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Triazolinyl-controlled radical polymerization as innovative route to poly(hydroxyethyl methacrylate)

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Summary

2,2'-Azoisobutyronitril (AIBN) initiated radical polymerization of trimethylsilyloxyethyl methacrylate (TMS-HEMA) was carried out in N,N-dimethylformamide (DMF) with the triazolinyl radical (T•) as additive. The latter effected a controlled polymerization process at least up to 60 % monomer conversion. The obtained poly(TMS-HEMA) with triazolin endfunctionality was applied to polymerize styrene, resulting in the formation of poly(TMS-HEMA)-*block*-polystyrene.

Introduction

In the synthesis of functional polymers, narrowing down the molecular weight distribution of homopolymers and making block copolymers by reinitiation through living or functionalized chain ends of the first block remain to be two important goals. For hydroxyethyl methacrylate (HEMA), anionic and group transfer polymerization (GTP) techniques have successfully been employed for making block copolymers with styrene using the silylated precursor, namely TMS-HEMA [1,2]. Such materials find use in biomedical applications. The triblock copolymer-poly(HEMA)-*block*-polystyrene-block-poly(HEMA) is one of the best known blood compatible materials [3]. Research to enhance the mechanical properties of these materials are ongoing as exemplified by several recent reports [4,5]. It is therefore important to develop a method that would facilitate the synthesis of block copolymers of HEMA and would offer greater flexibility regarding the choice of the second block. Recently, Matyjaszewski et al. published controlled polymerization of HEMA as well as TMS-HEMA by an atom transfer radical polymerization (ATRP) process [6]. This method was also applied for the preparation of poly(TMS-HEMA)-*block*-polymethylmethacrylate in the same report. However, the disadvantage of ATRP is the problem of copper removal from the products. To overcome this drawback of ATRP we used the triazolinyl radical as stable free radical additive [7,8] for controlled radical polymerization of TMS-HEMA. Further, the resulting triazolin endfunctionalized first block served to initiate the polymerization of styrene to obtain poly(TMS-HEMA)-*block*-polystyrene.

Experimental Section

Materials

Styrene and HEMA (Aldrich) were distilled under vacuum over calcium hydride prior to use.

Chlorotrimethylsilane (Aldrich) was used as received. DMF (Fisher Chemicals) was purified by stirring overnight with sodium hydroxide and filtering followed by distillation under reduced pressure over phosphorous pentoxide. AIBN (Fluka) was crystallized from methanol. Triazolinyl (T•) [9] and TMS-HEMA [1,2] were prepared according to the literature.

Homopolymerizations

Polymerizations were performed in DMF or toluene solution. In a 25 ml Schlenk flask fitted with a magnetic bar, dried and flashed with high purity argon, TMS-HEMA was transferred using a hypodermic syringe. To it was added the required volume of solvent (to make [M] = 1.0 mol / 1), required weight of AIBN (0.1, 0.25, 0.5 or 1.0 mol% of monomer) and triazolinyl (1.5 times of AIBN by moles) under a positive flow of argon. The solution was degassed by the usual 'freeze and thaw' technique for three times. The contents of the flask were allowed to come to room temperature and the flask was placed in an oil bath at 100 °C for ten minutes. The flask was then taken out and put into another oil bath heated to the polymerization temperature. The polymerization reaction was terminated by freezing the Schlenk flask in liquid nitrogen. The product mixture, immediately after it melted, was directly submitted for GPC and was scanned by NMR for conversion. Kinetic data were generated by doing polymerizations in several Schlenk flasks and terminating the process after different reaction times. Results of the experiments are shown in Table 1. Deprotection of the silyl groups could be easily done using a very mild acidic condition [1]. The poly(HEMA) obtained could be precipitated from a DMF solution in t-butyl methyl ether.

