SYNTHESIS OF TELECHELICS AND BLOCK COPOLYMERS VIA "LIVING" RADICAL POLYMERIZATION

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SUMMARY: Hydroxy-telechelic poly(methyl methacrylate)s of molecular weights below 5000 were obtained by atom transfer radical polymerization (ATRP) of methyl methacrylate followed by end-capping with allyl alcohol via atom transfer radical addition (ATRA). As initiators for the ATRP, monofunctional initiators with an additional hydroxy group in the molecule or bifunctional initiators were employed. The successful synthesis of the hydroxy-telechelic PMMA was proved by determination of their molecular weight using MALDI-TOF-MS. The efficiency of the end-capping reaction was determined by ^{1}H NMR spectroscopy using the allyl *N*-(4-tolyl)carbamate as end-capping agent. Block copolymers comprising a poly(ethylene oxide) (PEO) block and a poly(methyl methacrylate) (PMMA) block were prepared by ATRP using a macroinitiator on the PEO basis. The dormant species of the macroinitiator consists of the phenyl chloroacetate moiety which shows a high rate of initiation. The successful synthesis of the poly(ethylene oxide)-*block*-poly(methyl methacrylate) was proved by ^{1}H NMR spectroscopy; the ratios of EO/MMA repeating units in the feed and the copolymer were nearly equal.

Introduction

Living polymerization procedures in the ideal case show immediate initiation followed by propagation without termination and transfer reactions[1]. Therefore, these procedures are used in macromolecular engineering for the synthesis of complex macromolecular architectures, e.g., telechelics and block copolymers[2]. Different procedures were developed for the synthesis of both telechelics (Eq. 1 and 2) and block copolymers (Eq. 3 and 4) depending on the initiator (In) used. For the synthesis of telechelics with the functional groups Y, the end-capping of a living polymer prepared with a bifunctional initiator is the most common way (Eq. 1). Sequential introduction of the functional groups, i.e., one with the initiator and the other with the end-capping agent is an alternative route (Eq. 2). For the synthesis of A-B-A block copolymers, sequential addition of monomers to a bifunctional initiator is the most common way (Eq. 3). The use of macroinitiators is the method of choice when the two monomers are polymerized by different mechanisms (Eq. 4).

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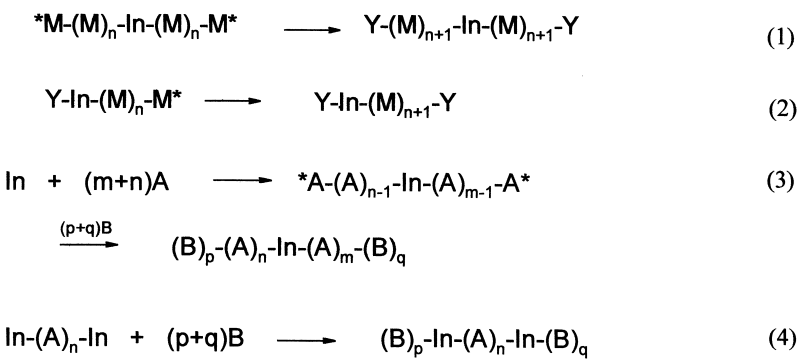


In the present comunication we report on the synthesis of hydroxy-telechelic poly(methyl methacrylate) by "living" free radical polymerization as represented by atom transfer radical polymerization (ATRP). In addition, the synthesis of poly(ethylene oxide)-*block*-poly(methyl methacrylate) by ATRP using a poly(ethylene oxide) macroinitiator will be presented.

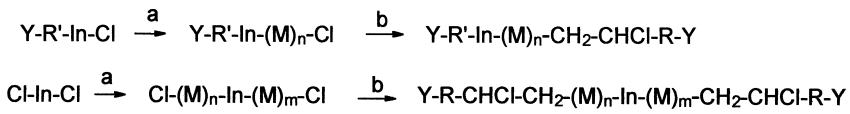
Results and discussion

In atom transfer radical polymerization, the initiator – an activated alkyl halide – reacts with a ligand-stabilized Cu(I)-species in a redox reaction transferring the halogen atom to result in an alkyl radical – the active species – and a Cu(II) species. The active species reacts with the monomer present in the system and the resulting radical is quenched again by the Cu(II) species to result in a new activated alkyl halide, the so-called dormant species. The equilibrium between active and dormant species is strongly shifted to the dormant species leading to a low stationary concentration of radicals. This low concentration of active species leads to a low probability of termination reaction by recombination or disproportionation because these reactions are second-order with respect to the radical concentration[3].

