2-Methyl-2-nitrosopropane as a new regulator of the polymer chain growth

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Aliphatic nitroso compounds are efficient regulators of the radical polymerization of methyl methacrylate through the ‘pseudoliving’ chain mechanism.

It is well known[1–5] that stable nitroxyl radicals, in particular, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and its analogues, can control the chain growth in the polymerization of styrene and methyl methacrylate (MMA). A significant disadvantage of the regulators is that they effectively influence the growth stage only at temperatures above 373 K. Thus, low-molecular stable radicals cannot be widely used under industrial conditions of polymer synthesis.

To control polymer chain growth in the radical polymerization of MMA, we proposed the use of 2-methyl-2-nitrosopropane (MNP), which is traditionally employed as a spin trap and can add active radical centres (including polymer radicals) with the formation of stable nitroxyl spin adducts directly in the reaction system.

2-Methyl-2-nitrosopropane was synthesised by a well-known procedure.[6] MMA, azobis(isobutyronitrile) (AIBN) and solvents were purified by standard procedures.[7] The physico-chemical constants of the compounds used were consistent with the published data. Samples for polymerization were prepared under a residual pressure of 1.33 Pa, the experimental details were described elsewhere.[8] The kinetics of polymerization was monitored by gravimetry, dilatometry and thermography.[9] The molecular weight (MW) of the polymer was determined by viscometry[10] and gel permeation chromatography 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 used as a detector. Tetrahydrofuran served as an eluent. For the calibration, narrow-disperse polystyrene standards[11] were used.

The data indicate that, on adding 0.01–0.05 mol% MNP, the initial rate of MMA polymerization decreased only slightly (Table 1). At the same time, this additive caused a noticeable decrease in the autoacceleration process. Moreover, a successive increase in the additive concentration from 0.01 to 0.05 mol% relative to MMA results in a gradual decrease of the polymerization rate at the autoacceleration stage (Figure 1, curves *2*–*4*) and almost comletely eliminates a gel effect which induces a spontaneous increase in the molecular weight and the composition inhomogeneity of polymers. Earlier,[12] we proposed the use of *N*-*tert*-butyl-α-phenylnitrone for controlling the radical polymerization of acrylic monomers. Note that MNP is a more efficient growth regulator because it actively affects the growth of polymer chains in much lower amounts (0.01–0.05 mol%). The addition of more than 0.1 mol% MNP to a monomer mixture gives rise to a considerable increase in the induction period (Table 1) and to strong inhibition of the overall process.

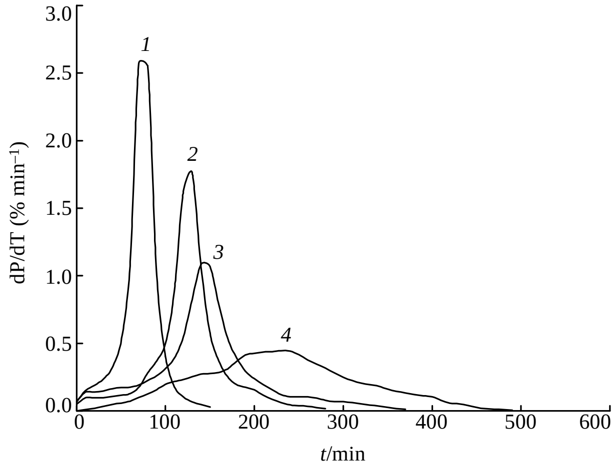
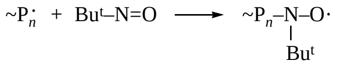


Figure 1 Differential kinetic curves of the polymerization of methyl methacrylate in the presence of MNP at 338 K; iniiator, [AIBN] = 0.1 mol%, MNP concentrations (mol%): (*1*) 0, (*2*) 0.01, (*3*) 0.02, (*4*) 0.05.

On the basis of the reactivity of nitroso compounds and a mechanism of ‘pseudoliving’ polymerization in the presence of nitroxyl radicals,[13] it is reasonable to assume that the controlled propagation of a macromolecular chain results from the interaction of MNP with polymeric (oligomeric) radicals to form stable nitroxyl radicals (**A**·):



$$\sim\!\mathrm{P}_n^{\boldsymbol{\cdot}} + \mathrm{Bu^t{-}N{=}O} \longrightarrow \sim\!\mathrm{P}_n{-}\underset{\displaystyle \mathrm{Bu^t}}{\underset{|}{\mathrm{N}}}{-}\mathrm{O}\boldsymbol{\cdot} \qquad (1)$$

A·

where $\sim\!\mathrm{P}_n^{\boldsymbol{\cdot}}$ is a macroradical containing *n* monomeric units.

This is the cause of an induction period observed in dilatometric studies. Nitroxyl spin adducts (**A**·) interact with growing radicals with the generation of labile terminal groups:

$$\sim\!\mathrm{P}_n^{\boldsymbol{\cdot}} + \boldsymbol{\cdot}\mathbf{A} \longleftrightarrow [\sim\!\mathrm{P}_n^{\boldsymbol{\cdot}} - - \boldsymbol{\cdot}\mathbf{A}] \qquad (2)$$

The lability of the chemical bond $[\sim\!\mathrm{P}_n^{\boldsymbol{\cdot}} - - \boldsymbol{\cdot}\mathbf{A}]$ is caused by the stability of the the nitroxyl radical [**A**·]. This stability is associated with electron density redistribution between oxygen and nitrogen atoms and also with steric hindrances from the *tert*-butyl group of nitroxyl. It is well-known that radical reactions are very sensitive to steric environments.