Block copolymerization

Attempts to isolate the homopolymer free of the monomer by precipitation was complicated due to the fact that poly(TMS-HEMA) has only one good non-solvent namely water. In water, the precipitated polymer often got partially hydrolyzed and the poly(HEMA) formed thereby absorbed water to form a gel that was difficult to dissolve back into an organic solvent for block copolymerization. However, addition of dry THF followed by evacuation several times was found to be a good technique in removing the remaining monomer sufficiently that no trace of the same could be detected by NMR-spectroscopy.
For block copolymerization the end functionalized homopolymer was first dissolved in styrene. The solution was degassed by the 'freeze and thaw' technique and put at 100 °C – 120 °C, preferably 120 °C. The block copolymers were converted into poly(HEMA)-*block*-polystyrene by treating the silylated block copolymers with dil. HCl in DMF according to the literature [1]. The copolymers could be precipitated in petroleum ether.

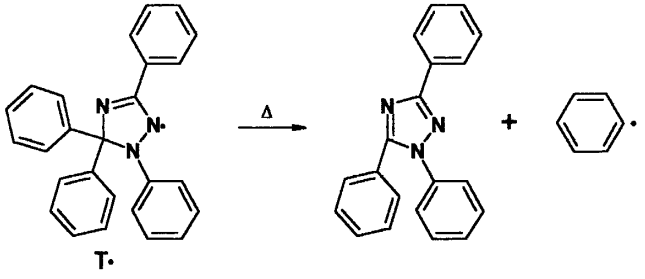
Analyses

Conversions were measured from ^{1}H-NMR-spectra using a 250 MHz Bruker NMR spectrometer. Molecular weight and molecular weight distributions were measured by GPC of the silylated polymer using SDV-gel columns in DMF with polystyrene standards.

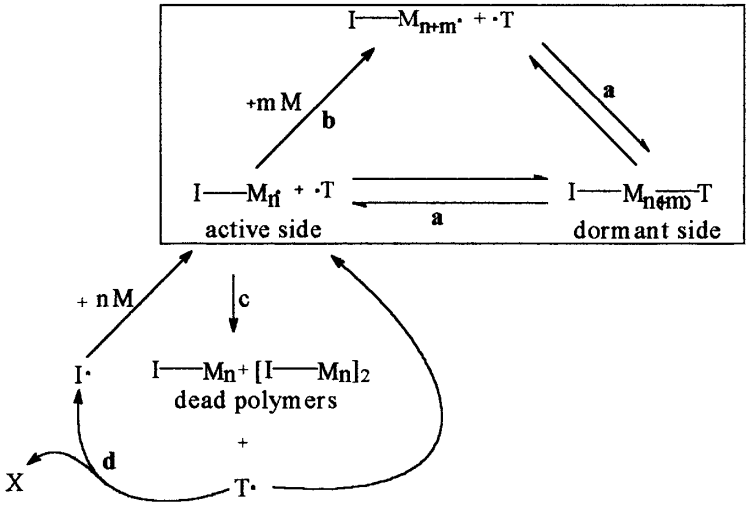
Results and Discussion

In our previous communications, the mechanism of self regulation offered by triazolinyl (T•, compare Scheme 1), a stable free radical (SFR), also known as a counter radical to the macroradical, has been discussed [7,8]. The essential features may be summarized here. In

controlled radical polymerization processes assisted by an added SFR, the amount of side reactions of the growing free macroradical is minimized by reducing its concentration in the equilibrium with the SFR (Scheme 2, path 'a'). Since unwanted side reactions of the free macroradical (Scheme 2, path 'c') cannot be suppressed quantitatively, the concentration of the SFR increases with time. In consequence the controlling equilibrium shifts, further to the dormant side, the polymerization gets slower and finally may stop. This problem restricted the suitability of the first SFR used in controlled polymerization, namely 2,2,6,6-tetramethylpiperidin-l-oxyl (TEMPO), to monomers like styrene [10] which is able to compensate the loss of growing centers by thermal initiation.



Scheme 1. Thermal decomposition of the free triazolinyl radical T•.

