Polymer Bulletin 53, 295–304 (2005)
DOI 10.1007/s00289-005-0352-y

Polymer Bulletin

Controlled radical polymerization of N,N-dimethylaminoethyl methacrylate using triazolinyl as counter radical

Nawel S. Khelfallah, Maxim Peretolchin, Markus Klapper (✉), Klaus Müllen

Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D-55128 Mainz, Germany
Email: klapper@mpip-mainz.mpg.de; Fax:+49-6131-379100

Received: 8 August 2004 / Revised version: 21 November 2004 / Accepted: 18 December 2004

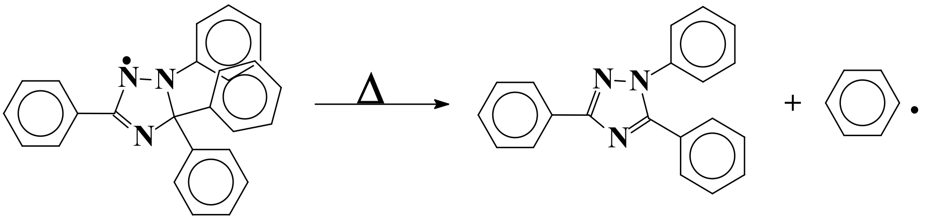
Summary

The role of the triazolinyl radical as additive for controlled radical polymerisation is investigated for N,N-dimethylaminoethyl methacrylate (DMAEMA) as polar monomer. A linear increase of the molecular weight with conversion and first-order kinetics are observed proving the controlled behaviour of the polymerization. The end-functionalisation of the obtained polymers was proven by both GPC und UV-spectroscopy. Furthermore, various amphiphilic block copolymers were obtained by chain extension with styrene, methyl methacrylate and ethyl methacrylate. In all cases monomodal GPC curves were obtained indicating an almost quantitative reinitiation.

Introduction

Since the first report by Georges et al. [1] dealing with the TEMPO-mediated free radical polymerization of styrene controlled radical polymerization has attracted great attention. Several methods for the control of radical polymerization have been developed and used for the synthesis of a large variety of polymers with controlled molecular weight and narrow polydispersities such as Atom Transfer Radical Polymerization (ATRP) [2,3], (ii) Reversible Addition-Fragmentation chain Transfer polymerization (RAFT) [4-6] and (iii) Stable Free Radical Polymerization (SFRP) using nitroxide as counter radical [7-9]. Their main advantages as compared to anionic, cationic and group transfer polymerization, are the less demanding reaction conditions.

Recently, we introduced the readily accessible triazolinyl radical (1,3,5,5-tetraphenyl-Δ^3-1,2,4-triazolin-2-yl) (**1**) (see scheme 1) as a new counter radical for controlled radical polymerization [10,11]. This compound serves as a useful alternative to nitroxides like 2,2,6,6 tetramethylpiperidinyl oxyl (TEMPO) which are limited to monomers undergoing a self-initiation or to N-tert-butyl-N-[1-diethylphosphono-(2,2-dimethylpropyl)]nitroxide which extended the scope of polymerizable monomers to acrylates [9,12,13]. Due to a well controlled decomposition mechanism of the triazolinyl radical, the concentration of growing macroradicals is adjusted during the polymerization (Scheme 1). [10,11] This unique behaviour can be explained through the "self-regulation concept" in which new initiating species (phenyl radicals) are formed allowing for the control of the radical polymerization. Such a process allows one to overcome the drawback of TEMPO mediated polymerisation wherein the concentration of free counter radicals slowly increases, thus leading to a shift of the equilibrium between TEMPO and growing macroradical versus TEMPO-adduct to the dormant side. This results in a drastic decrease in the rate of polymerization.



Scheme 1: Thermal decomposition of triazolinyl radical.

