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Polymer 46 (2005) 5–14
polymer
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ATRP of (meth)acrylates initiated with a bifunctional initiator bearing trichloromethyl functional groups and structural analysis of the formed polymer

Aleksandra Malinowska[b], Petr Vlček[a,*], Jaroslav Kříž[a], Luděk Toman[a], Petra Látalová[a], Miroslav Janata[a], Bohumil Masař[a]

[a]*Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic*
[b]*Institute of Organic and Polymer Technology, Wroclaw University of Technology, Wyspianskiego st. 27, 50-370 Wroclaw, Poland*

Received 19 August 2004; received in revised form 2 November 2004; accepted 3 November 2004
Available online 19 November 2004

Abstract

ATRP of methyl methacrylate (MMA), initiated with 1,3-bis{1-methyl-1-[(2,2,2-trichloroethoxy)carbonylamino]ethyl}benzene as a bifunctional initiator (BI) under CuCl catalysis was studied in the presence of 2,2′-bipyridine (bpy) or hexamethyltriethylenetetramine (HMTETA) ligands, in bulk or in toluene. With the bpy, the polymerization reaches only limited monomer conversions and products have broad MWDs. In contrast, polymerization in the presence of HMTETA is a well-controlled process, affords virtually quantitative conversion, giving PMMAs with narrow MWDs and predictable molecular weights within a range of more than one order of magnitude. NMR analysis of the prepared PMMA proved formation of linear polymers with im-measurable extent of chain branching or β-scission as undesired side reactions. The prepared α,ω-dichloro-PMMAs were used as macroinitiators for ATRP of *tert*-butyl acrylate (*t*-BuA), giving the corresponding triblock copolymers with narrow MWDs and molecular weights controllable in a wide range. Block copolymerizations were performed in dimethyl formamide (DMF) or acetone in the presence of pentamethyldiethylenetriamine (PMDETA) as ligand and could be accelerated by addition of metallic copper.

Keywords: ATRP; ABA triblock copolymers; Methyl methacrylate

1. Introduction

Methods of controlled or living polymerization are in fact the only ways leading to tailor-made polymers with predetermined molecular parameters, various microstructure or two-, three- or even multiblock copolymers having interesting application properties. For instance, methods of anionic polymerization initiated with a number of basic compounds, complex initiating systems, lanthanocenes, etc. [1–6], provide perfect control over the polymerization process. However, the methods require high purity of reaction systems and have often to be performed at low temperatures; this is why the experiments are time and labor-consuming and the prices of the products are quite high. To avoid these complications, various methods of controlled radical polymerization have been developed in the recent decade, having in comparison with anionic polymerization some important advantages. Thus, the polymerization utilizing iniferter agents [7], process with reversible addition–fragmentation chain transfer (RAFT process) [8,9], polymerization in the presence of stable, mostly nitroxide-type counter-radicals (TEMPO-mediated polymerization) [10–12] and atom-transfer radical polymerization (ATRP) [13,14] are available now and the field is under permanent rapid development.

The three-component ATRP initiating system contains an organo-halide-type initiator, catalyst in the form of a salt of transition metal in the lower oxidation state, and a complexing ligand based mostly on amine-type or organophosphorus compounds. The combination of a catalyst and

* Corresponding author. Tel.: +420 296 809 250; fax: +420 296 809 410.
E-mail address: vlcek@imc.cas.cz (P. Vlček).

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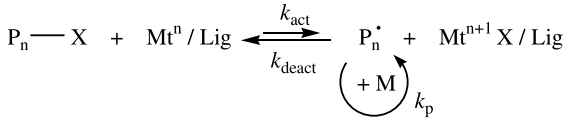
doi:10.1016/j.polymer.2004.11.004

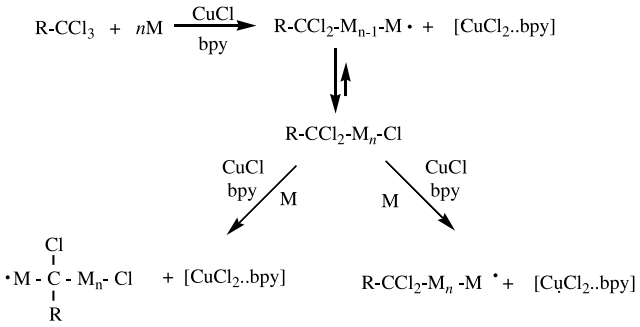


Scheme 1.

an appropriate ligand affects the redox potential of the system, leading to the equilibrium between dormant and active forms of growing chains, which minimizes an extent of termination reactions. Thus, the equilibrium between ω-halogenated polymer chain (dormant form) and growing free macroradical (active form), is the key step of ATRP, as simply described in the commonly accepted Scheme 1.

Alkyl halides, esters of haloacids or sulfonyl halides are the most frequently used initiators for ATRP of vinyl monomers like styrene, acrylates and methacrylates. The first successful attempts to achieve a controlled radical process were independently realized by Sawamoto and Matyjaszewski. Sawamoto's group [15] presented MMA polymerization, initiated with CCl_4 in the presence of $[RuCl_2(PPh_3)_3]$ as the metal 'catalyst' and methylaluminium bis(2,6-di-*tert*-butylphenoxide) ($MeAl(ODBP)_2$) as an activator, whereas Matyjaszewski and coworkers [16] described an initiating system for controlled styrene polymerization composed of 1-phenylethyl chloride (1-PECl) initiator, CuCl catalyst and 2,2′-bipyridine (bpy) ligand. Since that time, a huge number of studies have been performed, dealing with polymerization of various monomers initiated with a wide spectrum of initiating systems.

