Decomposition of Stable Free Radicals as "Self-Regulation" in Controlled Radical Polymerization

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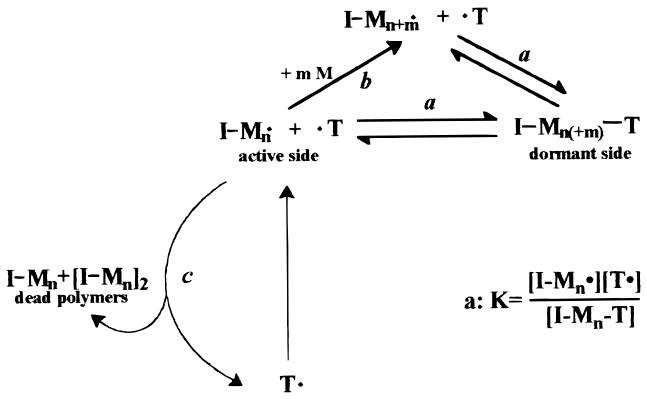
ABSTRACT: A new concept for controlled radical polymerization in the presence of stable free radicals is presented. Due to irreversible side reactions of free polymer radicals, the amount of dead polymer chains and, consequently, the concentration of stable free radicals increases during the polymerization reaction (Figure 1). Therefore, only monomers with the ability to constantly thermally initiate radical polymerization (e.g., styrene) to capture the excess counter radicals are susceptible to this type of polymerization. In contrast, we present a self-regulating process in controlled radical polymerization, which allows controlled radical polymerization of monomers with no spontaneous initiation. The increase of stable free radicals in our approach is prevented by slow decomposition of the counter radicals and by simultaneous formation of new initiating species. To prove this concept, two triazolinyl radicals (**4** and **7**) with different thermal stabilities have been studied. Their difference in stability shows a remarkable effect on their use as additives for the controlled radical bulk polymerization of styrene and MMA. The procession of the polymerization in the presence of spirotriazolinyl **7**, a stable radical, again strongly depends on the initiating properties of the monomer. While the polymerization of styrene is very well controlled, polymerization of MMA in the presence of spirotriazolinyl **7** could only be accomplished to very low conversions. In contrast, triazolinyl **4**, a less stable radical, is additionally able to effectively control the polymerization of MMA at comparably low temperatures.

Introduction

Recently, the development of controlled radical polymerization has attracted much attention.[1−8,10] The unique features of the simplicity of radical reactions combined with the advantages offered by living polymerizations made it one of the most extensively studied systems in industrial and in academic research. The idea of controlled radical polymerization is to avoid the bimolecular, irreversible termination reactions, typically obtained in a free radical polymerization (recombination, disproportionation, ...) by decreasing the number of growing radical chains at one time. Thus, although the reaction itself becomes comparably slow, the molecular mass can be very well controlled and very narrow molecular weight distributions can be obtained.[1]

One possibility to reach a controlled radical polymerization is to reversibly form a dormant species by the addition of stable free radicals to the radical polymerization (Figure 1).[2] The polymerization of styrene, mediated by the addition of 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO), became one of the most extensively studied systems of this kind.[3] For example, polystyrene with polydispersity indices around 1.1 have been obtained so far using this reaction. However, many questions remained unanswered. The TEMPO-controlled polymerization of styrene works well for low molecular weight polymers, typically below 10 000, but at higher masses and higher conversions, the degree of TEMPO end functionalization of the polymers seems to decrease dramaticaly.[4] More importantly, except for the polymerization of styrene and styrene derivatives, only a few monomers, mainly in random copolymers with styrene, were accessible to the TEMPO-controlled polymerization.[5] Remarkably, the polymerization of acrylates and methacrylates could not, or only with great effort, be accomplished.



I: initiator, **M**: monomer, **T•**: counter radical

Figure 1. Controlled radical polymerization and its side reactions.

An explanation for this behavior was offered by Fukuda et al.[6] The irreversible side reactions of free polymer-radicals (reactions c in Figure 1: recombination, disproportionation, ...) cannot be completely suppressed.[4,7] This has serious consequences for the polymerization reaction. The amount of dead polymer chains increases, leading to a broadening of the molecular weight distribution. More importantly, the concentration of the counter radicals in solution increases as well, leading to a shift of the polymerization equilibrium (reaction a) to the dormant side. Gradually, the polymerization reaction stops. However, this situation is avoided when styrene is used as monomer. Since styrene is able to undergo thermal initiation, the newly formed radical chains take part in the polymerization equilibrium as well and capture free counter radicals again. Thus, the thermal initiation of styrene prevents the increase of stable free radicals in solution and the polymerization equilibrium remains at a point where

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controlled polymerization is still effective. Furthermore, since the polymerization depends on the formation of new radical chains, the TEMPO-controlled polymerization proceeds with the same rate as the thermally initiated radical polymerization of styrene.