Another important aspect is that nitroxides typically undergo an elimination reaction when attached to methacrylates resulting in hydroxylamine and a double-bond containing polymer. In the triazolinyl case such a reaction is not possible. The applicability of the triazolinyl radical (**1**) as a very efficient additive for the controlled radical polymerization of monomers other than styrene has already been demonstrated for methyl methacrylate [10,11] and hydroxyethyl methacrylate [14]. These results encouraged us to use the triazolinyl radical as a counter radical for the controlled radical polymerization of N,N-dimethylaminoethyl methacrylate (DMAEMA). This monomer has already been polymerized via living anionic polymerization [15,16] and group transfer polymerization (GTP) [17,18]. Recently, a controlled radical polymerization of DMAEMA has been also achieved using ATRP [19,20] and RAFT [4,21]. However, all the above methods have some drawbacks such as the necessary purity of the solvent and of the monomer for anionic polymerization and GTP, the difficulty of completely removing the metal catalyst for ATRP and the unpleasant odor of the sulfur containing compounds produced by RAFT. Poly(dimethylaminoethyl methacrylate) and quaternized-poly(dimethylaminoethyl methacrylate) are attractive as water-soluble polymers due to their large variety of applications in the environmental protection field or in pharmacy as drug delivery systems [22,23] so that any contamination with metal ions such as copper or nickel should be avoided. Moreover, amphiphilic block copolymers of DMAEMA are of interest as they can form micelles and act as stabilisers in dispersion polymerization [24,25]. However, a practical synthesis of block copolymers is still a major challenge.

Experimental section

Materials

Commercial N,N-dimethylaminoethyl methacrylate (DMAEMA) (Fluka) was distilled over CaH_2 and stored at –20°C under argon prior to use. Azobisisobutyronitrile (AIBN) was recrystallized from methanol. The triazolinyl free radical (**1**) was synthesized according to the method described in the literature [26].

Polymerization of DMAEMA

Typically, a 50 ml Schlenk was charged with 100 mmol (15.7 g) of N,N-dimethylaminoethyl methacrylate, triazolinyl free radical (**1**) (0.13 mmol, 0.048 g) and AIBN (0.1 mmol, 0.0164 g). The amounts of counter radical and initiator were chosen to give a molar ratio triazolinyl/AIBN of 1.3. [10,11] The solution was degassed by several freeze-thaw cycles under reduced pressure. For the kinetic measurements aliquots of 1.5 ml were taken under inert atmosphere. The solutions were immersed in a preheated oil bath at 95 °C. After 10 min when the colour of the solution changed from deep dark to nearly colourless, the solutions were placed in an oil bath maintained at 70 °C to perform the polymerization. After the required reaction time the reaction was stopped by cooling the tubes. The obtained polymer were isolated by evaporating the excess monomer at high vacuum and finally dried under vacuum at 40 °C for 3 days. The conversion was determined gravimetrically after freeze drying and drying under vacuum. ^{1}H-NMR spectroscopy was also used to determine the conversion by comparison of the integrals of the signals at 4 ppm assigned to the CH_2 group of the ester unit and the residual vinyl protons of the monomer at 5.5-6 ppm.

Chain extension and block copolymer formation were carried out by heating a mixture of end-functionalized poly(dimethylaminoethyl methacrylate) and the corresponding monomer. The reaction temperatures depended on the monomer (methacrylates 70 °C, styrene 120 °C).

Characterization

The polymers were dissolved in THF and precipitated from hexane at low temperature to remove any residual monomers and counter radical. GPC measurements were performed on a Waters device equipped with a Styragel column using DMF as eluent. The temperature was maintained at 50 °C during all SEC experiments. ^{1}H-NMR spectroscopy was performed on a Bruker AX300 spectrometer using $CDCl_3$ or CD_2Cl_2 as solvent.