Among others, polyhalogenated compounds of the general formula R-CX_3, where X stands for halogen and R can be hydrogen, halogen or various organic substituents, were tested, in which at least one of the halogen atoms can be released and generate primary radical capable of initiation of polymerization. These compounds are mostly commercially available, inexpensive and can be simply purified by common methods like distillation. By the way, in Sawamoto's pioneering work [15], CCl_4 initiator was used for MMA polymerization (see above). In the following work of the same authors [17], MMA polymerization was initiated with 1,1,1-trichloroacetone, α,α-dichloroacetophenone and with ethyl 2-bromo-2-methylpropanoate in toluene in combination with the $[RuCl_2(PPh_3)_3]$ catalyst



Scheme 2.

and $MeAl(ODBP)_2$ activator. It was found that all these systems initiate polymerization with a linear dependence of molecular weights on monomer conversion producing thus polymers with narrow MWD's. Also, semilogarithmic plots of monomer consumption vs. time are linear up to conversions exceeding 80%. All these findings thus indicate a controlled process. α,α-Dichloroacetophenone gave PMMA with the narrowest MWD ($M_w/M_n = 1.15$), initiation with ethyl 2-bromo-2-methylpropanoate led to a polymer with a broader MWD ($M_w/M_n = 1.34$); in the latter case, according to a slightly non-symmetric shape of the MWD curve, the broadening the MWD might originate from a rather slow initiation reaction. Based on ^{1}H NMR end-group analysis the authors assume that α,α-dichloroacetophenone can behave as a bifunctional initiator, giving a polymer with chlorine end-group on both the ends. The idea is corroborated by the existence of the peak at 3.2 ppm observed in the spectrum belonging to a methine proton in the $–CH_2–(C_6H_5CO)–CH–CH_2–$ group generated if α,α-dichloroacetophenone acts as a bifunctional initiator.

Destarac et al. studied ATRP of styrene [18] from both the kinetic and mechanistic points of view, initiated with various polychloroalkane-type initiators of the general formula $RCCl_3$, and catalyzed with CuCl in the presence of bpy ligand. With respect to the R group, two kinds of the initiators were tested: (i) those with CCl_3 group activated by an adjacent electron-withdrawing group, for instance methyl trichloroacetate or 1,1,1-trichloro-2,2,2-trifluoroethane, and (ii) non-activated, in which R is of alkyl type, like 1,1,1-trichlorononane or 2,2,2-trichloroethyl pivalate. It was found that all the compounds used are active initiators in ATRP of styrene, however, the type of R group affects the rate of polymerization. Generally, the activated initiators initiate polymerization with a higher reaction rate, whereas non-activated ones lead to slow polymerizations. The obtained kinetic data together with the results of both the NMR and SEC analyses led to the conclusion that some of the activated initiators can behave as bifunctional and the non-activated polychloroalkanes act mostly as monofunctional initiators. The two possible pathways are shown in Scheme 2.

In another work [19], ATRP of MMA and methyl acrylate (MA), initiated with various R-CCl_3-type initiators in combination with CuCl and bpy was investigated; also here, the effect of the R group on polymerization kinetics and functionality of the initiator used was found. A deviation in the dependence of M_n on monomer conversion was observed in MMA polymerization initiated with bifunctional initiators (CCl_4, methyl 2,4,4,4-tetrachlorobutanoate), giving a polymer with terminal halide groupings and central CCl_2 moiety. The CCl_2 group can be activated in the presence of the catalyst and generate an additional radical capable of initiation leading to formation of grafts. However, model studies using 2,2-dichloroethanol and 2,2-dichloropropane showed that this initiation is very slow and, therefore, the extent of grafting is probably rather low. Thus,

Table 1
ATRP of MMA initiated with BI at 90 °C in the presence of bpy or HMTETA ligands

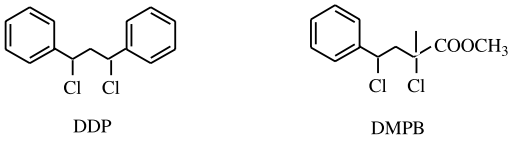
Run[a]	Ligand	Solvent	Time (h)	Conversion (%)	M_n	M_w/M_n
1	bpy	Bulk	6	80	13,700	1.41
2	bpy	Toluene[b]	6	70	8900	1.78
3	HMTETA	Toluene[b]	15	65	4400	1.31
4	HMTETA	Bulk	3	95	4900	1.14
5	HMTETA	Toluene[c]	6	84	8600	1.14
6	HMTETA	Toluene[c]	8	90	8700	1.12

[a] BI/CuCl/$CuCl_2$/ligand/MMA mole ratio: 1—1:1:0:2:100; 2—1:1:0:2:100; 3—1:1:0:1:50; 4—1:1:0.5:1:50; 5—1:1:0:1:100; 6—1:1:0.5:1:100.
[b] Toluene/MMA = 1:1.
[c] 1.8:1 (v/v).

the above-mentioned deviation in the M_n evolution was explained on the basis of possible β-scission of chains with the central CCl_2 group, giving non-active polymer with terminal C=C double bond on one hand and a new macroradical on the other (see below). The hypothesis was corroborated by ^1H NMR analysis of the product, which evidenced the presence of CH_2 protons of a vinyl group.

In the paper dealing with ATRP of styrene and MMA initiated with (chloromethyl) benzene (MCT) or (dichloromethyl)benzene (DCT) under the CuCl/bpy catalysis, Hoecker and coworkers [20] documented that functionality of polyhalogenated initiator can also be dependent on the monomer used. Thus, by addition of the first styrene unit onto DCT, symmetrical molecule of 1,3-dichloro-1,3-diphenylpropane (DDP) is formed, having 2 equiv. chlorine atoms, both capable of initiation of styrene polymerization. On the contrary, the reaction of DCT with MMA leads to methyl 2,4-dichloro-2-methyl-4-phenylbutanoate (DMPB), having two chlorine atoms with different degrees of activation and thus different initiation efficiencies toward MMA (see Scheme 3). The chlorine adjacent to the carbonyl group is more activated and, consequently, the initiation of MMA polymerization proceeds—at least prevailingly—at this site. The hypothesis is corroborated by kinetic analysis of styrene and MMA polymerizations initiated with MCT or DCT.