This explanation, as reasonable as it is, bears a problem. The thermal initiation of styrene is essential to achieve a controlled polymerization. Going one step further, this means that all monomers, which are not able to initiate a radical polymerization on their own, will not be suitable candidates for the TEMPO-controlled radical polymerization.

A first solution to this problem was proposed by Fukuda et al. and Matyjaszewski et al.[8] They pointed out, that systems, in which the dissociation of the polymer−counter radical adduct I−M_n−T, but no spontaneous initiation, occurs, can be "awakened" by the continuous addition of further initiator I•. As has been shown, the polymerization rate could be increased by this method by a factor of up to 3. Additionally, no appreciable broadening of the molecular weight distribution was observed. But the continuous addition of one reactant represents a further complication to the controlled radical polymerization. We therefore present a different approach to the above problem: instead of continuous addition of initiator we introduce a counter radical that decomposes by releasing new initiating species (Figure 4).

Experimental Section

Materials. All chemicals were purchased from Aldrich. Benzoyl peroxide (BPO) was recrystallized from diethyl ether. Styrene (S) and methyl methacrylate (MMA) were stirred over CaH_2 for 12 h and distilled in vacuo prior to use. All other chemicals were used as received without further purification.

1,3,5,5-Tetraphenyl-Δ^3-1,2,4-triazolin-2-yl (**4**) and 1′,3′-diphenylspiro[9*H*-fluorene-9,5′-[Δ^3-1,2,4-triazolin]-2-yl] (**7**) were prepared and characterized according to the literature.[9]

Polymerization. A typical polymerization procedure was carried out as follows: Polystyrene was prepared in a controlled radical polymerization of styrene (10 mL) with BPO (24.2 mg, 0.1 mmol) in the presence of triazolinyl free radical **4** (56.1 mg, 0.15 mmol). A 25 mL Schlenk tube, fitted with magnetic bar, was three times heated in vacuo and argon flushed. Styrene was injected into the vessel and degassed by the "freeze and thaw" technique (three times), prior to the addition of the initiator and the additive. The sealed Schlenk tube was placed in an oil bath maintained at 130 °C. The reaction was allowed to continue for the reaction times listed in Table 1. Samples of 1−2 mL volume were taken at intervals, diluted with THF and precipitated in 100 mL of methanol. The polystyrene was dried at 50 °C in a vacuum oven.

PMMA samples were prepared in a similar way. After addition of the radical **4**, the deeply colored solution was placed in an oil bath and maintained at 90 °C for 5 min. The nearly colorless solution was then cooled to the desired reaction temperature, and the reaction was allowed to proceed as above.

Analyses. Monomer conversions of the polymerization reactions were measured by GC, using *n*-octane as the internal standard. Molar masses and distributions were measured by gel permeation chromatography (GPC) using PI-gel columns in THF with polystyrene standards.

ESR experiments were carried out on a Bruker ESP-300 spectrometer, operating at X-band frequency (9−10 GHz) with 100 kHz field modulation. The spectra were measured at different temperatures with a Bruker variable temperature unit ER 4111 VT.

Results and Discussion

The research in "counter radical" controlled polymerization, until now, focused mainly on (nitroxide) radicals with very high stability, especially at high reaction temperatures and in solution. In contrast, we tried to reduce the stability of the counter radical in the reaction media. The counter radical should fulfill two requirements. First, it should be stable enough to take part in the equilibrium of the controlled radical polymerization (reaction a in Figure 1) without decomposition. Second, when the concentration of counter radicals increases during the polymerization reaction, the tendency toward decomposition by formation of new initiating radicals I• should increase as well.