Results and discussion

The polymerization of DMAEMA was carried out with and without triazolinyl (table 1) in order to compare the polymerisation kinetics by measuring the conversion and the evolution of the molecular weights and to prove the controlled character of the polymerization. One of the requirements of such a polymerization is a reaction following first-order kinetics, indicating that the number of active species remains almost constant during the polymerization. This can be evidenced by plotting $\ln([M]_0/[M])$ versus time. $[M]_0$ and $[M]$ are the initial and the present monomer concentrations in the bulk. In the case of N,N-dimethylaminoethyl methacrylate, figure 1 clearly demonstrates that the plot of $\ln([M]_0/[M])$ versus time is nearly linear. This proves also the almost complete absence of irreversible bimolecular termination reactions.

However, in the presence of the triazolinyl radical the rate of polymerization is drastically reduced which is typical for controlled processes.

In Figure 2 the molecular weight of the polymer are plotted as a function of conversion (figure 2). Compared to the molecular weights obtained in the conventional manner without additive, where high molecular weight polymers are formed almost immediately, the presence of triazolinyl strongly affects the

Table 1: Radical polymerization of DMAEMA (100 mmol) carried out in the presence of triazolinyl (0.13mmol) using AIBN as initiator and a ratio of triazolinyl/AIBN of 1.3.

Polymerization Time [h]	Conversion		M_n 10^{-3}	M_w 10^{-3}	M_w/M_n
	By Gravimetry	By NMR			
0.25	7.6	8	52.2	72	1.32
0.5	10.8	11	57.9	79.9	1.38
0.75	13.6	16	63.7	92.3	1.45
1	17	17	72.6	106.7	1.47
1.5	22	21	81.4	127	1.56
2	27	23	93	149	1.61
2.5	29	26	97	158	1.63

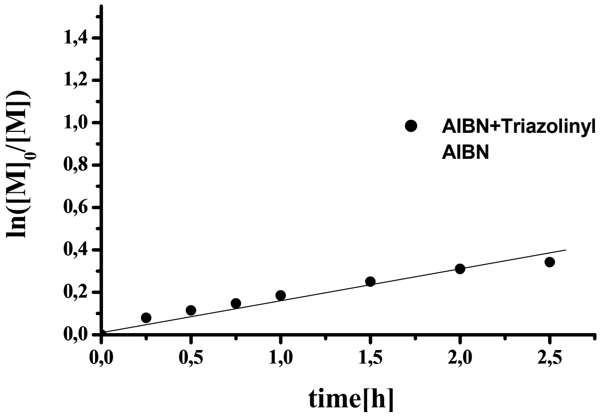


Figure 1: Bulk polymerization of N,N-dimethylaminoethyl methacrylate at 70 °C using AIBN as initiator, plot of $\ln([M]_0/[M])$ versus time.

polymerization of DMAEMA. The linearity of the plot indicates that the transfer reactions typical for DMAEMA polymerization are minimized. Otherwise one would observe a constant molar mass already at an early stage. The observed deviations from the linearity at high conversion are due to changes in the termination rate arising from differences in chain length and viscosity as reported already by Fukuda et al. [27].

It should be noted that at low conversions (< 5 %) the detected molecular weights are too high. This is a result of the preheating process in the first 10 minutes. To obtain a fast initiation by using AIBN as initiator we had to heat the mixture up to 95 °C. This guarantees a fast decomposition of the initiator but one loses control over the polymerization process in the initial state. As proven already in other publications the molecular weights are determined by the concentration of AIBN. One can assume that also a few chains are initiated by the triazolinyl radical, however as the decomposition of the AIBN is much faster almost all chains are started by the azoinitiator. [11,28]

During the preheating period a change of colour is observed indicating the coupling reaction between initiator radicals or poly(N,N-dimethylaminoethyl methacrylate) macroradicals and the triazolinyl radical. The decomposed initiator can start the polymerization in bulk very rapidly leading to the formation of relatively high