Recently, we synthesized a novel type of bifunctional ATRP initiator with two trichloromethyl groups as the active sites [21] by reaction of an aromatic diisocyanate with 2,2,2-trichloroethan-1-ol. As has been mentioned in the foregoing paper, synthesis of the initiator proceeds very smoothly and, due its insolubility in aliphatic hydrocarbons, the product can be easily isolated and purified. Moreover, the aromatic initiator moiety is easily detectable with UV and, therefore, its presence in polymer chains can be verified by SEC with UV detector. This is very helpful for kinetic and mechanistic studies. In this work, we present results of MMA polymerization and preparation of MMA/*t*-BuA block copolymers using this initiator and catalyzed with CuCl in the presence of various amine ligands.



Scheme 3.

2. Experimental part

2.1. Materials

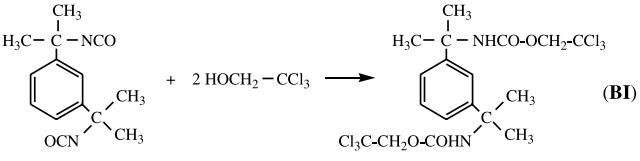
MMA and *t*-BuA (Fluka, >99%) were twice vacuum distilled with CaH_2; the second distillation was performed just prior to use. CuCl (Fluka) was purified with acetic acid according to the literature [22], $CuCl_2$, bpy, HMTETA and PMDETA (Aldrich) were used as received. Toluene was purified by distillation in the presence of sodium benzophenone complex, hexane by distillation with CaH_2, DMF and acetone (Fluka) were degassed by stripping with dry argon. 1,3-Bis(1-isocyanato-1-methylethyl)benzene, and dibutyltin dilaurate were used as received, 2,2,2-trichloroethan-1-ol was dried with molecular sieves and distilled.

2.2. Preparation of the initiator

1,3-Bis{1-methyl-1-[(2,2,2-trichloroethoxy)carbonylamino]ethyl}benzene (BI) was prepared by condensation of 1,3-bis(1-isocyanato-1-methylethyl)benzene with a twofold molar excess of 2,2,2-trichloroethan-1-ol, catalyzed with dibutyltin dilaurate in toluene at 50 °C (Scheme 4) and isolated and purified by precipitation in hexane [21]. Its structure was checked by elemental and ^1H NMR analyses.

2.3. Polymerization and copolymerization

Polymerizations were performed in 25- or 50-ml flasks equipped with a three-way stopcock and magnetic stirrer



Scheme 4.

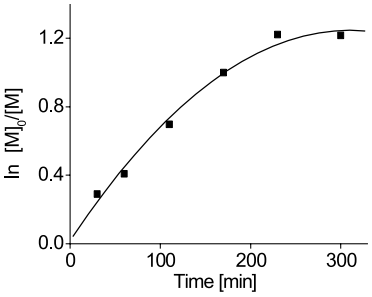


Fig. 1. ln[M_0]/[M] vs. time plot of MMA polymerization, run 2, Table 1.

under argon. Typically, (Table 1, run 3): 100 mg (0.184 mmol) of BI, 18 mg (0.184 mmol) of CuCl and 12 mg (0.092 mmol) of $CuCl_2$ were placed into a 25-ml flask with magnetic stirrer and degassed by evacuation at room temperature and flushing with argon; the procedure was repeated three times. Then, 0.05 ml (0.184 mmol) of HMTETA, 2 ml (18.7 mmol) of MMA and 2 ml of toluene were added with gas-tight syringes under argon; the mixture was cooled in a dry-ice-bath and repeatedly evacuated and flushed with argon. Finally, the flask was immersed into an oil bath (90 °C) and polymerized for 8 h. Polymerization was terminated by cooling down to room temperature, the mixture was diluted with 14 ml of THF and the formed polymer was isolated by two precipitations in a 80/20 (v/v) methanol/water mixture. The monomer conversion was determined either by GC or gravimetrically.

Block copolymerization (Table 3, run 5): 0.6 g of PMMA macroinitiator (0.063 mmol) with $M_n = 9400$ and $M_w/M_n = 1.13$, 6 mg of CuCl (0.063 mmol) and 4 mg of Cu powder (0.063 mmol) were placed into a 25-ml flask and degassed in the same way as in homopolymerization. Then, 0.013 ml (0.063 mmol) of PMDETA, 1.86 ml of *t*-BuA (12.72 mmol) and 0.46 ml of acetone were added with syringes and the mixture was repeatedly evacuated and flushed with argon (see above). After that, the flask was immersed into a 60 °C oil bath and polymerized for 5 h. The product was isolated in the same way as in the homopolymerization and dried in vacuo at 40 °C.

2.4. Analyses of polymers

Molecular weights of polymers and copolymers were measured by SEC (Labora HP-5001, Czech Republic) in

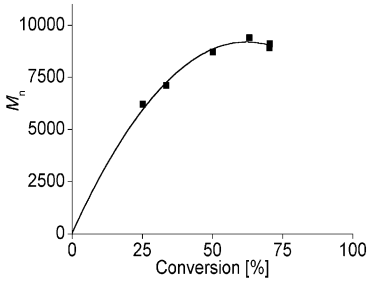


Fig. 2. M_n vs. conversion plot in MMA polymerization, run 2, Table 1.

