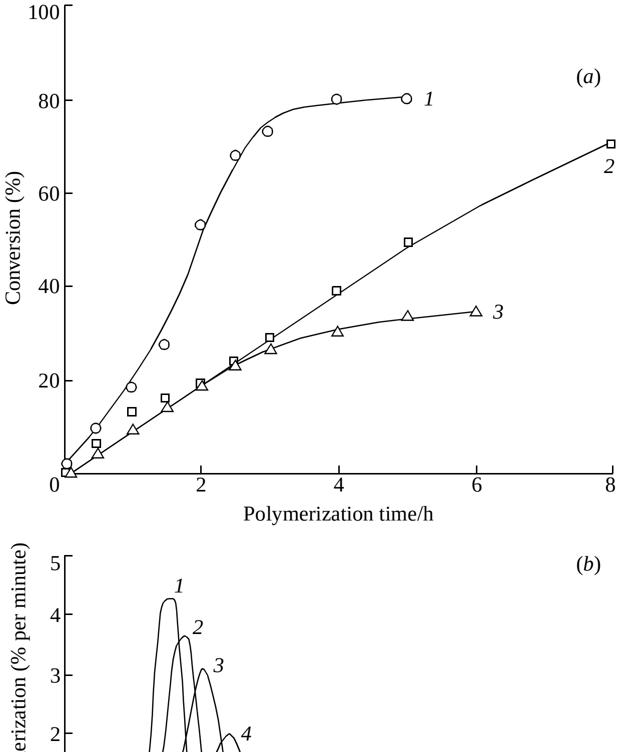


Figure 1 (*a*) Integral and (*b*) differential kinetic curves of methyl methacrylate polymerization. Initiator: DPC (0.1 mol%) at (*a*) 323 and (*b*) 338 K. BPT content (mol%): (*a*) *1*, 0; *2*, 0.06; *3*, 0.1; (*b*) *1*, 0; *2*, 0.02; *3*, 0.03; *4*, 0.04; *5*, 0.05; *6*, 0.06.

Table 1 Rate of MMA polymerization in the presence of BPT at 323 K.

Oxidising agent or initiator (mol%)	BPT concentration (mol%)	Rate of polymerization, $V/10^{-4}$ mol dm^{-3} s^{-1}
Ag_2O	0.4	0.24
PbO_2 (0.4)	0.4	0.45
DPC (0.1)	—	5.34
	0.06	3.54
	0.1	3.13
AIBN (0.1)	—	1.22
	0.4	1.18

It is fundamentally important that the addition of BPT to the system, after an initial increase in the rate of polymerization, resulted in a subsequent decrease in the rate, and the process reached a steady state (Figure 1, curve *6*).

These kinetic data and the kinetics of MMA polymerization in the presence of 1-*tert*-butyl-3-phenylnitrone and nitroso compounds[4-6] allowed us to suggest that the polymerization can proceed *via* a ‘pseudo-living’ chain mechanism[7–12] in the presence of BPT.

The relationship between the molecular weight (MW) of polymer products and conversion can afford more comprehensive information on the mechanism of the polymer chain growth. Figure 2 indicates that a pronounced increase of MW, which was observed at the gel-effect point for PMMA synthesised using DPC as an initiator, is not observed on the addition of BPT to the polymerizate. In the presence of the oxytriazene, the number-