Table 1. Polymerization of Styrene and MMA in the Presence of Triazolinyl 4 and 7[a]

no.	additives	time (h)	conv. (%)	$10^{-3}M_n$	$10^{-3}M_w$	M_w/M_n
1	BPO (0.1 mmol)	0.25	8	7.1	12.9	1.86
	7 (0.15 mmol)	0.5	17	16.9	23.3	1.37
	St (87.6 mmol)	0.75	24	23.4	32.5	1.39
	140 °C	1	29	28.1	39.1	1.40
		1.5	39	38.1	51.5	1.35
		2	45	42.8	61.5	1.43
		3	57	54.6	76.9	1.41
		4	71	59.1	87.8	1.49
2	BPO (0.1 mmol)	0.25	18	18.7	34.2	1.82
	4 (0.15 mmol)	0.5	28	25.6	43.2	1.68
	St (87.1 mmol)	0.75	36	31.9	52.5	1.65
	140 °C	1	45	36.4	59.6	1.63
		1.5	55	41.8	70.4	1.69
		3	80	59.9	101.8	1.69
3	BPO (0.1 mmol)	22	2			
	7 (0.15 mmol)					
	MMA (103 mmol)					
	65 °C					
4	BPO (0.1 mmol)	1	6	30.0	30.4	1.22
	4 (0.15 mmol)	2	16	44.6	61.6	1.38
	MMA (103 mmol)	3	21	55.9	83.8	1.50
	65 °C	4	32	63.2	100.0	1.58
		7	48	78.7	125.9	1.60

[a] Key: BPO, benzoyl peroxide; St, styrene; MMA, methyl methacrylate. M_n and M_w determined by gel permeation chromatography (in tetrahydrofuran using polystyrene or poly(methyl methacrylate) standards).

Our primary work dealt with the preparation of homopolymers and block copolymers by controlled radical polymerization in the presence of triazolinyl radicals.[10] The triazolinyl radicals **4** and **7** were synthesized according to Neugebauer et al.[9] by ring closure of N-phenylbenzohydrazonyl chloride (**1**) with either α-phenylbenzylamine (**2**) or 9-amino-9*H*-fluorene (**5**) respectively, followed by oxidation of the triazolin systems by $K_3Fe(CN)_6$ (Figure 2). Both systems are very stable and can be stored and handled at room temperature for months without even a trace of decomposition products.

Spirotriazolinyl **7** is an extremely stable radical even at high temperatures and in solution. At 100 °C in toluene for 30 h, no decrease in ESR intensity was observed (Figure 3). Its application to controlled radical polymerization will, therefore, similar to the TEMPO system mentioned above, depend strongly on the initiating abilities of the monomer used.

In contrast, triazolinyl **4** decomposes (Figure 4) with a half-lifetime of about 20 min under the conditions used. Therefore, the triazolinyl radical **4** fulfills the requirements mentioned above: it is stable on the time scale of the equilibrium of the controlled radical polymerization (**4** only needs microseconds to capture a growing polymer radical chain) but is not stable on the time scale of the whole polymerization reaction.

The thermal decomposition of **4** proceeds via release of a phenyl radical **9** to a stable aromatic triazol compound **8** (identified by mass spectrometry), as shown

