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Sterically hindered aliphatic amines in the controlled synthesis of polystyrene

E. V. Kolyakina, V. V. Polyanskova, and D. F. Grishin★

Research Institute of Chemistry,
N. I. Lobachevsky Nizhny Novgorod State University,
23 building 5, prosp. Gagarina, 603950 Nizhny Novgorod, Russian Federation.
Fax: +7 (831 2) 65 8162. E-mail: grishin@ichem.unn.runnet.ru; grishin@ichem.unn.ru

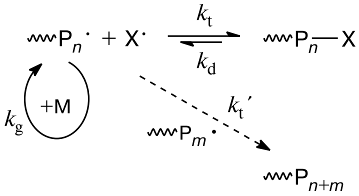
The kinetic features of radical polymerization of styrene in the presence of primary and secondary aliphatic amines combined with benzoyl peroxide and the molecular-mass characteristics of the resulting polymers were studied. In the presence of peroxide initiators, aliphatic amines, as potential sources of stable aminoxyl radicals, provide the synthesis of polystyrene with a controlled molecular mass without gel effect at a relatively high rate.

Key words: controlled radical polymerization, polystyrene, styrene, di(*tert*-butyl)amine, *tert*-butylamine, block copolymerization.

Controlled "living" synthesis of polymers is an actively developed line of synthetic polymer chemistry. This method opens up broad or even unique opportunities for molecular design, *i.e.*, preparation of polymers with a complex architecture and a specified set of properties. Most of "living" radical polymerization processes are based on the reversible inhibition of polymerization involving stable radicals. Low-molecular-weight aminoxyl radicals, for example, 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) and di(*tert*-butyl)aminoxyl[1—3] and sterically hindered aminoxyl radicals based on spin traps generated *in situ*[4—8] are used most often as reversible inhibition agents.

Aminoxyl radicals are efficient acceptors of free radicals, including polymeric ones, over a broad temperature range. An important distinctive feature is the reversibility of their interaction with a series of growing macroradicals at certain temperatures, which opens up prospects for controlling the lifetime of the polymer chain (Scheme 1).

Scheme 1



The following designations are used in Scheme 1: $\sim\!\sim P_n{}^{\cdot}$ is the growing macroradical; $X^{\bullet}$ is a stable aminoxyl radical; M is the monomer; k_d is the rate constant for dissociation of the [$\sim\!\sim P_n$—X] adduct; k_t is the rate constant for recombination of the aminoxyl radical with the growing radicals; k_g is the growth rate constant; $k_t{}'$ is the recombination rate constant of two growing radicals.

Polymerization in the presence of aminoxyl radicals allows one to control the kinetic parameters and prepare narrow-disperse polymers with a specified molecular mass and block copolymers. The polymerization behavior in the presence of aminoxyl radicals depends on the radical structure. It has been found[9,10] that by using sterically hindered aminoxyl radicals, it is possible to reduce the polymerization temperature from 120 to 90 °C. In the case of using a series of high-molecular-weight aminoxyl radicals formed upon the reaction of spin traps with the growing radical, the controlled synthesis of polymers proceeds in the kinetic mode and temperature conditions as close as possible to the industrial process conditions.[4—8] In this case, "living" radical polymerization may proceed not only for styrene or its analogs but also for a broad range of other monomers.

Despite all advantages, "living" polymerization has not been practically implemented as yet due to some shortcomings and limitations. The most significant of these are high cost and complexity of industrial synthesis of controlling additives.

In this paper, we propose an original approach in which aminoxyl radicals are formed *in situ* from sterically hindered amines. In the presence of oxidants, primary and secondary amines are known[11—13] to be oxidized, in particular, yielding aminoxyl radicals (Scheme 2).

As the oxidant, we chose benzoyl peroxide (BP), which is extensively used in industry to initiate polymerization processes.

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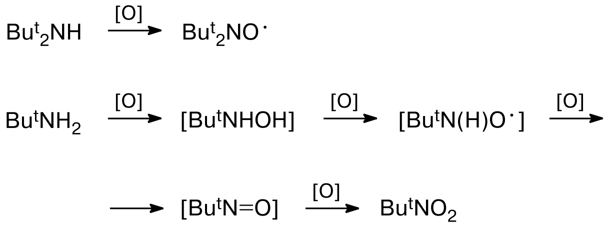
Scheme 2



The purpose of this work is to study polymerization features of styrene (St) in the presence of a binary controller initiator based on a primary (*tert*-butylamine, TBA) or secondary (di(*tert*-butyl)amine, DBA) aliphatic amine and BP.