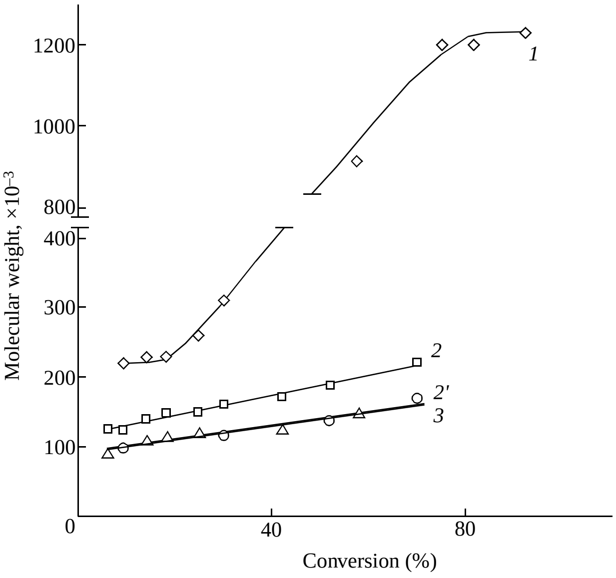


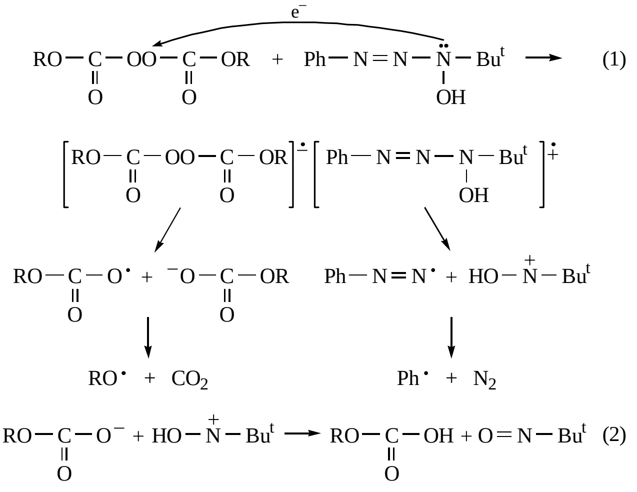
Figure 2 (*1*)–(*3*) Viscosity-average and (*2*′) number-average molecular weight of poly(methyl methacrylate) as a function of conversion at 323 K. Initiator: DPC (0.1 mol%). BPT concentrations (mol%): (*1*) 0, (*2*) and (*2*′) 0.06, (*3*) 0.1.

average and viscosity-average molecular weights increase as a linear function of conversion. In this case, the MW values are somewhat lower than those of the polymers prepared without the additive (Table 2). The gel-permeation chromatograms (GPC) of samples synthesised in the presence of BPT are unimodal and shifted towards higher MW values as the conversion increases (Figure 3).

The MW of polymers, synthesised in the presence and in the absence of BPT additives are essentially different at 20–25% conversion. This fact is consistent with the kinetics of chain growth under conditions of ‘pseudo-living’ radical polymerization[1,6] and can be explained by the direct participation of BPT at the stages of chain growth and termination. The kinetic study indicates that the introduction of the oxytriazene into the system significantly reduces the gel effect (Figure 1) and hinders both the bimolecular chain termination and uncontrollable molecular-weight growth of the polymer.

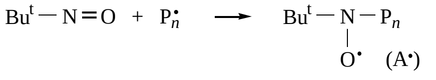
The coefficient of polydispersity (P_N) of the polymer was changed only slightly during the process (Table 2), as distinct from the samples prepared using DPC without adding the oxytriazene. The fact that the polydispersity coefficient in the system did not increase with conversion is consistent with the absence of the gel effect at high degrees of conversion. These data may indicate that the number of propagating chains remained unchanged in the polymerization process, and only the length increased. Such properties are characteristic of the growth through the ‘pseudo-living’ chain mechanism.

When a peroxide reacts with the oxytriazene, one-electron transfer takes place to result in active radicals (RO· and Ph·), which are capable of initiating polymer chain growth, and a nitroso compound:



R = $C_{16}H_{33}$

2-Methyl-2-nitrosopropane formed by reactions (1) and (2) interacts with polymeric (oligomeric) radicals ($\sim P_n^{\bullet}$) to form a stable nitroxyl radical (A·):



$$\mathrm{Bu^t{-}N{=}O + P_n^{\bullet} \longrightarrow Bu^t{-}\underset{\displaystyle O^{\bullet}}{N}{-}P_n \quad (A^{\bullet})} \qquad (3)$$

Table 2 Molecular-weight characteristics of poly(methyl methacrylate). Initiator: DPC (0.1 mol%) at 323 K.

Conversion (%)	M_n	M_w	M_η	P_N
14	162000	284000	261000	1.8
53	230000	641000	548000	2.8
72	519000	1488000	1337000	>2.9
12[a]	96000	148000	139000	1.5
31[a]	117000	190000	177000	1.6
50[a]	130000	218000	203000	1.7
70[a]	170000	338000	222000	1.8

[a] The samples were synthesised in the presence of 0.06 mol% BPT.