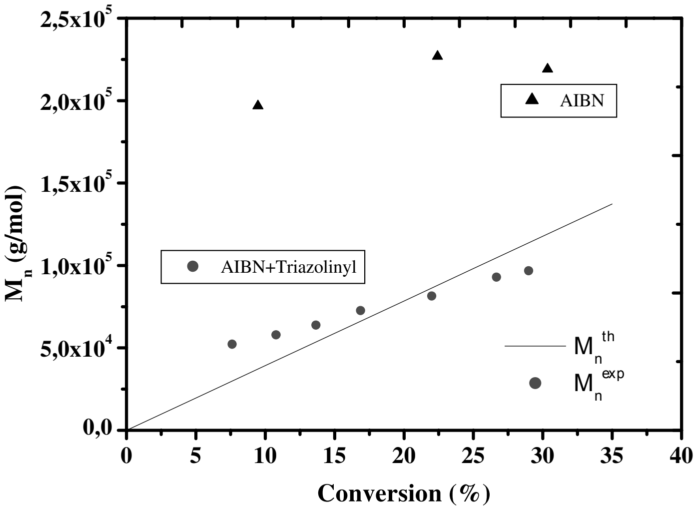


Figure 2: Evolution of experimental molecular weight with conversion for the controlled as well as for the free radical polymerization of DMAEMA at 70 °C.

molecular weight polymers. Later, after being back to 70 °C, the equilibrium between active and dormant species controls the polymerization and the process can proceed in a controlled fashion. This aspect explains why the plot of M_n versus conversion does not start from zero as it has been reported for styrene [10,11]. After a few minutes the well controlled decomposition of the triazolinyl radical [10, 11] (Scheme 1) maintains the concentration of growing macroradical constant. In contrast to the polymerization in the presence of TEMPO which strongly depends on the self-initiating ability of the monomer the triazolinyl radical does not depend on the initiating properties of the monomer.

During the polymerization the polydispersities remained relatively high (~1.5-1.6) in comparison to the corresponding controlled polymerisation of styrene (M_w/M_n = 1.3) [10]. This is typical for a relatively slow deactivation/activation process [27]. The slight increase of the polydispersity index at higher conversion is a consequence of some irreversible side reactions which can not be completely suppressed. This leads on one hand to the formation of dead polymer chains, on the other hand it lead to new growing chains which are initiated by the phenyl radicals generated by the self-regulation process.

Next to the linear evolution of M_n with conversion and the formation of polymers with low polydispersities a high degree of end-functionalization is crucial because it allows for an efficient block copolymerization. In order to investigate the end-groups the P(DMAEMA) synthesized in the presence of triazolinyl radical several analytical techniques such as UV-spectroscopy and GPC were applied.

As is shown in figure 3 the P(DMAEMA)s exhibits a strong UV-absorption band localized at around 290 nm. This is attributed to the triazolinyl endgroup, since the DMAEMA unit and the azoinitiator do not exhibit any absorption in this region.

Assuming that the triazolinyl end group has almost the same absorption coefficient as the model compound 1,3,5,5-tetraphenyl-Δ^3-1,2,4-triazoline (λ = 290 nm: ε = 79300 $l*mol^{-1}*cm^{-1}$ in dioxane) (scheme 2) the degree of end-functionalisation of the polymers can be readly calculated.