Results and Discussion

It was found that introduction of ~2.0—4.0 mol.% DBA into the system results in degeneration of the gel effect (Fig. 1). A decrease in the rate at the self-acceleration stage is possible due to both a pseudoliving reaction mechanism[2] and participation of the amine in chain transfer.[14]

When the secondary DBA is replaced by primary TBA in the same concentration, the positive effect on the kinetic parameters of polymerization is not so pronounced. In this case, the time it takes to reach the limiting conversion substantially increases (Fig. 2) and the initial rate of polystyrene (PS) synthesis in the presence of amine in concentrations below 4.0 mol.% remains rather high. As the amine concentration increases to 4.0 mol.%, the process rate is low starting from ~30% conversion. On further increase in the TBA concentration (8.0 mol.%), the inhibiting action of the additive becomes more pronounced and visible, starting from low conversions of monomer into the polymer.

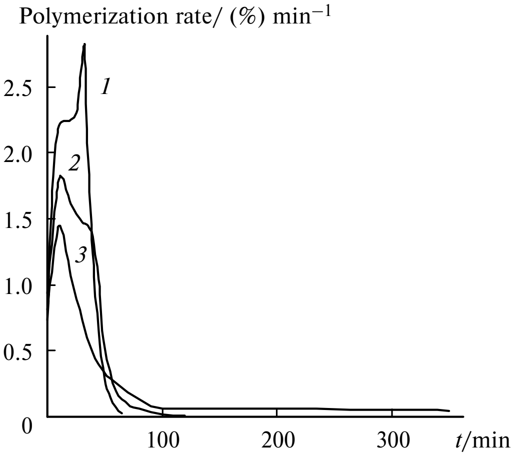


Fig. 1. Differential curves of St polymerization in the presence of 0 (*1*), 1 (*2*), and 2 mol.% (*3*) DBA at 100 °C. BP as the initiator (1 mol.%).

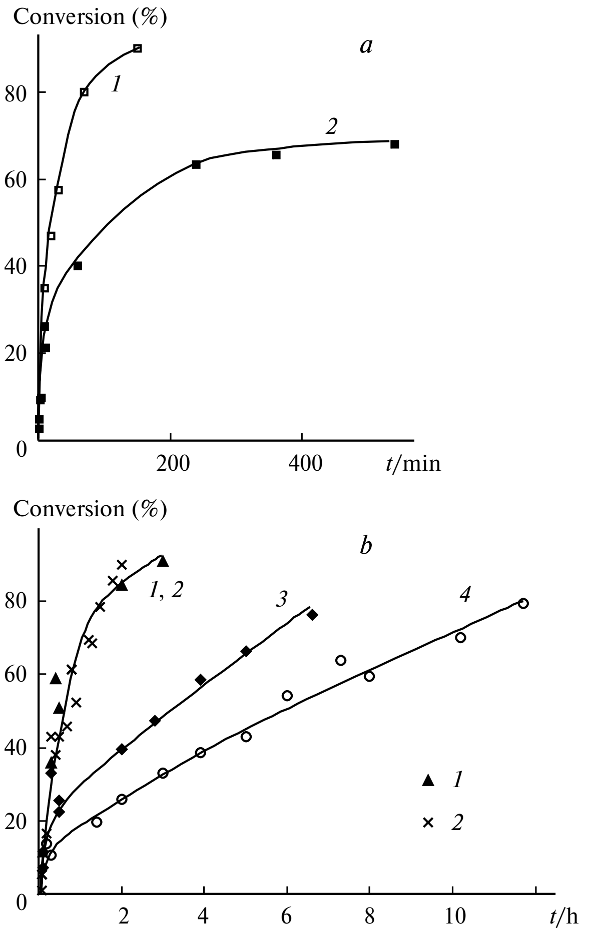


Fig. 2. Integral kinetic curves for St polymerization in the presence of DBA (*a*) and TBA (*b*) at 100 °C: the DBA concentration is 1 (*1*) and 2 mol.% (*2*); the TBA concentration is 0 (*1*), 1 (*2*), 4 (*3*), and 8 mol.% (*4*). BP as the initiator (1 mol.%).