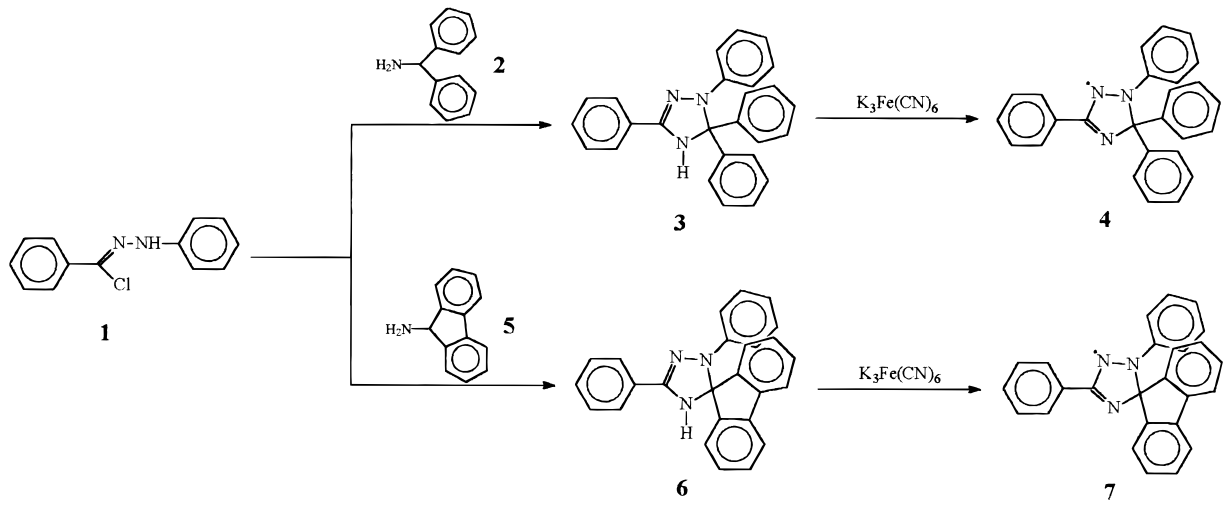

Figure 2. Synthesis of triazolinyl-radicals **4** and **7**.

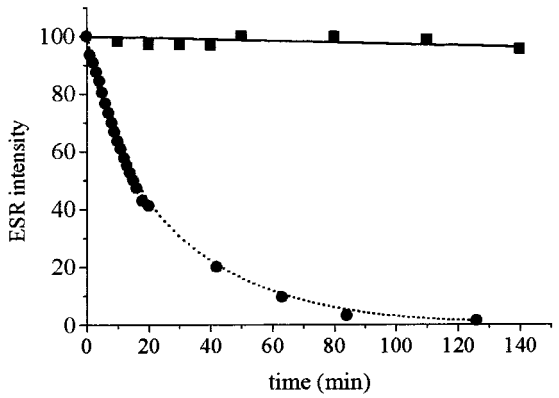

Figure 3. Normalized ESR intensity of (●) triazolinyl **4** and (■) spirotriazolinyl **7** in toluene at 100 °C.

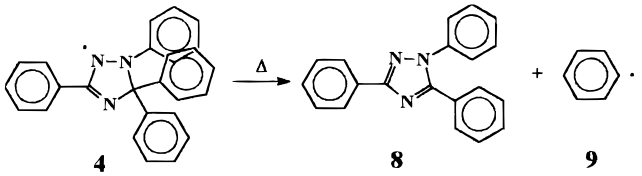

Figure 4. Thermal degradation of triazolinyl **4**.

in Figure 4. Since phenyl radicals are known to initiate radical polymerization, this behavior is of crucial importance to the use of **4** in controlled radical polymerization. A decrease of the counter-radical concentration during the polymerization is prevented not only by decomposition of triazolinyl radicals but also by formation of new starting radicals. Not all excess triazolinyl **4** is irreversibly removed from the polymerization mixture (by thermal degradation), since half of the excess will be captured by the new growing radical polymer chains, initiated by phenyl radicals. Therefore, the concentration of free counter radicals in solution does not depend on possible initiating properties of the monomer, but on the properties of the triazolinyl **4**.

To verify this assumption, a model reaction for the early stage of the polymerization was performed. The decomposition of azobis(isobutyronitrile) (AIBN) in toluene in the presence of 1.5 mol equiv **4** at 100 °C was observed. The calculated half-lifetime of AIBN at this temperature is about 30 min.[11] The FD mass spectrum obtained after 60 min is shown in Figure 5 with several peaks assigned.

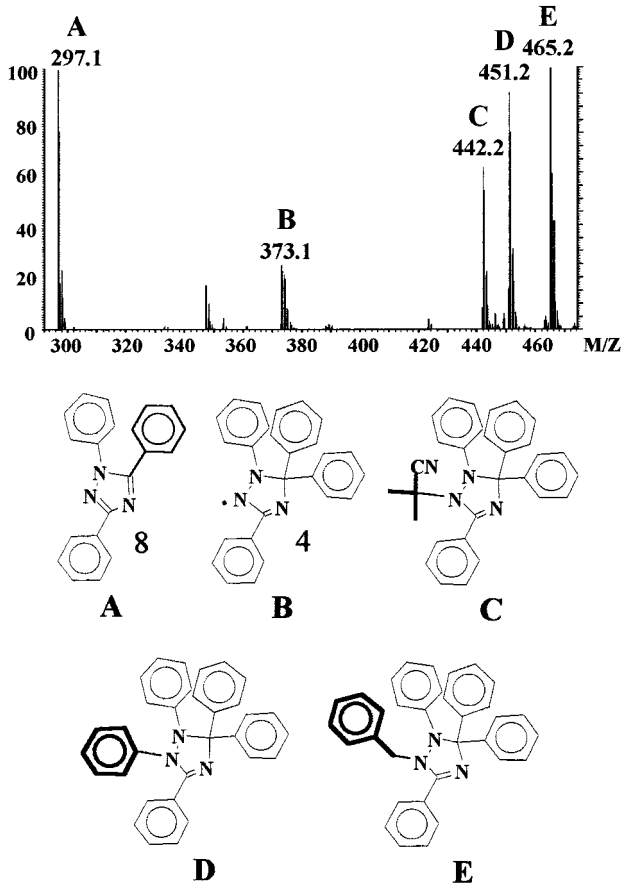

Figure 5. FD mass spectrum of AIBN, decomposed in the presence of **4** in toluene at 95 °C.