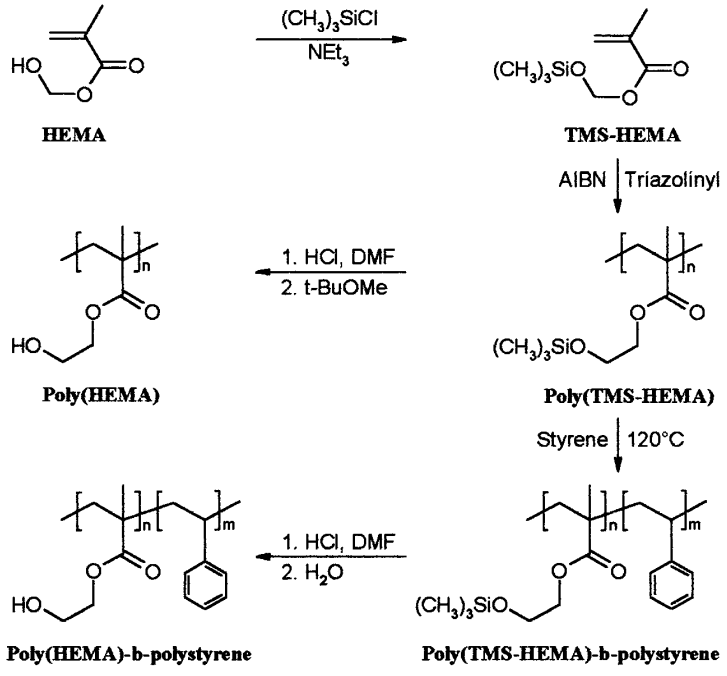


Scheme 2. SFR controlled radical polymerization and the self regulation mechanism of triazolinyl T•.

In difference to nitroxide-type radicals the free triazolinyl T•, slowly decomposes over the period of polymerization as described schematically in Scheme 2, path 'd'. Thereby, superfluous SFR is removed from the controlling equilibrium and its excess never rises to an extent which stops the polymerization. In addition, an initiating phenyl radical I• is formed upon every decomposition of triazolinyl T• (Scheme 1) and the loss of active centers is partially compensated. In consequence thermal initiation is no longer necessary to hold up the concentration of active centers.

Though recent publications with new types of nitroxides report success in the controlled radical polymerization of acrylates [10-13] these SFRs still fail in the case of methacrylic monomers. The results on employing triazolinyl for the controlled polymerization of methylmethacrylate (WMA) [7,8] were very encouraging and tempted us to examine the

suitability of triazolinyl stable free radical for controlled radical polymerization of other (meth)acrylic monomers. Hydroxyethyl methacrylate (HEMA) was an obvious choice.
We observed however, that the monomer is not amenable to controlled polymerization while the silylated precursor (TMS-HEMA) is. Under similar experimental conditions as described herein for TMS-HEMA, the narrowest molecular weight distribution that could be achieved with unprotected hydroxyethyl methacrylate is 2.0.
Usually silylation is employed to protect functional groups bearing a reactive hydrogen that can be harmful to the initiator or propagating chain end. Protection and polymerization is thus essential for anionic polymerization of functional monomers [14]. In contrast, radical chain propagation is usually not affected due to the presence of protic hydrogen. However, silylation improves the lipophilicity of a hydrophilic monomer thereby allowing solution polymerization in non-polar solvents and also altering the reactivity of the monomer towards copolymerization. Silylation has been explored as a method for improving the reactivity of hydrophilic monomers or materials when the reaction medium is non-polar or the other reactants are lipophilic [15,16].
Since we could not achieve the controlled polymerization of HEMA with the triazolinyl SFR as additive, we anticipated that silylation of the monomer might be fruitful in optimizing its reactivity. Furthermore, in the case of HEMA the removal of the corresponding ethyleneglycol dimethacrylate is difficult and a contaminated monomer results in network formation during the polymerization. The prevention of this is yet another reason to use the silylated precursor (TMS-HEMA) which is easy to purify. We have found this method to be successful in making the monomer HEMA amenable to controlled radical polymerization. Consequently, our work deals with the controlled polymerization of TMS-HEMA to synthesize poly(TMS-HEMA) of narrow molecular weight distribution carrying triazolinyl end groups. These will further serve to initiate the polymerization of styrene under the formation of block copolymers (Scheme 3).