THF (flow rate 1 mL/min) at 20 °C with a separation system composed of two 300×8 mm columns (PSS Germany) filled with SDV gel (bead size 5 μm, porosity 10^5 and 10^6 Å), equipped with a differential refractometer Labora RIDK 102 and UV detector Labora LCD 2040 adjusted at 260 nm. The system was calibrated with PMMA standards (PSS Germany) and its separation range was from 10^3 to 10^6 Da. Eluograms were treated using professional software Caliber (Polymer Laboratories) as PMMA [23] or poly(*t*-BuA) [24].

2.5. NMR analysis

For a structural analysis of PMMA, ^{1}H, ^{13}C and ^{1}H–^{13}C correlation spectra of a 10% solution of the product in $CDCl_3$ were measured with a 300 MHz Bruker Avance 300 NMR spectrometer at 330 K, using both an inverse-detection and direct-detection broad-band probe. All spectra were measured with quadrature detection in F2, ^{1}H NMR with 32 kpoints without exponential weighting and ^{13}C 1D NMR with 64 kpoints and using 1 Hz exponential broadening. 2D correlation spectra were measured with 2048 points in F2 and 256 (HETCOR) or 128 (COLOC) increments in F1. Sine-bell weighting function was applied in both dimensions. The numbers of scans/increment were 112 for HETCOR (12 h) and 1120 for COLOC (60 h), respectively.

To determine chemical composition, ^{1}H NMR spectra of 5% solutions of the copolymers in $CDCl_3$ were measured at 300.13 MHz on a Bruker Avance DPX 300 spectrometer at 330 K using hexamethyldisiloxane (HMDS) as an internal standard, with pulse width 15.3 μs (90° pulse), relaxation delay 10 s, spectral width 6000 Hz, acquisition time 1.36 s, 16 scans. Compositions of copolymers were calculated from the integrated relative intensities of the peaks at 3.58 ppm (OCH_3 in MMA), and 1.42 ppm ($OC(CH_3)_3$ in *t*-BuA).

3. Results and discussion

3.1. MMA homopolymerization

3.1.1. Polymerization in the presence of bipyridine ligand

As was already mentioned in the foregoing paper [21], the efficiency of BI was first tested in a combination with CuCl/bpy complex at 90 °C. When polymerized in bulk at the BI/CuCl/bpy/MMA mole ratio 1:1:2:100, MMA conversion reaches about 80% within 6 h, giving a polymer with slightly broadened MWD and M_n higher than the theoretical value (Table 1, run 1). In toluene (a volume equal to that of the monomer was added), the reaction is somewhat slower so that the MMA conversion is 70% after 6 h (run 2) Also here, the BI/CuCl/bpy/MMA mole ratio was 1:1:2:100. Again, molecular weight of the product does not correspond to the theoretical predictions, and MWD is even broader than in the foregoing case. The reaction

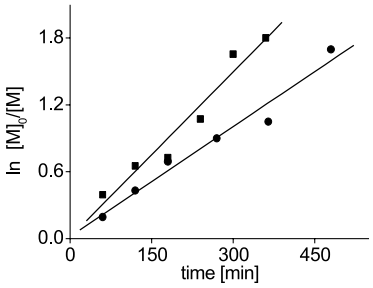


Fig. 3. ln[M_0]/[M] vs. time plots of MMA polymerizations; Table 1, squares—run 5, circles—run 6.

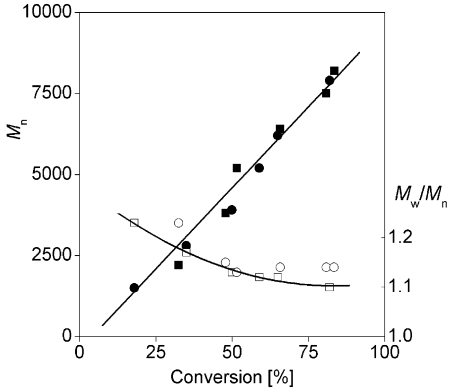


Fig. 4. Dependence of M_n (solid symbols) and M_w/M_n (empty symbols) for MMA polymerizations, Table 1, squares—run 5; circles—run 6.

mixtures were heterogeneous in both the experiments, as expected. Kinetic study of the polymerization in toluene shows, that the ln [M_0]/[M] vs. time plot exhibits a downward curvature at conversions higher than ca. 60% (Fig. 1) indicating termination of the process. Also, the molecular weight of the polymer virtually does not increase at conversions higher than 60% (Fig. 2). Thus, the polymerization is ill-controlled under these conditions.

3.1.2. Polymerization in the presence of HMTETA

With this ligand, the reaction mixtures were virtually homogeneous with a small amount of a solid portion depending on the starting reaction conditions. The experiment, in which the mole ratio BI/CuCl/HMTETA/MMA = 1:1:1:50 was used, proceeded in toluene (volume equivalent with respect to MMA) in an un-controlled way, attaining within 15 h only ca. 65% monomer conversion. The formed polymer had a slightly broadened MWD ($M_w/M_n = 1.31$) with a hint of bimodality (Table 1, run 3). In the presence of DMF (toluene/DMF volume ratio was 1/1), the reaction was somewhat faster and MMA was consumed almost completely within 10 h; however, the polymer with a broad MWD ($M_w/M_n = 1.39$) exhibiting a hint of bimodality was again obtained. (This experiment is not presented in the table). In bulk, and in the presence of $CuCl_2$ ($Cu^I/Cu^{II} = 2$), the polymerization is distinctly faster, reaching almost complete monomer conversion within 3 h and giving the product with a narrow MWD (run 4, $M_w/M_n = 1.14$). The polymerizations, in which the MMA/BI ratio was 100, performed in the presence or absence of $CuCl_2$ gave almost the same results (runs 5 and 6); high monomer conversions were attained and polymers with narrow MWDs were obtained in both the cases. The semilogarithmic conversion plots in Fig. 3 show that both the polymerizations are controlled processes; as expected, the reaction in the presence of $CuCl_2$ is somewhat slower than that in its absence. Also, molecular weights of the formed PMMAs increase linearly with conversions in both the cases (Fig. 4), following fairly the theoretical values.