The triazolinyl radical **4** gives a signal at *m*/*z* 373.1. The decomposition product **8** shows a peak at *m*/*z* 297.1. At *m*/*z* 465.2 the coupling product of triazolinyl **4** with benzyl radicals, resulting from transfer reactions of the initiator to the solvent toluene, can be assigned.

The peaks at *m*/*z* 442.2 and 451.2 can be assigned to the coupling product of triazolinyl radicals with AIBN and phenyl fragments, respectively. Thus, the spectra confirms the above arguments: the excess of **4**, which is not captured by the fragments coming from the decomposition of AIBN, partly decomposes by release of phenyl radicals, which again captures the remaining triazolinyl **4**.

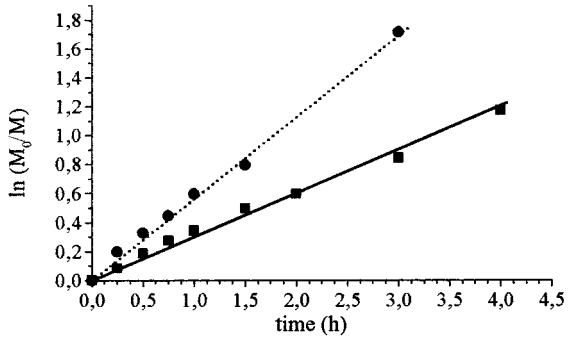

Figure 6. Semilogarithmic time−conversion plot for the bulk polymerization of styrene in the presence of **4** (●) or **7** (■) at 140 °C.

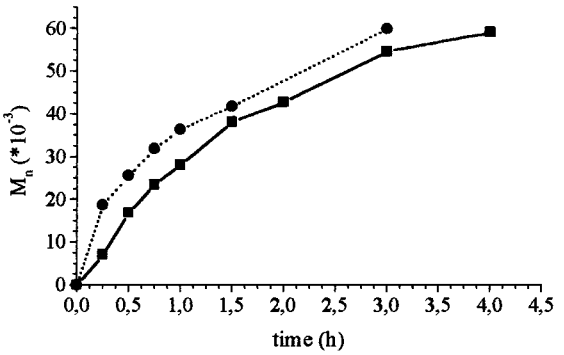

Figure 7. Development of the molar mass versus reaction time for the bulk polymerization of styrene in the presence of **4** (●) or **7** (■) at 140 °C.

Polymerization Reactions. The triazolinyl radicals **4** and **7** were submitted to the bulk polymerization of styrene. Benzoyl peroxide (BPO), which is known to initiate not only by benzoyloxy but also by phenyl radicals,[11] was used as the initiating system. Both radicals show a strong influence on the polymerization reaction. Typical results are summarized in Table 1.

A criterion often used to characterize a controlled polymerization in contrast to free radical processes is a linear increase of the conversion with reaction time. As can be seen from Figure 6, by addition of triazolinyl radicals **4** and **7,** both polymerization reactions fulfill this criterion. Furthermore, both radicals can clearly be distinguished from each other since the polymerization in the presence of spirotriazolinyl **7** gives a markedly smaller slope than the reaction with triazolinyl **4**.

In addition, a clear increase of the molar mass with increasing reaction time is observed (Figure 7). At same reaction times, the values of the molar masses for spirotriazolinyl polymers are lower than those of the corresponding triazolinyl polymer.