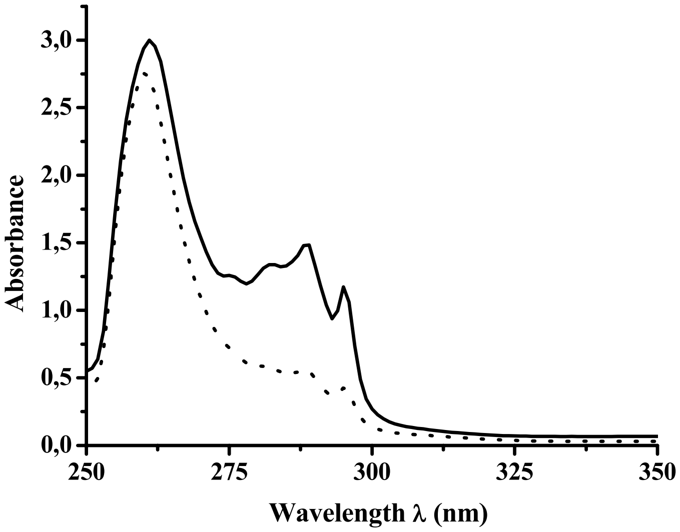
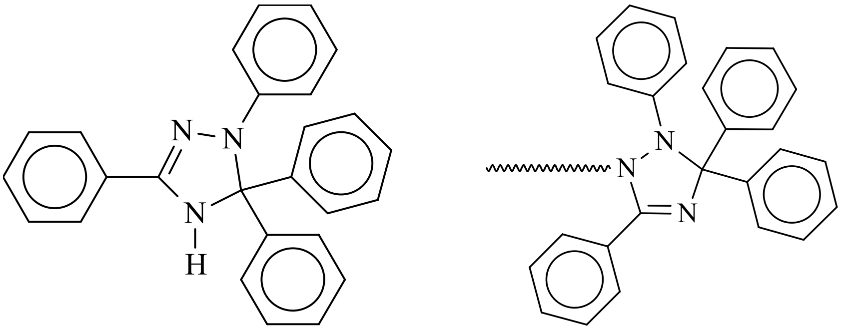


Figure 3: UV-absorption spectra of P(DMAEMA) M_n =52000 (solid line) and 73000 (dotted line) measured in dichloromethan.



Scheme 2: 1,3,5,5-Tetraphenyl-Δ^3-1,2,4-triazoline and polymer with a triazoline end group.

From the molecular weight obtained from GPC and UV-spectroscopy a degree of end functionalisation of about 81 % for a M_n of 52000 is obtained. The degree of end-functionalization is strongly dependent on the molecular weight of the polymer. Thus, when increasing the molecular weight up to M_n =73000, the UV-absorption is much more decreased than expected and a degree of end-functionalisation of 52 % is calculated. This clearly indicates that for obtaining well-defined block copolymers the conversion and the molecular weight of the first block should not be too high.

Additionally, GPC elugrams were recorded using UV-detection at 280 nm in DMF. As can be seen in figure 4 the size exclusion chromatography traces (M_n =52000) measured by UV-detection match the corresponding RI-curve and are almost symmetrical, proving the presence of triazoline units at the end of almost each P(DMAEMA) chain. UV-curves are converted considering that there is only one detectable unit per chain resulting in a number average, not in a weight average. When testing the ability of the triazolinyl end group to reinitiate a polymerisation, the

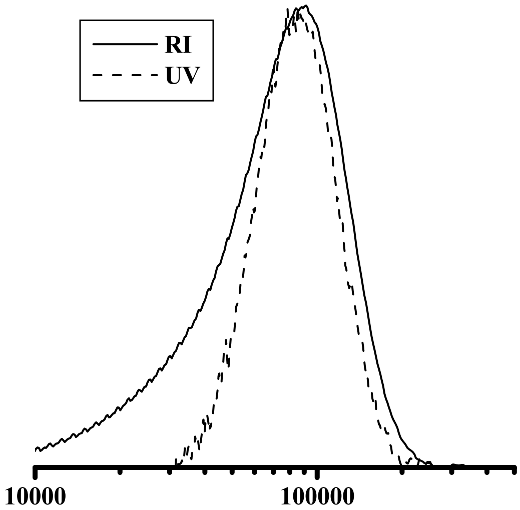


Figure 4: Molecular mass distribution from GPC analysis using RI and UV-detection at λ=280 nm.

obvious experiment was to demonstrate a chain extension with DMAEMA. Therefore, a low conversion P(DMAEMA) (M_n=52000) was heated at 70 °C in the presence of DMAEMA monomer. After 2 h the polymer solution became more viscous. The obtained polymer was analysed by GPC showing that the initial molecular weight was shifted toward higher molar masses (M_n=92000). The GPC curves remains monomodal, clearly indicating a quantitative reinitiation of the P(DMAEMA) chains. One can conclude that P(DMAEMA) end-functionalized with triazolinyl radicals should give block copolymers by simple reinitiation in the presence of other monomers.