The observed differences in the type of influence of primary and secondary amines on the St polymerization kinetics correlate with the results of ESR studies of these systems. The ESR spectrum of the St + BP + DBA polymerization system exhibits a triplet with the splitting constants at nitrogen a_N = 15.5 G corresponding to di(*tert*-butyl)aminoxyl. These results suggest that the stable aminoxyl radicals formed *in situ* (see Scheme 2) would directly affect the chain propagation step (see Scheme 1).

Theoretically, primary amines are also able to produce aminoxyl radicals upon oxidation at one of the reaction steps (see Scheme 2). Nevertheless, we did not detect intermediate aminoxyl radicals in the St + BP + TBA system by ESR. Probably, this is due to the fact that some other processes involving the amine and BP as the oxidant can proceed under the chosen conditions, and the formation of aminoxyl radicals is not the major reaction route.

Table 1. Initial rate of St polymerization at 60 °C in the presence of BP (1 mol.%) and amines (TBA and DBA)

Amine	Concentration (mol.%)	Initial polymerization rate $\cdot 10^4$/mol L^{-1} s^{-1}
—	—	1.2
TBA	1	1.1
	2	0.9
	4	0.7
	8	0.6
DBA	1	2.3
	2	2.3

The kinetic parameters of St polymerization in the presence of TBA and DBA at low conversions were estimated by analyzing the initial sections of the kinetic curves using dilatometric data at 60 °C (Table 1).

It was found that introduction of TBA in various concentrations into the polymerization system does not affect substantially the initial process rate. Although the rate of synthesis of macromolecules decreases, it still remains commensurable with the rate of BP-initiated polymerization without TBA. A rather pronounced inhibition of the polymerization has been noted on the addition of TBA in a concentration of 8.0 mol.%: the initial rate of the macromolecule synthesis decreases almost twofold.

The addition of secondary amines increases somewhat the initial rate of St polymerization in the presence of the peroxide initiator (see Table 1). This increase in the St polymerization rate in the presence of DBA is apparently due to additional radical formation in the system caused by the reaction of amine with the peroxide according to single-electron transfer pattern, resulting in accelerated peroxide decomposition.[15]

Table 2. Molecular-mass characteristics of PS synthesized in the presence of amines at 100 °C (BP concentration, 1 mol.%)

Amine	Concentration (mol.%)	Conversion (%)	$M_n \cdot 10^{-3}$	$M_w \cdot 10^{-3}$	M_w/M_n
—	—	91	20	41	2.1
TBA	1	17	28	35	1.3
	1	43	31	42	1.5
	1	86	56	107	1.7
	2	28	22	29	1.3
	2	83	31	113	3.6
	4	25	20	35	1.7
	4	66	37	127	3.4
	8	11	36	50	1.4
	8	70	92	265	2.9
DBA	2	10	12	17	1.4
	2	21	13	24	1.9
	2	40	21	38	1.9
	2	68	25	55	2.2

Note. M_n and M_w are the number-average and weight-average molecular masses, respectively, M_w/M_n is the polydispersity factor.

The molecular-mass characteristics of the PS obtained in the presence of primary and secondary amines are presented in Table 2. The plots for the PS viscosity-average and number-average molecular masses and the PS molecular-mass distribution (MMD) are shown in Figs 3 and 4.

As follows from the obtained data (see Fig. 3, *a*), the introduction of 2 mol.% DBA into the polymerization system results in a straight-line dependence of the molecular mass on the conversion, which is a typical feature of controlled radical polymerization. As the conversion of St increases, the MMD mode regularly shifts toward higher-molecular-mass products (see Fig. 4, *a*). However, it is noteworthy that the polydispersity of PS samples obtained in the presence of DBA is relatively high and increases during polymerization (see Table 2); note also a substantial broadening of the MMD curves. Most likely, the increase in the polydispersity factor during polymer-