Scheme 3. Silylation of HEMA, controlled polymerization steps and deprotection of the silyl group

The triazolinyl radical was used as the stable free radical additive along with AIBN initiator

for the solution polymerization of TMS-HEMA in DMF or toluene. The monomer concentration was kept constant at 1.0 mol / 1 for the study. The amount of utilized AIBN was between 0.1 mol% and 1.0 mol% of the monomer concentration. The concentration of triazolinyl was always kept 1.5 times of that of AIBN. Experimental data and typical results are shown in Table 1.

Table 1. Results of the polymerization of TMS-HEMA with and without addition of triazolinyl T•.

Exp.	Conditions[a]	Time / h	Conv. / (%)	$M_{n,SEC}$	M_w/M_n
1[b]	In toluene at 70 °C	5	52	129300	1.90
	[AIBN]/[M] = 0.0025	20	95	127400	1.95
2	In DMF at 66 °C	38	94	35400	1.58
	[AIBN]/[M] = 0.005				
3	In DMF at 66 °C	38	97	22900	1.60
	[AIBN]/[M] = 0.01				
4	In toluene at 66 °C	73	85	41500	1.50
	[AIBN]/[M] = 0.005				
5	In toluene at 66 °C	65	91	26100	1.54
	[AIBN]/[M] = 0.01				
6	In DMF at 84 °C	3.8	3	n. d.	n. d.
	[AIBN]/[M] = 0.001	5.5	25	59300	1.90
		7.5	35	69200	1.80
		12	57	104600	1.83
7		6.9	1	n. d.	n. d.
		8.0	5	22500	1.19
	In DMF at 70 °C	8.8	19	38600	1.48
	[AIBN]/[M] = 0.0025	9.5	22	45700	1.32
		11	41	55400	1.43
		12	60	58200	1.47
		21	84	62100	1.49

[a] [TMS-HEMA] = [M] = 1 mol / l; [T•]= 1.5 [AIBN]; [b] Reference experiments without triazolinyl
n. d.: not detected

Experiment 1 in the table was carried out without addition of triazolinyl. As is typical for a free radical polymerization the molecular weight is independent of conversion. Molecular weight distributions of M_w / M_n around 2 are observed by SEC. In comparison, the results of the experiments with triazolinyl show its controlling influence on the polymerization. This outcome can either be recognized by the narrower molecular weight distributions or the developing molecular weights with conversion or both, depending on the experimental conditions and will be discussed in the following.

First however, experiments 2 and 3 shall be compared with 4 and 5, respectively. The resulting molecular weights and their distributions are in the same range for similar degrees of conversion, but the polymerization rate in DMF is obviously about twice as high as in toluene under otherwise similar conditions. The reason for this observation was not investigated here but the influence of aromatic solvents on the polymerization rate constant in free radical polymerization of MMA has to be mentioned in this regard [17]. It is ascribed to possible charge-transfer interactions between the aromatic solvent and the growing centers