Using the BI bifunctional initiator and CuCl/HMTETA catalysis, molecular weight of PMMA can be controlled stoichiometrically within a range of more than one order of magnitude (Table 2), keeping MWDs symmetric and narrow. The polymerizations are mostly performed in bulk; addition of $CuCl_2$ is recommended when the MMA/BI mole ratio is ≤ 100 (runs 1 and 2). At higher excess of monomer over the initiator (runs 3–5), concentration of active radicals is sufficiently low and, thus, the addition of Cu^{II} salt is not needed. Nevertheless, the process is slow at MMA/BI ratios exceeding 500, so that the monomer conversion is not quantitative even in a 10-h polymerization (run 5). However, it can be reasonably assumed that higher conversion would be attained in a longer polymerization time.

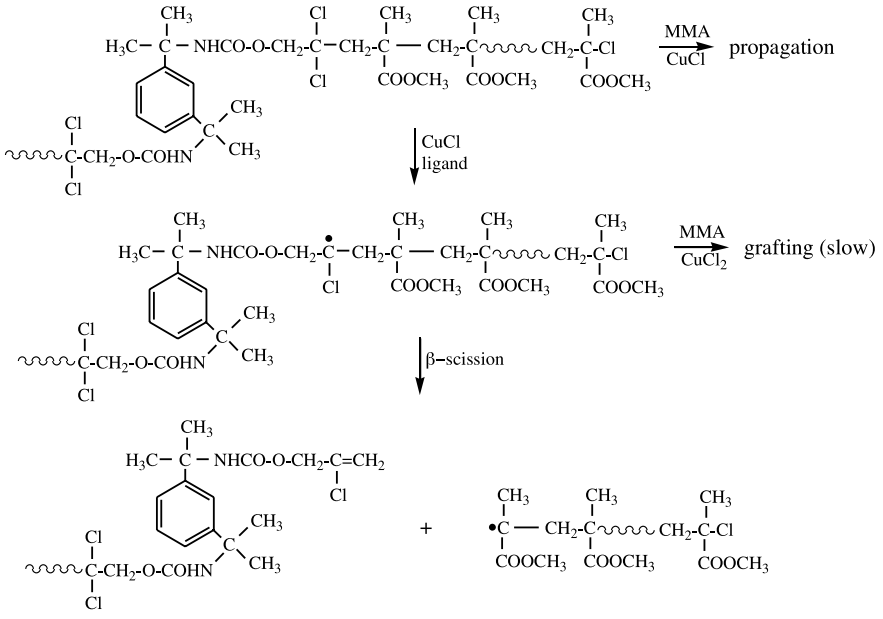
3.1.3. NMR analysis of PMMA structure

As was already mentioned in Section 1, ATRP, initiated with polyhalogenated initiators, may be accompanied by the splitting-off of the second chlorine atom from the CCl_2 moiety forming an additional free radical which can start grafting of the chain. Moreover, the polymer with the radical 'inside' the chain can undergo a β-scission, giving rise to two polymer chains: one of them is terminated with a

Table 2
Controlling the molecular weights of PMMA prepared by ATRP initiated with BI in bulk at 90 °C

Run	MMA/BI (m/m)	X[a] mole ratio	Time (h)	Conversion (%)	M_n	M_w/M_n
1	50	1:1:0.5:1	3	95	4800	1.14
2[b]	100	1:1:0.5:1	8	90	9400	1.13
3	200	1:1:0:1	3	96	19,600	1.16
4	500	1:1:0:1	9	95	48,400	1.17
5	1000	1:1:0:1	10	80	72,500	1.21

[b] In toluene, toluene/MMA = 1.8/1 (v/v).



Scheme 5.

vinyl double bond and the other with a free radical. The process is demonstrated in Scheme 5. To obtain more information about the structure of the formed PMMA and about the extent of the mentioned side reactions, a low-molecular-weight PMMA with $M_n = 2900$ was analyzed by NMR.

The structure was checked using ^1H and ^{13}C NMR spectra and ^1H–^{13}C correlation spectra. In assigning the signals, the numbering used is as in Scheme 6 (corresponding to half of the structure); the protons have the same numbers as the attached carbons. ^1H NMR spectrum of the PMMA product is shown in Fig. 5 in comparison with that of the used initiator. The signal assignment relies on COSY and TOCSY correlation (not shown).

Fig. 6 compares ^{13}C NMR spectrum of the initiator (APT technique, CH_3 and CH signals up, CH_2 and C signals down) with two types of ^{13}C NMR spectra of the product: (i) DEPT spectrum showing only carbons with attached protons (CH_3 and CH signals up, CH_2 signals down) and (ii) ordinary ^{13}C NMR spectrum (in the inverse-gated mode retaining additive signal intensities). The signal assignment relies on the ACD C-NMR simulation program, consistency with DEPT spectrum and with ^1H–^{13}C correlation spectra. Again, no double-bonded aliphatic carbons or branching units are present. The signal assignment is fortified by two types of ^1H–^{13}C correlation. Fig. 7 reproduces ^1H–^{13}C HETCOR correlation spectrum showing correlations between protons and directly attached carbons.