The results confirm the mechanism proposed above. The controlled polymerization in the presence of the stable spirotriazolinyl **7** depends on the formation of new radicals by the thermal initiation of styrene, a comparably slow process, to prevent an increase of free triazolinyl radicals in solution and, consequently, to prevent the polymerization coming to a stop. A completely different situation exists for the polymerization in the presence of triazolinyl **4**. Again the polymerization proceeds via a controlled pathway. However, the radical **4** has two possibilities to prevent an increase of free radical concentration in solution. First, by slow thermal reinitiation of the monomer and second, in contrast to the spiro-triazolinyl **7** controlled polymerization, the counter radical itself possesses the ability to control its free concentration in solution by decomposing and at the same time forming new initiating radicals. The triazolinyl **4** controlled polymerization of styrene is independent of the slow thermal initiation of styrene but has a self-regulating mechanism.

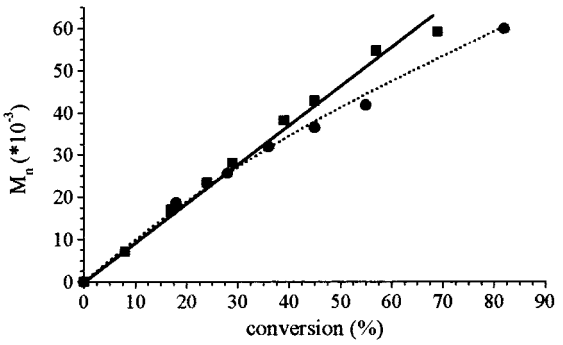

Figure 8. Development of the molar mass versus conversion for the bulk polymerization of styrene in the presence of **4** (●) or **7** (■) at 140 °C.

A further criterion often used to define a controlled polymerization processes is an increase of the molecular weight versus conversion. The dependence of the molar mass upon yield for the polymerization of styrene in the presence of counter radicals **4** or **7** is reported in Figure 8. Clearly, both polymerization reactions show an increase of molar mass; therefore, both can be referred to as controlled polymerizations.

Polymers obtained in the spirotriazolinyl **7** controlled polymerization show a linear increase of the molar mass up to high conversions. The molar mass depends on the number of polymer chains. Therefore, a linear increase suggests a constant number of growing radical chains. Since thermal initiation of styrene accounts for the loss of polymer chains due to irreversible termination reactions, this is in agreement with the mechanism proposed above. The total amount of stable spirotriazolinyl **7** and therefore the number of growing polymer chains remain constant during the whole reaction period.

Polymers obtained in a triazolinyl **4** controlled polymerization show different behavior. For up to 35% conversion, only small deviations from the same linear increase of the molar mass versus conversion, as compared to the case of polymers prepared in the presence of **7**, are observed. For higher conversion, the molar mass diverts from linearity to lower molecular weights (but still clearly increases). This behavior suggests an increase in the number of growing polymer chains. The formation of dead polymer chains formed by irreversible termination reactions in the radical polymerization are not only compensated, but additional initiating species are formed, since both thermal initiation of styrene and decomposition of triazolinyl **4** with formation of initiating species must be taken into account.

Additionally, the development of the polydispersity index (PDI) versus conversion was observed (Figure 9). The polydispersity index for the spirotriazolinyl **7** controlled polymerization decreases from 1.8 to values around 1.3, well below the theoretical limit of 1.5 for the free radical polymerization processes. The molar mass distribution remains narrow up to high conversions.

For polymerization controlled by the triazolinyl **4** the PDI decreases as well with increasing conversion, as

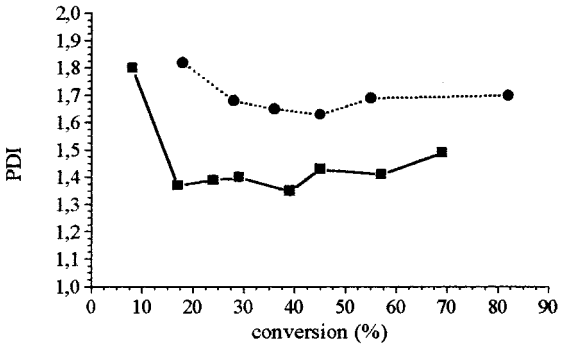

Figure 9. Development of the polydispersity index versus conversion for the bulk polymerization of styrene in the presence of **4** (●) or **7** (■) at 140 °C.

expected for a controlled radical polymerization. Values of about 1.6 were reached, at least well below PDIs of 2.5 obtained in a comparable uncontrolled radical polymerization.

The explanation for the different behavior of the two radicals in the polymerization reaction is the same as before. The polymerization in the presence of the stable spirotriazolinyl **7** is very well controlled, since thermal initiation of styrene accounts for dead polymer chains. The polymerization in the presence of **4** is somewhat *less* controlled, since the loss of dead polymer chains is overcompensated by decomposition/reinitiation of the counter radical and the thermal initiation of styrene. Nonetheless, the process still remains controlled, as has been shown above.