and might explain the lower polymerization rate in toluene. This suggested to use DMF as solvent in the kinetic experiments 6 and 7 which are treated next.
To affect a fast initiator decomposition the reaction mixtures have initially been heated to 100 °C for 10 minutes. Nevertheless, an inhibition period is observed for both experiments as can be seen in Figure 1. In this phase the triazolinyl SFR present in a large excess is able to scavenge all other generated radicals and the polymerization equilibrium (Scheme 2, path 'a') is on the dormant side. Due to the aforementioned self regulation process (Scheme 2, path 'd') the excess of free triazolinyl is torn down with increasing reaction time. The controlled polymerization process begins when the excess of triazolinyl SFR to all other radical species falls below a certain level. Now the equilibrium has shifted to the active side and steady chain propagation is the dominating reaction. Further based on the self regulation the still remaining excess of triazolinyl SFR serves to compensate termination processes (Scheme 2, path 'c') by the generation of initiating phenyl radicals (Scheme 2, path 'd'). Accordingly, the data taken from Table 1 result in a linear behavior of ln $[M_0]$ / [M] vs. time up to high conversion as depicted in Figure 1. This clearly shows the controlled character of the triazolinyl mediated polymerization of TMS-HEMA.
The second criterion for a controlled polymerization is shown to be fulfilled in Figure 2. There, a growth of polymer chains is established by the increase of molar mass with conversion. The development of the experimentally determined molecular weights does not begin in the origin of the graph. This is explained through the "uncontrolled" growth of a small amount of high molecular chains during the initial heating phase at 100 °C. Besides, the dependence of the molecular weight upon conversion deviates from linearity towards smaller values. This is due to the self regulation based formation of new chains throughout the polymerization process.

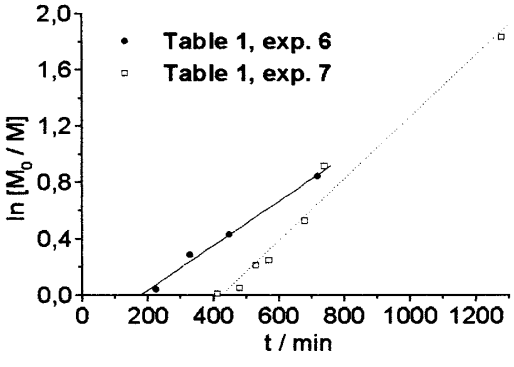


Figure 1. Polymerization of TMS-HEMA ([M] = 1 mol / l) in DMF. Logarithmic plot of conversion vs. time.
• = exp. 6: [AIBN] / [M] = 0.0010, T = 84°C.
□ = exp. 7: [AIBN] / [M] = 0.0025, T = 70°C.

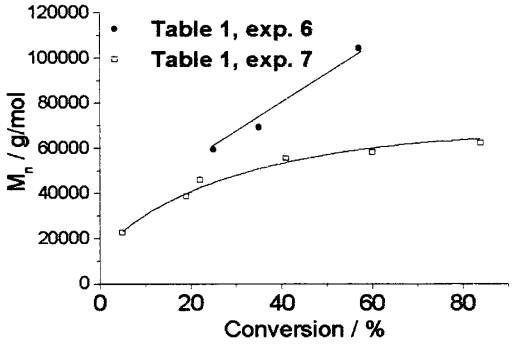


Figure 2. Molecular weight vs. conversion in triazolinyl mediated polymerization of TMS-HEMA.
• = exp. 6: [AIBN] / [M] = 0.0010, T = 84°C.
□ = exp. 7: [AIBN] / [M] = 0.0025, T = 70°C.

Reduction in the concentration of free triazolinyl rests upon its thermal decomposition. Therefore, identifying a temperature for the best control is an important task for a triazolinyl assisted polymerization. We observed that so far as a relatively narrow molecular weight distribution is concerned the process works better at 70 °C (experiment 7) than at 84 °C (experiment 6). With M_w / M_n = 1.8 – 1.9 the molecular weight distributions of the poly(TMS-HEMA) resulting from experiment 6 are similar to the ones of experiment 1

without addition of triazolinyl. In opposition to that the polymers formed at 70 °C in the presence of triazolinyl show molecular weight distributions between M_w / M_n = 1.2 at 5 % conversion and M_w / M_n = 1.5 at 84 %. The increasing tendency of the molecular weight distribution in dependence on the degree of conversion is based on the growing number of macromolecules resulting from the self regulation.

Table 2. Preparation of poly(TMS-HEMA)-*b*-polystyrene. Homopolymerization: [M] = 1.0 mol / l, [AIBN] = 2.5×10^{-3} mol / l, [T•] = 3.8×10^{-3} mol / l, solvent DMF, 70°C. Block copolymerization with styrene in bulk at 120°C.