The uniform reinitiation as a result of reverse reaction (2) leads to the occurrence of a ‘pseudoliving’ polymerization mechanism. In this case, the chain growth proceeds *via* sequential insertion of the monomer at the labile bond $[\sim\!\mathrm{P}_n^{\boldsymbol{\cdot}} - - \boldsymbol{\cdot}\mathbf{A}]$:

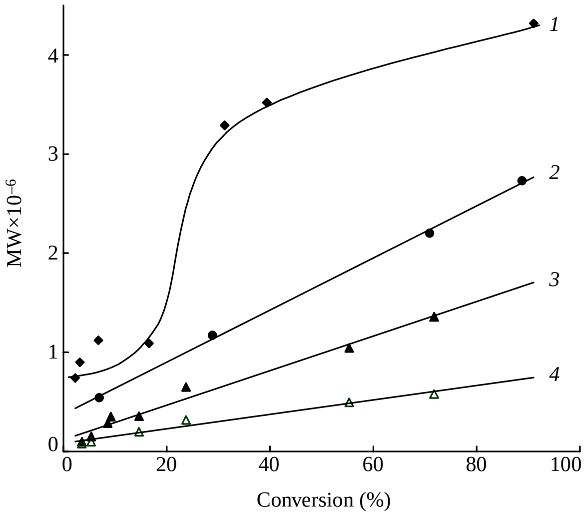
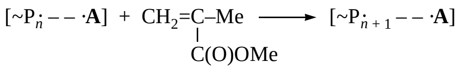


Figure 2 Molecular weight (MW) of poly(methyl methacrylate) as a function of conversion: (*1*)–(*3*), viscosity-average MW; (*4*) number-average MW; initiator, [AIBN] = 0.1 mol%. MNP concentrations (mol%): (*1*) 0, (*2*) 0.01, (*3*) and (*4*) 0.02.



$$[\sim P_{n}^{\cdot} - - \cdot \mathbf{A}] + CH_2{=}\underset{C(O)OMe}{C}{-}Me \longrightarrow [\sim P_{n+1}^{\cdot} - - \cdot \mathbf{A}] \quad (3)$$

Another explanation of the polymerization mechanism of MMA in the presence of MNP can be given in terms of the secondary catalytic inhibition of the polymerization of vinyl monomers by nitroxyl radicals, which was considered in detail by Smirnov.[14]

In order to examine this mechanism under particular conditions, the molecular-weight distribution of the samples prepared in the presence of various MNP concentrations and the molecular weights of polymeric products as functions of the degree of conversion were studied. We found that the chromatograms of poly(methyl methacrylate) (PMMA) samples are unimodal, and the mode is regularly shifted towards the high-molecular region with increasing time of polymerization. This indicates that the polymerization is accompanied by a continuous rise of the average MW of the polymer. In addition, the number-average and viscosity-average molecular weights are linear functions of the conversion up to high degrees of conversion (Figure 2). This demonstrates that the number of propagating chains is constant during the overall process. The MW data indicate that almost all polymeric chains are able to reinitiate and to grow *via* the 'pseudoliving' chain mechanism up to high degrees of conversion. The coefficient of polydispersity (the ratio between the weight-average and number-average molecular weights) of the polymer varies to some extent in the course of the process (Table 1). An insignificant increase in the coefficient of polydispersity (higher than 1.5) with conversion can be associated with bimolecular chain termination, which lead to formation of an amount of a 'dead polymer' simultaneously with the 'living' mechanism of polymerization.

Table 1 Characteristics of the polymerization of MMA and the polymer formed in the presence of MNP; initiator, [AIBN] = 0.1 mol%, T = 323 K.

Entry	MNP concentration (mol%)	Induction period/ min	Initial rate/ 10^{-4} mol dm^{-3} s^{-1}	Conversion (%)	Coefficient of polydispersity
1	0	0	1.22	11.8	2.0
2	0.01	0	0.94	—	—
3	0.02	~25	0.59	3.6	1.6
4	0.02	~25	0.59	5.4	1.8
5	0.02	~25	0.59	14.7	2.2
6	0.02	~25	0.59	71.7	2.2
7	0.05	~50	0.55	—	—
8	0.1	~180	0.37	—	—

Thus, MNP as a potential source of stable radicals directly participates in the stage of polymer chain growth and controls the rate of the process and the molecular-weight characteristics of PMMA in a relatively 'soft' temperature range (323–338 K). An important feature of this growth regulator is that, in contrast with other regulators,[1–5] stable radicals capable to control the polymeric chain growth are formed directly in the course of polymerization by the interaction of the polymeric macroradicals with the additive. This additive is more efficient as a polymerization modifier than TEMPO and other stable radicals. In controlling the polymeric chain propagation, MNP slightly decreases the rate of polymerization and hence can outperform other regulators of radical polymerization.[2–5,14]

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