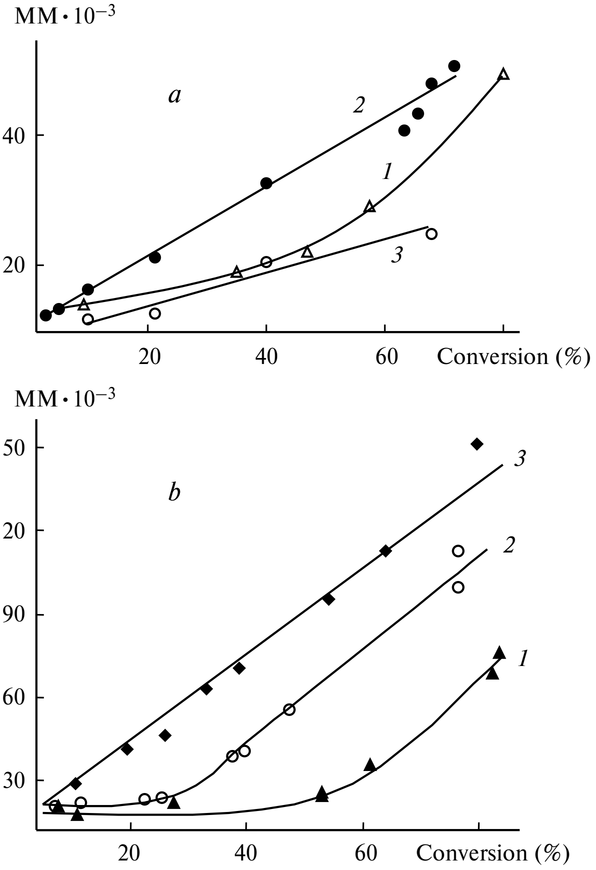


Fig. 3. *a*. Viscosity-average (*1*, *2*) and number-average (*3*) molecular masses (MM) of PS *vs.* conversion: the DBA concentration is 1 (*1*) and 2 mol.% (*2*, *3*). *b*. Viscosity-average molecular mass of PS *vs.* conversion: the TBA concentration is 2 (*1*), 4 (*2*), and 8 mol.% (*3*). Conditions of synthesis: 100 °C, BP as the initiator (1 mol.%).

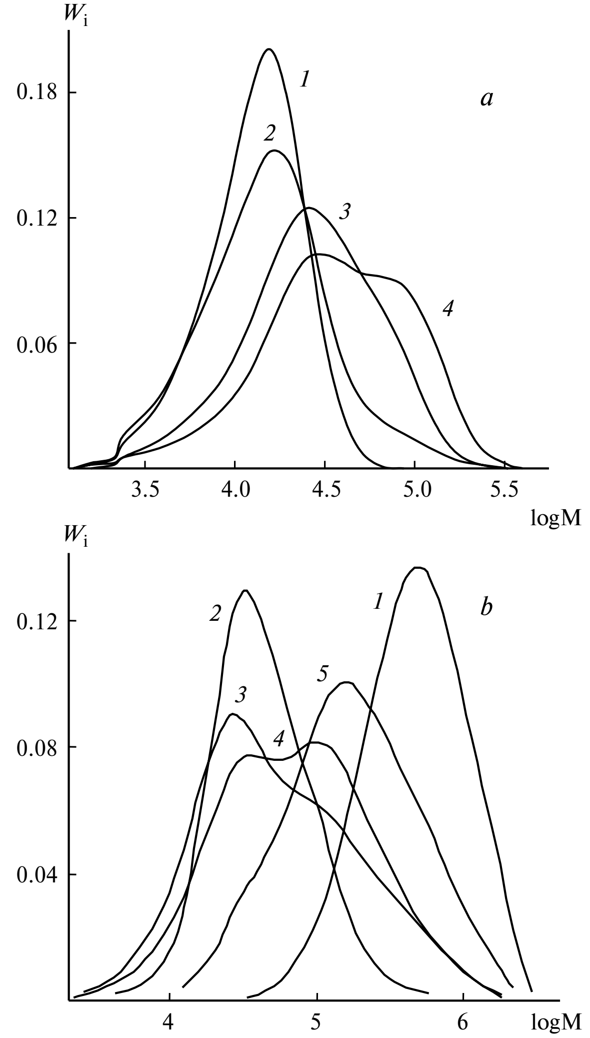


Fig. 4. *a*. Molecular-mass distribution (MMD) curves of PS with different conversions: 10 (*1*), 21 (*2*), 40 (*3*), and 68% (*4*). Synthesis conditions: 100 °C, BP (1 mol.%) and DBA (2 mol.%). *b*. MMD curves for PS: the TBA concentration is 0 (*1*), 1 (*2*), 2 (*3*), 4 (*4*), and 8 mol.% (*5*); the conversion is 84 (*1*), 86 (*2*), 83 (*3*), 66 (*4*), and 70% (*5*). Synthesis conditions: 100 °C, thermal (*1*) and substance (*2—5*) initiation, BP (1 mol.%).

ization is due to participation of the amine in a number of side processes (chain transfer, induced peroxide decomposition, and so on) mentioned above.