Exp.	8	9	10
$M_{n,\,P(TMS\text{-}HEMA)}$ / (g / mol)	55400	66000	66000
$M_{n,\,P(TMS\text{-}HEMA)\text{-}b\text{-}PS}$ / (g / mol)	143300	113100	91300
$(M_w / M_n)_{P(TMS\text{-}HEMA)}$	1.43	1.42	1.42
$(M_w / M_n)_{P(TMS\text{-}HEMA)\text{-}b\text{-}PS}$	2.04	2.39	1.98
Time / h	2	2	1

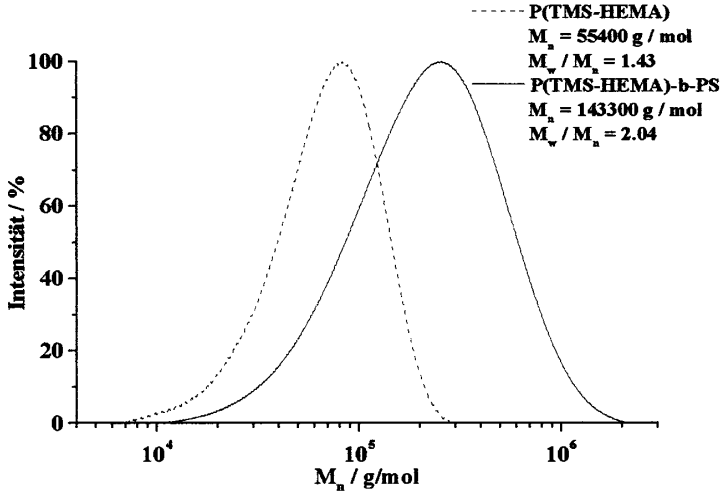


Figure 3. GPC traces of poly(TMS-HEMA) macroinitator vs. resulting poly(TMS-HEMA)-*b*-polystyrene. Taken from experiment 8, eluent DMF, calibration with PS-standards.

Next to the fulfillment of the kinetic criteria and narrow molecular weight distributions the reversible termination of the chain ends of the homopolymers formed in a controlled radical polymerization should allow their application as macroinitiators for the synthesis of block copolymers. We checked the re-initiation of the previously synthesized poly(TMS-HEMA) in the presence of styrene at 120 °C. The results of the block copolymerization of typical samples are shown in Table 2. For all these samples a distinct increase of the molecular weight and a unimodal GPC curve after the block copolymerization was obtained. This is also illustrated in Figure 3, which shows the GPC traces of the poly(TMS-HEMA) starting block and the poly(TMS-HEMA)-*b*-polystyrene resulting from experiment 8. These results clearly indicate that P(TMS-HEMA) obtained by triazolinyl controlled radical

polymerization is basically suited as initiator for the formation of block copolymers.

Conclusion

Silylation of the hydroxyl group of HEMA was found to be a necessity for the free radical approach towards controlled polymerization. The problem with HEMA is that it often contains ethyleneglycol dimethacrylate as an impurity which requires much effort to be removed and results in crosslinking of the poly(HEMA). We observed that using the trimethylsilyl protected monomer helps in two ways. Firstly TMS-HEMA could be distilled free of the dimethacrylate and secondly the monomer was amenable to triazolinyl controlled radical polymerization without the disadvantage of heavy metal removal as existing in ATRP. The triazolinyl SFR gave rise to the first-order kinetics of the TMS-HEMA polymerization up to high conversion with a steady molecular weight increase. The reversible linkage of the triazolinyl to the chain ends of the obtained poly(TMS-HEMA) was used to initiate the polymerization of styrene under formation of poly(TMS-HEMA)-*b*-polystyrene. Since the applied polymerization mechanism is of radical nature it provides the possibility of making block copolymers with a wider variety of monomers than accessible with anionic or group transfer polymerization techniques.

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