Additionally, we applied both radicals to the polymerization of MMA. As can be seen from Table 1, a controlled polymerization of MMA in the presence of triazolinyl **4** to high conversions and high molecular weights can be achieved. As we previously reported,[10] the molecular weight shows an increase when plotted versus conversion while polydispersity indices decrease to 1.2, well below the theoretical limit of 1.5 for free radical polymerization. In contrast, the addition of spirotriazolinyl **7** inhibits the polymerization. Only very low conversion could be obtained after 22 h, even with variation of the temperature up to the boiling point of MMA.

These results further support the proposed mechanism. The controlled polymerization in the presence of spirotriazolinyl **7** strongly depends on the initiating abilities of the monomer. Since MMA does not have this ability, the polymerization is stopped at a very early stage. In this case, the counter radical functions as inhibitor. In contrast, triazolinyl **4** does not depend on the initiating properties of the monomer, since the radical itself possesses the ability to control its own free concentration in solution. For styrene, this ability adds to the initiating properties of the monomer and results in a "less" controlled reaction, compared to a completely stable radical, e.g., spirotriazolinyl **7** or TEMPO. The advantage of this radical becomes apparent for non-initiating monomers, such as MMA. A controlled radical polymerization now only depends on the strength of the bond between counter radical and polymer, since the radical itself compensates for shifts in equilibrium concentrations. Triazolinyl **4**, therefore, is able to polymerize monomers that cannot, or only with further complications (e.g., adding further additives, adding further initiator), be polymerized with completely stable radicals.

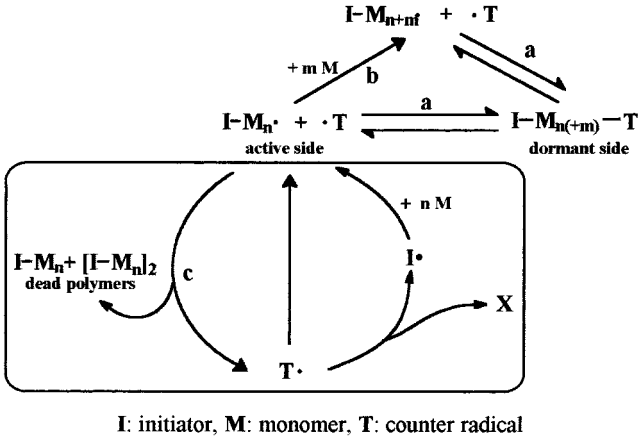

Figure 10. Controlled radical polymerization in the presence of triazolinyl **4**.

Conclusion

It has been shown that the addition of spirotriazolinyl **7** to the bulk polymerization of vinylic monomers is very much comparable to the known TEMPO-controlled polymerization. While the controlled polymerization of styrene proceeds remarkably well, a polymerization of MMA could not be accomplished. Spirotriazolinyl **7** depends on continuous initiating properties of the monomer (thermal initiation in the case of styrene).

In contrast, triazolinyl **4**, with a slightly reduced stability in contrast to **7**, has the ability to reduce its own free concentration in solution and therefore to establish a self-regulating reaction cycle (Figure 10).[12] The possibility of initiating a controlled polymerization is independent of the monomer properties. Consequently, monomers such as MMA, which are not accessible to the controlled radical polymerization using stable radicals such as spirotriazolinyl **7** or TEMPO, at least not easily, have the chance to be submitted to a controlled radical process. Thus, "stable counter radicals" with a somewhat reduced stability at the desired reaction temperature show promise in achieving a controlled radical homopolymerization of a greater range of vinylic monomers and, finally, in producing block copolymers of completely different monomers by controlled radical polymerization of both blocks.

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(12) A theoretical simulation, performed by A. H. E. Müller (University of Mainz, Germany) using the program "Predici" (CiT GmbH, v. 4.7) further supported the concept of a self-regulating process in controlled radical polymerization. For the polymerization of MMA in the presence of spirotriazolinyl **7**, typical conversions of lower than 10% were predicted before the reaction stops. In contrast, a well-controlled polymerization was predicted when a slow decomposition of the triazolinyl counter radical **4** was taken into account. These and other theoretical results will be discussed in detail in a later publication.

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