Several block copolymers eg. poly(dimethylaminoethyl methacrylate)-block-polystyrene, poly(dimethylaminoethyl methacrylate)-block-poly(methyl methacrylate), poly(dimethylaminoethyl methacrylate)-block-poly(ethyl methacrylate) were made. In these experiments a monomer e.g. methyl methacrylate was heated at 70 °C in the presence of end-functionalized P(DMAEMA) (M_n=54000) synthesized using triazolinyl and AIBN as counter-radical and initiator respectively at low conversion. Figure 5 shows that the molecular weight is shifted to higher molar masses, due to the formation of the block copolymer P(DMAEMA)-b-PMMA. The GPC traces remain monomodal, however, the obtained block copolymers have a relatively high polydispersity compared to the homopolymer. This can be ascribed to a slow reinitiation rate of the end-functionalized P(DMAEMA) in comparison to the polymerization rate of the second monomer MMA.

In a similar way block copolymers with ethylmethacrylate (EMA) and styrene were obtained. In the case of styrene the polymerization of the second block was performed at 120 °C. It should be mentioned that, although the end-functionalization of the first P(DMAEMA) is not complete, the monomodal GPC traces strongly in all cases indicate a high yield of block copolymers (figure 6). Possibly, the degree of end-functionalisation is higher than calculated from the UV-spectra, since the accuracy of the determination is limited due to the low concentration of the UV-active groups and due to the structural difference of model compound and polymer end-group. It should

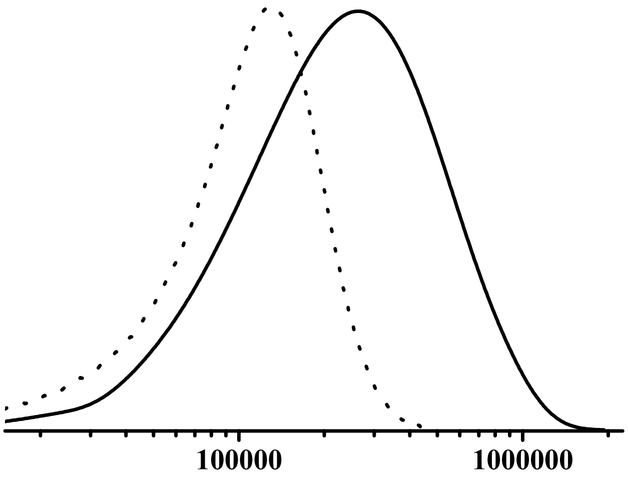


Figure 5: GPC-Plot of the block copolymer P(DMAEMA)-b-PMMA measured in DMF P(DMAEMA) (solid line) and P(DMAEMA)-b-PMMA (dotted line).

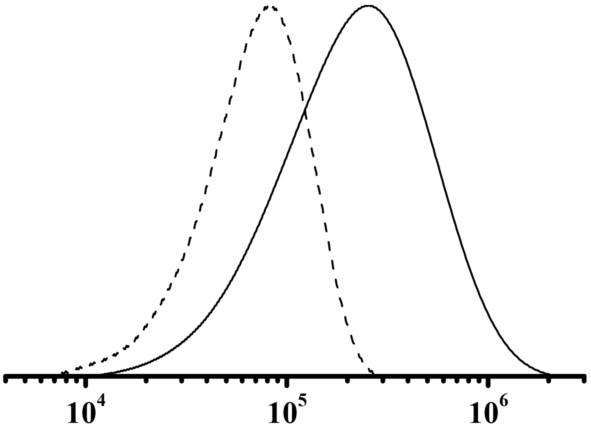


Figure 6: GPC-Plots of a P(DMAEMA) precursor (dotted line) and the resulting block copolymer with styrene (solid line).