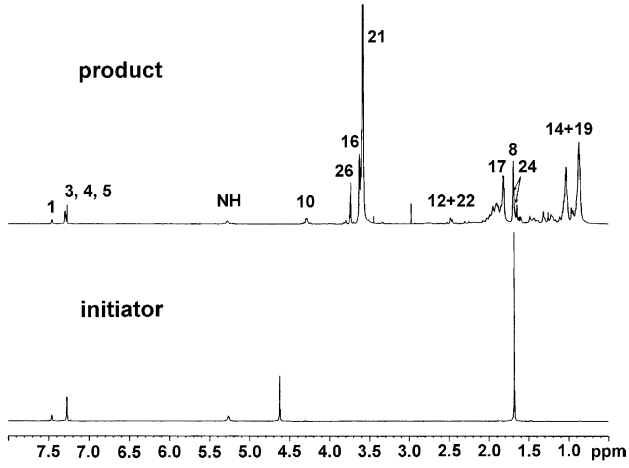
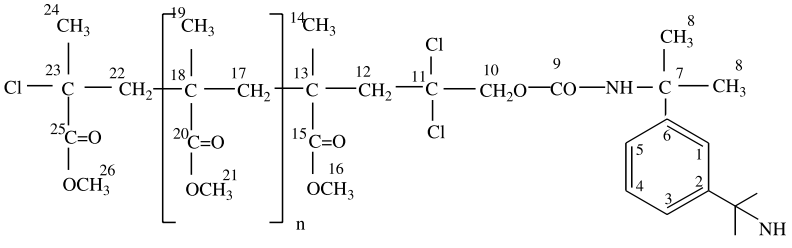


Fig. 5. ^1H NMR spectra of the product and initiator (5% in $CDCl_3$, 330 K), spectrum simulation using the ACD H-NMR program and on consistency with ^1H–^{13}C correlation spectra. It has to be noted that no protons attached to double bonds can be observed in the spectrum.



Scheme 6.

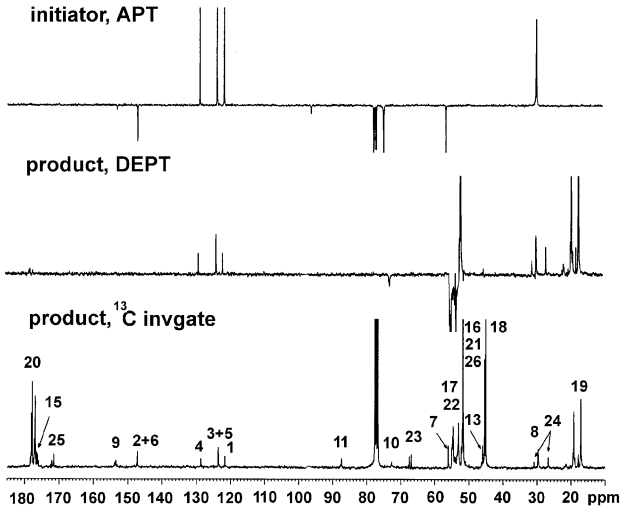


Fig. 6. ^{13}C NMR spectrum of the initiator (APT, above) compared with DEPT (middle) and inverse-gated (bottom) ^{13}C NMR spectra of the product (10% in $CDCl_3$, 330 K).

For multiple-bond $^{1}H–^{13}C$ correlation, we tried several types of 2D spectra, including HMBC and its modifications, but found the classic long-range $^{1}H–^{13}C$ COLOC to be the most reliable. This spectrum tuned to three-bond correlation is reproduced in Fig. 8. It is well-known that not every expected cross-peak is necessarily developed in this type of spectra, its intensity being dependent both on the magnitude of the $^{3}J_{C–H}$ coupling constant and on the ^{1}H T_2 relaxation time. Nevertheless, most of the long-range correlations expected according to Scheme 6 are detected in Fig. 8.

In particular, combination of 1D and 2D spectra gives

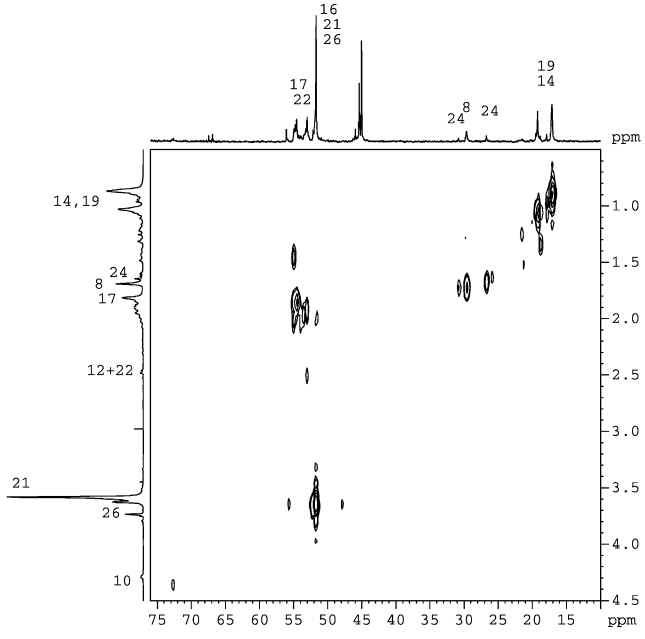


Fig. 7. $^{1}H–^{13}C$ (HETCOR) correlation spectrum of the product (10% in $CDCl_3$, 330 K).