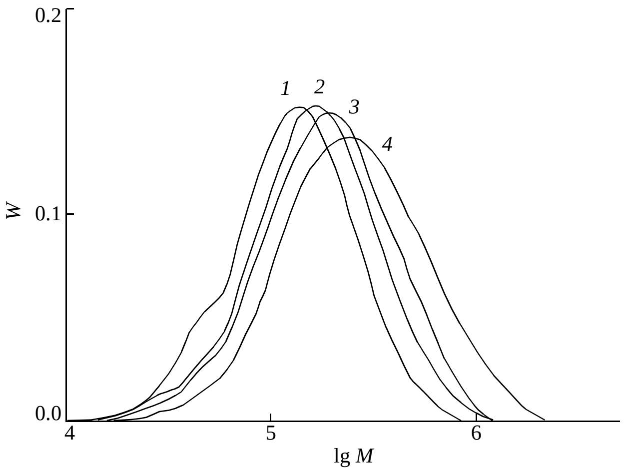


Figure 3 Molecular-weight distribution curves of poly(methyl methacrylate) at 323 K. BPT content 0.06 mol%. Conversion (%): (*1*) 12, (*2*) 31, (*3*) 50, (*4*) 70. *W* is the mole fraction.

The formation of nitroxyl radicals in the polymerization was found by EPR spectroscopy. In the EPR spectra, a triplet was detected with the constant at nitrogen 15.6 oersted. The signal corresponds to the stable radical A·, the product of reaction (3).

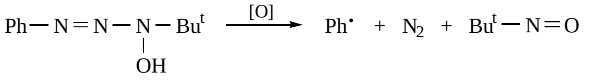
The stable spin adduct A· interacts with a growing polymeric radical to form a labile link, reaction (4). The subsequent chain growth occurs through a stepwise mechanism by successive events of the scission of a terminal labile link, the addition of monomeric units (mM) and the formation of a new labile link:

$$\sim P_n^{\bullet} + {}^{\bullet}A \longrightarrow [\sim P_n - - A] \qquad (4)$$

$$[\sim P_n - - A] + mM \longrightarrow [\sim P_{n+m} - - A] \qquad (5)$$

This chain growth mechanism is responsible for the absence of a gel effect and an increase in the number-average MW with increasing conversion.

An indirect support to the above initiation mechanism is provided by the fact that BPT does almost not affect the kinetics of polymerization and the molecular-weight characteristics of the polymer with the use of azobis(isobutyronitrile) (AIBN) as an initiator in place of DPC. Azo compounds, unlike acyl peroxides, cannot oxidise oxytriazenes,[13] and hence reactions (1)–(5) do not proceed. On the contrary, lead and silver oxides used as oxidants react with BPT to form phenyl radicals, which initiate polymerization, and nitroso compounds, which can control chain propagation:[6,13]



$$\mathrm{Ph{-}N{=}N{-}\underset{\displaystyle OH}{N}{-}Bu^t \xrightarrow{[O]} Ph^{\bullet} + N_2 + Bu^t{-}N{=}O} \qquad (6)$$

Low rates of polymerization and low conversions observed in this case (Table 1) result to some extent from a poor solubility of lead and silver oxides in the monomer and, as a consequence, from the heterogeneity of the system. Temperature changes in the range 30–100 °C have no effect on the polymerization.

Thus, we can conclude that BPT makes it possible to perform the controlled synthesis of PMMA up to high conversions with the formation of polymers with low coefficients of polydispersity.

It is of both theoretical and practical importance that the polymerization proceeds under mild conditions (50–65 °C) without gel formation. Moreover, a reasonably high rate is maintained during the course of polymerization. Stable nitroxyl radicals were employed to control the polymer-chain growth in pseudo-living polymerization.[14,15] As a rule, these radicals are sterically hindered low-molecular-weight nitroxyls [for example, 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) and its analogues], which are used at elevated temperatures. When 1-*tert*-butyl-3-phenylnitrone is added to the system, 2-methyl-2-nitrosopropane, which forms in reactions (1) and (2), reacts with the growing radicals to form nitroxyl radicals having a high-molecular-weight tail [reaction (3)]. Probably, this high-molecular-weight nitroxyl forms a less stable bond with a PMMA radical, as compared to the common nitroxyls, and hence provides an opportunity to control the molecular weight of the resulting polymer under significantly milder conditions.

BPT was synthesised by a published procedure.[16] The kinetics of polymerization was monitored by gravimetry, dilatometry and thermography. The molecular weight of the polymer was determined by viscometry and GPC using a set of five styrogel columns with pore diameters of 10^5, 3×10^4, 10^4, 10^3 and 250 Å (Waters, USA). An R-403 differential refractometer (Waters) was employed as a detector. Tetrahydrofuran served as an eluent. For the calibration, narrow-disperse polystyrene standards were used.[17]

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