also be noted that there is no indication of a lower molecular weight fraction for a homopolymer of the second monomer which can be possibly formed by phenylradicals from the decomposition of the triazolinyl radical. This indicates that the block formation is almost perfect and termination reactions leading to free triazolinyl radical are avoided.

^{1}H-NMR spectroscopy was used to complete the characterization of the formed block copolymers. As can be seen in figure 7 for the case of P(DMAEMA)-b-PMMA, the characteristic resonances of both blocks are clearly detectable. The composition of the blocks can either be estimated by ^{1}H-NMR spectroscopy comparing the resonances of the two methyl groups a and d, or by GPC. The results are given in table 2. The deviation between both methods can be explained by the use of polystyrene as standard for GPC.

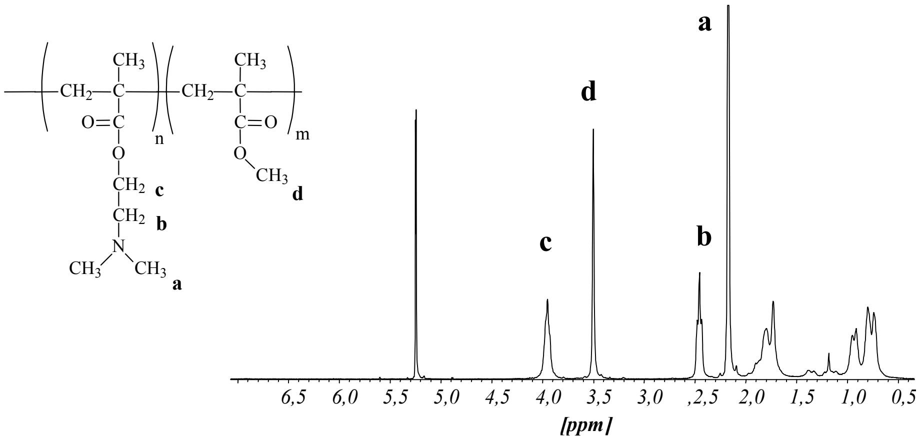


Figure 7: ^{1}H-NMR spectrum (300 MHz) of the block copolymer P(DMAEMA)-b-PMMA (CD_2Cl_2).

Table 2: Characteristic of P(DMAEMA) block copolymer using P(DMAEMA) (M_n=54000) as macroinitiator (block A).

Monomer B	Conv %	M_n of diblock polymer (GPC)	PD	Ratio A/B by GPC	Ratio A/B by ^{1}H NMR
MMA	17	83000	2.03	1.18	1.4
Styrene	13	138300	1.87	0.42	0.33
EMA	15	91000	1.95	0.97	1.05

Conclusion

Well defined poly(dimethylaminoethyl methacrylate)s were prepared by controlled radical polymerization in the presence of triazolinyl as counter radical. The obtained polymers have narrow polydispersities and are highly end-functionalized. The presence of triazolinyl at the chain end was proven by GPC using UV-detection, by UV-spectroscopy and by reinitiation experiments. P(DMAEMA)-b-PMMA, P(DMAEMA)-b-PEMA and P(DMAEMA)-b-PS block copolymer were synthesized and characterized by GPC and ^{1}H-NMR spectroscopy.