Interesting features have been revealed while examining the molecular-mass characteristics of the PS synthesized in the presence of TBA (see Fig. 3, *b* and 4, *b*; Table 2). It follows from the data presented in Fig. 3, *b* that the introduction of 8.0 mol.% amine induces a linear increase of the viscosity-average molecular mass *vs.* conversion. This attests indirectly to a controlled mechanism of the polymerization. However, as the additive concentration decreases (to 2—4 mol.%), the contribution of uncontrolled process increases and, therefore, the plot for the molecular mass *vs.* conversion acquires two sections and a kink typical of polymerization processes accompanied by gel effect. In the initial section, the PS molecular mass remains almost invariable, while for higher conversions, it sharply increases. When TBA and the initiator are taken in equal concentrations (1.0 mol.%), the dependence of the molecular-mass characteristics of the polymer on the conversion is S-shaped, which is typical of the usual (uncontrolled) radical polymerization with gel effect.

The character of influence of TBA on the MMD and the polydispersity factors of the polymers are also determined by the additive concentration (see Fig. 4, *b*). Indeed, upon the addition of amine in low concentrations (1.0 mol.%), the polydispersity factors of the PS are relatively low (see Table 2) and the MMD is unimodal. With a higher amine concentration, starting from a 40% conversion, the MMD curves are substantially broadened and become bimodal (see Fig. 4, *b*, curves *3—5*). This suggests that in this case, chain propagation follows two parallel mechanisms (involving two active sites). The polydispersity factors of the polymers obtained in the presence of 2—8 mol.% TBA at high conversions are also greater than those of the samples synthesized without the additive (see Table 2). This increase in the polydispersity following the introduction of amine is probably due to side processes, in particular, chain transfer on the amine and other reactions of the amine with BP characteristic of this type of system. On the one hand, it is possible that 2-methyl-2-nitropropane resulting from amine oxidation with BP is accumulated and takes part in polymerization (see Scheme 2). As the amine concentration increases, the contribution of side processes involving these compounds increases, resulting in the bimodal distribution and greater polydispersity of the samples. On the other hand, when this process is carried out at a high amine concentration, peroxide might be completely consumed; as a result, conventional thermal polymerization of St takes place, which may cause an increase in the PS polydispersity (see Table 2). This is confirmed by the fact that an increase in the TBA concentration entails a considerable increase in the molecular mass of PS (see Fig. 3, *b*), a bimodal MMD, and a shift of the mode to higher masses comparable with the molecular mass of the PS obtained upon thermal initiation (see Fig. 4, *b*).

An important characteristic feature of the pseudoliving polymerization is that the polymers isolated from the reaction mixture are able to initiate further polymerization. In order to test the initiating activity of the PS prepared in the presence of 2 mol.% DBA, we synthesized polystyrene—polymethyl methacrylate block copolymers (PS—PMMA) at 100 °C using PS-macroinitiators with different conversions. The molecular-mass characteristics of the block copolymers are summarized in Table 3.

The obtained PS—PMMA block copolymers were washed out from homopolymers by successive selective

Table 3. Block copolymerization results in the PS-macroinitiator—MMA system at 100 °C

Macro-initiator	Conver-sion (%)	Homopolymer (wt.%)		Block copolymer (wt.%)	$M_n \cdot 10^{-3}$	M_w/M_n	PS fraction in the block copolymer (wt.%)
		PS	PMMA				
PS-18600	36	35	6	59	43	3.9	59
PS-25200	31	17	15	68	70	5.5	39

extraction. For PS and PMMA, θ-solvents were used (cyclohexane and acetonitrile, respectively) and the removal of homopolymers was monitored by IR spectroscopy (see Table 3). It can be seen that the copolymer is the major product; however, the fraction of PS and PMMA homopolymers is also high, which implies a substantial contribution of thermal initiation.

The molecular-mass characteristics and the MMD of the block copolymerization products obtained in the presence of macroinitiators show some specific features (see Table 3 and Fig. 5). For example, the molecular masses of block copolymer samples are higher than the molecular mass of the initial macroinitiator. However, it is noteworthy that the synthesized block copolymers have a rather broad polydispersity.