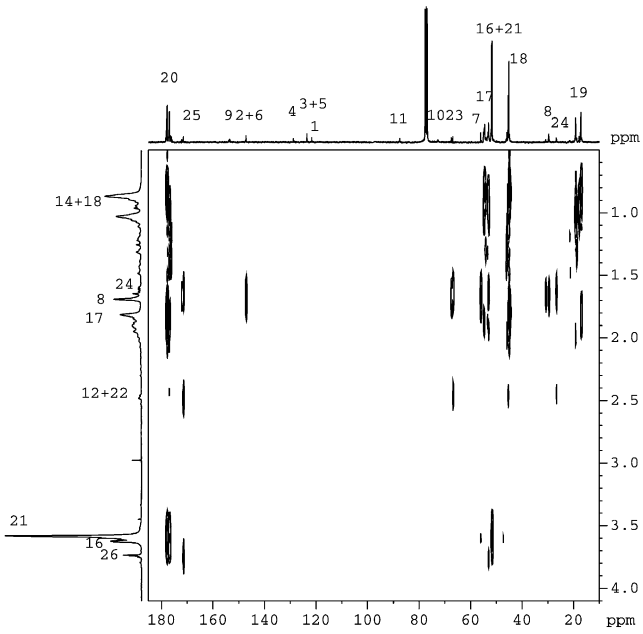


Fig. 8. Relevant part of $^{1}H–^{13}C$ long-range correlation spectrum (COLOC) of the product (10% in $CDCl_3$, 330 K).

assurance that the end unit (carbons 22–26 in Scheme 6) has the assumed structure. We start with proton 24, which corresponds to a shifted methyl signal, according to simulation. Direct correlation in $^{1}H–^{13}C$ HETCOR assigns the corresponding carbon signal. 1D DEPT135 spectrum confirms that this really is a methyl signal. Now COLOC shows that next to methyl 24 is carbon 23, which has no signal in either DEPT or HETCOR, i.e. it is a quaternary carbon. Its position shows that it must be attached to one chlorine atom, according to simulations. Owing to sufficiently large $^{3}J_{C–H}$ coupling constant, protons 24 correlate with carbonyl carbon 25, which has a predicted position. This carbon 25 further correlates in COLOC with signal 25 identified in proton spectrum and DEPT as O-methyl signal. Further, signal 24 correlates in COLOC with 22, which is a neighboring CH_2 group (assigned by proton and DEPT spectra).

In a similar way, all other (more trivial) signals were assigned. Unfortunately, the group of carbons 10, 11, 12 could not be assigned in such direct way. The reason is that the signals are somewhat broadened and the coherences are destroyed by relaxation during correlation experiments. Nonetheless, we can see that there is only one signal 11 of a quaternary carbon (compare DEPT and ordinary ^{13}C spectrum) with a position properly shifted relatively to that of the initiator. The next signal 10 is a CH_2, according to DEPT, again in the predicted position.

Combining all the techniques mentioned, we can conclude that the polymer structure corresponds to that of Scheme 6. The product is clearly linear, without any branching at carbon 11 or any unsaturated unit, which could be produced by chain disproportionation or β-scission.

Table 3
Synthesis and characterization of poly(*t*-BuA-*b*-MMA-*b*-*t*-BuA) copolymers

Run	PMMA		M:I[a]	Cu[b]	Time (h)	Conversion (%)	Copolymer			
	M_n	M_w/M_n					SEC			
							M_n	M_w/M_n	M_n (NMR)	M_n (theor.)
1	7300	1.11	300	–	18	27	19,300	1.13	17,800	17,700
2	7300	1.11	300	–	18	62	26,100	1.19	31,400	31,100
3	7300	1.11	300	1	14	90	38,300	1.56[c]	–	41,000
4	8700	1.11	200	–	14	35	19,500	1.10	17,400	18,500
5	9400	1.13	200	1	5	90	31,900	1.19	32,300	30,700
6	4200	1.15	400	1	15	41	37,300	1.15	25,100	25,000
7	4200	1.15	400	2	11	61	51,100	1.24	35,500	34,400
8	4800	1.15	800	4	25	50	71,000	1.27	55,600	53,500

Conditions: PMMA/CuCl/PMDETA = 1/2/2 (runs 1–3), or 1/1/1 (runs 4–8), T = 70 °C (run 1), 90 °C (runs 2, 3), 60 °C (runs 4–8); DMF (runs 1–3), acetone (runs 4–8), solvent concentration: 25% vol. per *t*-BuA.
[a] *t*-BuA/PMMA mole ratio.
[b] Cu/CuCl mole ratio.
[c] Bimodal MWD.

3.2. Synthesis of poly(t-BuA-b-MMA-b-t-BuA) copolymers

Poly(methyl methacrylate)s, prepared in the way mentioned above, are linear and symmetric, having C–Cl groupings on both the ends and, therefore, they can be used as α,ω-bifunctional macroinitiators of ATRP of other monomers. Thus, attempts have been made to polymerize *t*-BuA with various PMMA macroinitiators under catalysis with CuCl/PMDETA combination in the presence of polar solvents, DMF [25] or acetone [26,27], leading to the corresponding triblock copolymers. The results are summarized in Table 3. Runs 1–3 were performed in the presence of DMF. At 70 °C (run 1), the polymerization is slow; 27% conversion is obtained after 18 h. However, molecular weight of the resulting polymer corresponds to the expected value and polydispersity is narrow. At 90 °C, reaction is faster reaching 62% conversion within the same time interval giving again PMMA with a narrow MWD and M_n near to the theoretical value. The attempt to accelerate this polymerization by copper addition (run 3) failed. Monomer conversion is almost quantitative in 14 h, but the formed polymer had broadened MWD with a distinct hint of bimodality. Polymerization in the presence of acetone at 60 °C and without Cu addition (run 4) proceeds somewhat faster than that in DMF; nevertheless, monomer conversion is still low in 15 h. Perceptible improvement was observed in run 5, polymerized in the presence of one equivalent of Cu relative to CuCl under otherwise the same conditions. Here, the *t*-BuA conversion is almost quantitative within 5 h and the corresponding triblock copolymer is formed with a narrow MWD and expected molecular weight. Under these reaction conditions, lengths of poly(*t*-BuA) blocks in copolymers can be controlled stoichiometrically in fairly broad range, as documented in runs 5–8. An addition of a higher amount of Cu is recommended when the *t*-BuA/PMMA macroinitiator mole ratio is higher than 200. Anyway, the polymerization requires a long reaction time when the *t*-BuA/PMMA macroinitiator mole ratio = 800 and Cu/CuCl ratio = 4 are used (run 8). The prepared triblock copolymers are precursors of amphiphilic copolymers with variable lengths of the outer hydrophilic blocks of poly(acrylic acid) after selective hydrolysis of the poly(*t*-BuA) blocks.