As a number of amphiphilic AB block copolymers of N,N-dimethylaminoethyl methacrylate, which are typically not well accessible via conventional radical polymerization or nitroxide-mediated radical polymerization, were synthesized, we could demonstrate that triazolinyl radicals are also applicable in the controlled polymerization of polar monomers. Additionally, triazolinyl radicals have some advantages over other counter radicals, especially for the polymerization of methyl methacrylate, butyl methacrylate and tms-hydroxyethyl methacrylate. All these monomers cannot be successfully polymerised either with TEMPO or with the nitroxide SG-1, recently applied in many cases [12,13].

References

1 Georges MK, Veregin RPN, Kazmaier PM, Hamer GK. Macromolecules 1993, 26:2987.
2 Matyjaszewski K, Xia JH. Chem. reviews 2001, 101(12):3689.
3 Kamigaito M, Ando T, Sawamoto M. Chem. reviews 2001, 101(9): 2921.
4 Chiefari J, Chong YK, Ercole F ,Krstina J, Jeffery J, Le TPT, Mayadunne RTA, Meijs GF, Moad CL, Moad G, Rizzardo E, Thang SH. Macromolecules 1998, 31:5559.
5 Moad G, Mayadunne RTA, Rizzardo E, Skidmore M, Thang SH. Macromolecular Symposia 2003, 192:1-12.
6 Rizzardo E, Chiefari J, Mayadunne RTA, Moad G. Thang S. Macromolecular Symposia 2001, 174:209-212.
7 Veregin RPN, Odell PG, Michalak LM, Georges MK. Macromolecules 1996, 29:2746.
8 Drockenmuller E, Catala JM. Macromolecules 2002, 35:2461.
9 Couvreur L, Lefay C, Belleney J, Charleux B, Guerret O, Magnet S. Macromolecules 2003, 36:8260.
10 Colombani D, Steenbock M, Klapper M, Müllen K. Macromol Rapid Commun 1997, 18: 243.
11 Steenbock M, Klapper M, Müllen K, Bauer C, Hubrich M. Macromolecules 1998, 31:5223.
12 Farcet C, Charleux B, Pirri R. Macromolecules 2001, 34:3823.
13 Farcet C, Lansalot M, Charleux B, Pirri R, Vairon JP. Macromolecules 2000, 33:8559.
14 Dasgupta A, Brand T, Klapper M, Müllen K. Polymer Bulletin 2001, 46:131.
15 Antoun S, Teyssié P, Jérôme R. Macromolecules 1997, 30:155.
16 Antoun S, Teyssié P, Jérôme R. Macromolecules 1997, 30:1556.
17 Oh JM, Lee HJ, Shim HK, Choi SK. Polymer Bulletin 1994, 32:149.
18 Beatle PM, Rowan L, Mykytiuk J, Billingham NC, Armes SP. Polymer 1997, 34: 1561.
19 Zhang X, Xia JH, Matyjaszewski K. Macromolecules 1998, 31:5167.
20 Lee SB, Russell AJ, Matyjaszewski K. Biomacromolecules 2003, 4:1386.
21 Rizzardo E, Chiefari J, Chong BYK, Ercole F, Krstina J, Jeffery J, Le TPT, Mayadunne RTA, Meijs GF, Moad CL, Moad G, Thang SH. Macromolecular Symposia 1999 143:291.
22 Chen, Du FS, Wu ZQ, Huang L, Li ZC, Li FM. Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) 1997, 38:534.
23 Cho SH, Jhon MS, Yuk SH, Lee H. J. Polym. Sci., Part B: Polym. Phys. 1997, 35:595.
24 Baines FL, Armes SP, Billingham NC. Macromolecules 1996, 29:3416.
25 Baines FL, Armes SP, Billingham NC, Tuzar Z. Macromolecules 1996, 29:8151
26 Neugebauer FA, Fischer H, Krieger C. Angew Chem 1989, 101:486.
27 Fukuda T, Goto A, Ohno K. Macromol Rapid Commun 2000, 21:151.
28 Klapper, M, Brand T, Steenbock M, Müllen K, ACS Symposia 2000, 768:152, Editor Matyjaszewski K