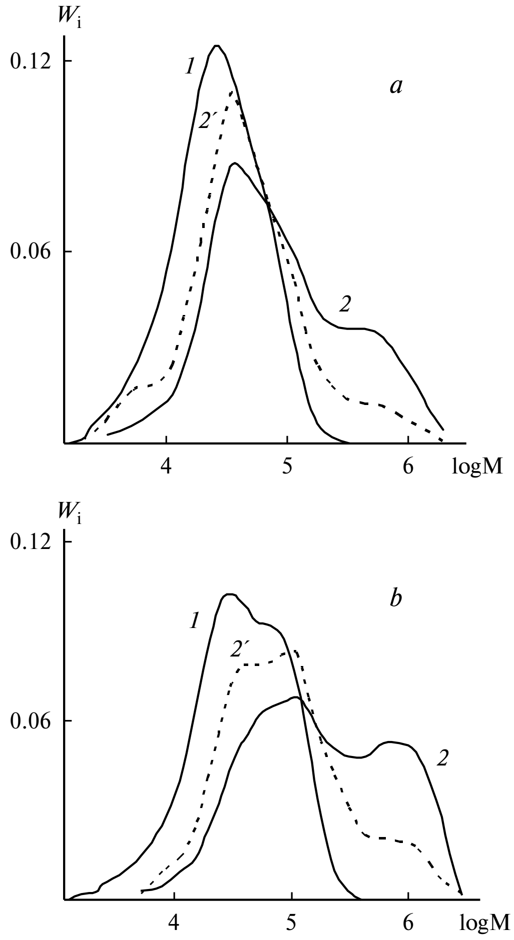


Fig. 5. MMD curves for macroinitiators PS-18600 (*a*) and PS-25200 (*b*) and PS—PMMA block copolymer samples synthesized at 100 °C based on these initiators: (*1*) macroinitiator; (*2*, *2′*) block copolymer. The curves were obtained with a refractometric (*1*, *2*) and UV (*2′*) detector.

The GPC data for the block copolymerization product (see Fig. 5) demonstrate that the refractometric and photometric MMD curves have different shapes. This attests to an inhomogeneity of St distribution in the molecules with different molecular masses. Molecules with lower molecular mass contain more St. It can also be seen from Fig. 5 that absorption typical of the styrene groups is also present for much longer macromolecules compared to those contained in the initial PS. This result indicates unambiguously that block copolymerization follows a somewhat more complicated route than the St homopolymerization in the presence of DBA. This is indicated by the polymodal MMD curves of the block copolymerization products. Nevertheless, the results confirm the fact that the PS molecules synthesized in the presence of DBA remain active and capable of initiating the methyl methacrylate (MMA) polymerization to give block copolymers.

To conclude, our studies demonstrated that binary systems based on primary and secondary aliphatic amines combined with benzoyl peroxide represent original controller initiators of polymer chain propagation in the polymerization of styrene.

Experimental

Di(*tert*-butyl)amine was synthesized by a known procedure,[16] TBA was a commercial chemical. Amines, the initiator (BP), St, and the solvents were purified by standard procedures.[17—20] The physicochemical characteristics of all of the compounds corresponded to published data.

The samples were prepared as follows: the monomer was placed into glass tubes, degassed three times by freezing the tubes in liquid nitrogen, and polymerization was carried out at a residual pressure of 1.3 Pa. Polymerization kinetics was measured by weight, dilatometric,[21] and thermographic methods.[22]

The macroinitiators for block copolymerization were prepared from styrene in the presence of BP (1.0 mol.%) and DBA (2 mol.%) at 100 °C. The macroinitiator synthesis was planned to ensure complete consumption of BP present in the system ($\tau_{1/2}$ = 25 min at 100 °C). The synthesized macroinitiator was freeze-dried from chloroform to remove the remaining St and added to MMA. The PS and MMA mixture was kept for ~150 h at 100 °C.

The molecular masses of polymers were determined by viscometry[23] and by GPC on a setup containing a set of styrogel columns with pore diameters of 10^5, $3 \cdot 10^4$, 10^4, 10^3, and 250 Å (Waters, USA) with an R-403 differential-refractometric (Waters) and UV detectors using THF as the eluent. Calibration was done against narrow-disperse polystyrene standards.[24] ESR studies were carried out on an AE-4700 instrument. Manganese ions in the magnesium oxide crystal lattice were used as the reference for magnetic field calibration.

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