In all the block copolymerizations presented above, the PMMA macroinitiators are quantitatively consumed in the *t*-BuA polymerization and, consequently, the prepared triblock copolymers are not detectably contaminated with PMMA homopolymer. This is documented by SEC eluograms of the copolymers and of the corresponding

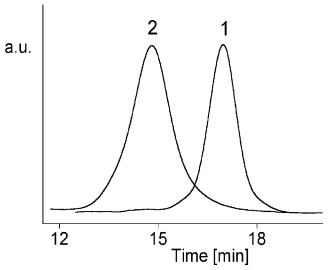


Fig. 9. SEC eluograms of the copolymer (2) and the corresponding PMMA macroinitiator (1), Table 3, run 5.

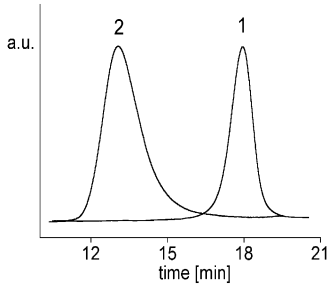


Fig. 10. SEC eluograms of the copolymer (2) and the corresponding PMMA macroinitiator (1), Table 3, run 8.

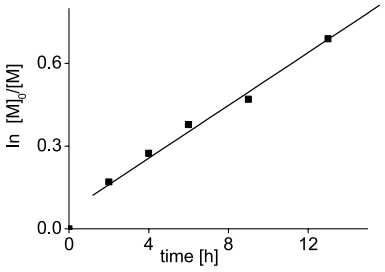


Fig. 11. ln[M_0]/[M] vs. time plot of *t*-BuA polymerization initiated with PMMA macroinitiator, (M_n=4800, M_w/M_n=1.15), otherwise the same conditions as in run 6, Table 3.

PMMA macroinitiators (runs 5 and 8) in Figs. 9 and 10. Moreover, ln[M]$_0$/[M] vs. time plot of the *t*-BuA polymerization initiated with PMMA (M_n=4800, M_w/M_n=1.15) under otherwise the same conditions as in run 6, is linear at least in the measured range, indicating a constant content of growing species within the process (Fig. 11). Also, M_n of the formed polymer increases linearly with increasing monomer conversion (Fig. 12) and, at the same time, polydispersity slightly decreases. Both these features support the statement that ATRP of *t*-BuA is a 'living' and controllable process under the given conditions.

4. Conclusions

The novel type of bifunctional initiator with trichloromethyl active groups was used for polymerization of MMA and synthesis of poly(*t*-BuA-*b*-MMA-*b*-*t*-BuA) copolymers, catalyzed with CuCl in the presence of amine-type ligands. With bipyridine, MMA polymerization is not well controlled, MWDs of products are broadened and molecular weights do not follow theoretical predictions. In contrast, polymerization in the presence of HMTETA proceeds in a 'living' manner, giving PMMAs with narrow MWDs and M_n values near to the theoretical ones. Under the optimized conditions, molecular weight of PMMA can be controlled in the range from 4800 to 72,500, i.e. more than one order of magnitude, keeping MWDs narrow. NMR analysis of polymers showed that they are linear and symmetric with respect to the initiator moiety which means that the possible side reactions, grafting and/or β-scission of the chains, do not proceed in a detectable range. Thus, the initiator acts as a non-activated type in sense of the conclusions of Destarac et al. [18], nevertheless, the polymerization is, under well-chosen conditions, sufficiently rapid. The formed α,ω-dichloro-PMMAs can initiate ATRP of *t*-BuA, leading to corresponding triblock copolymers with variable lengths of the blocks. The block copolymerization has to be performed in the presence of PMDETA ligand and a polar solvent. The best results gave polymerizations in acetone, affording block copolymers with narrow MWDs and predictable molecular weights. However, the reaction is slow and has to be accelerated by addition of metallic copper, in particular, if the *t*-BuA/PMMA macroinitiator mole ratio is higher than 200. Thus, the novel initiator, which can be easily prepared by a simple reaction of isocyanate groups with alcohol, is a good tool in ATRP synthesis of polymers and block copolymers based on (meth)acrylates.

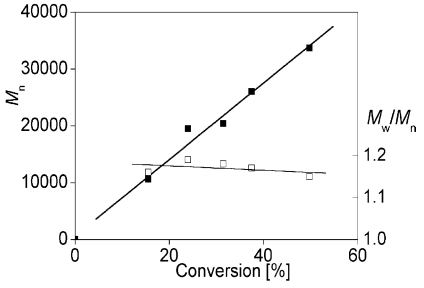


Fig. 12. Development of M_n (solid symbols) and M_w/M_n (empty symbols) with conversion in *t*-BuA polymerization initiated with PMMA; experiment from Fig. 11.

Acknowledgements

Financial support of this work from the Grant Agency of the Czech Republic (grant 203/01/0513) and from the Academy of Sciences of the Czech Republic (project AVOZ 4050913) is highly appreciated. One of the authors (A.M.) thanks the IUPAC (project 2002-047-1-400) and Academy of Sciences of the Czech Republic for financing her postgraduate stay in the IMC, Prague.

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