Hydroxy-telechelic poly(methyl methacrylate)

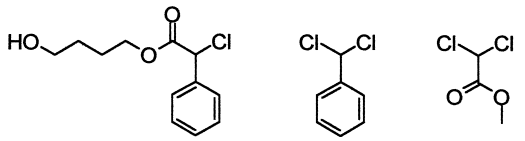
For the preparation of telechelics by ATRP, two routes were developed. The first route (Scheme 1) starts with a monofunctional initiator which is substituted with an additional functional group Y, such as hydroxy group or *N*-(4-tolyl)carbamate moiety. Atom transfer radical polymerization using these monofunctional initiators leads to a heterotelechelic polymer with Y and Cl as functional end-groups. Atom transfer radical addition (ATRA) to an α-olefin bearing a functional group Y leads finally to the telechelic end product. Since the halogen atom in the ATRA product is not activated, this reaction is considered to be an end-capping reaction.

In the second route (Scheme 1), a bifunctional initiator was employed for the ATRP of methyl methacrylate and the chloro-telechelic polymer obtained was subjected to an end-capping reaction by atom transfer radical addition with an α-olefin bearing the functional group Y. After successful end-capping, a telechelic end product with functional groups Y is obtained.



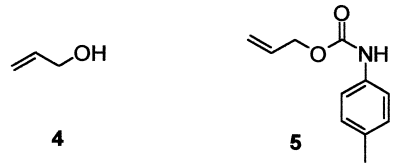
Scheme 1: Synthesis of telechelics starting with the monofunctional initiator Y-R′-In-Cl and the bifunctional initiator Cl-In-Cl using the end-capping agent CH_2=CH-R-Y: *a* ATRP, *b* ATRA

The monofunctional initiator used in this investigation is derived from chloro(phenyl)acetyl chloride which, when treated with butane-1,4-diol, results in 4-hydroxybutyl chloro(phenyl)acetate (**1**). As bifunctional initiators, dichloro(phenyl)methane (**2**) and methyl dichloroacetate (**3**) were employed.



1 **2** **3**

As end-capping agents, allyl alcohol (**4**) and the respective allyl *N*-(4-tolyl)carbamate (**5**) were used. It is expected that the end-capping reaction follows an atom transfer radical addition reaction of the chloro-telechelic oligomers to the end-capper.



4 **5**

In order to evaluate the influence of a high initiator concentration which is necessary to prepare oligomers and the influence of functional groups in the initiator, 4-hydroxybutyl chloro(phenyl)acetate (**1**), dichloro(phenyl)methane (**2**), and methyl dichloroacetate (**3**) were used for the polymerization of methyl methacrylate. For a partial compensation of the high radical concentration, an inert solvent, e.g., butyl acetate, was employed. GPC analysis (Fig. 1) of these oligomers revealed that a controlled polymerization is possible; in all cases, the

calculated and the experimental molecular weights were close and the polydispersity index was smaller than 1.5.

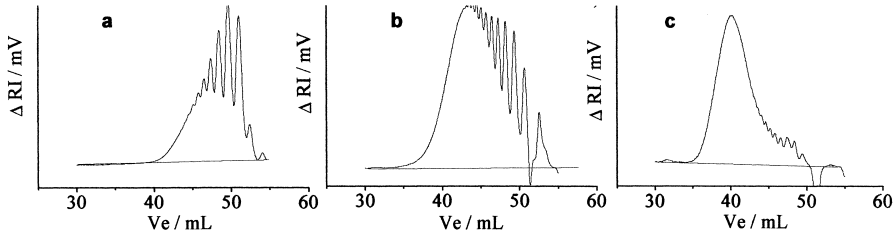
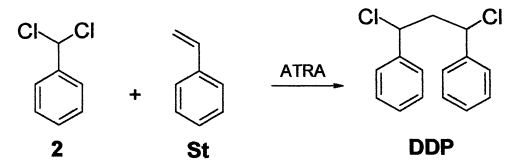
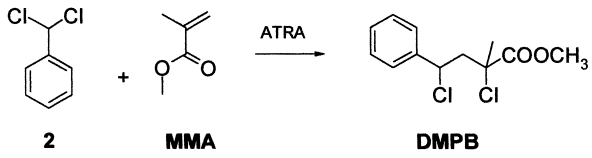


Fig. 1 GPC plots of oligo(methyl methacrylate)s: (a) In = **2**; M_n = 550, M_w/M_n = 1.22; (b) In = **3**; M_n = 950, M_w/M_n = 1.46; (c) In = **1**; M_n = 1900, M_w/M_n = 1.36



(5)



(6)

For **2** and **3**, however, the question arises whether the chain growth reaction occurs bidirectionally or not. The application of **2** as an initiator to the "living" radical polymerization of styrene is the most evident conclusion if a bidirectional chain growth is desired. Upon addition of the first styrene molecule, 1,3-dichloro-1,3-diphenylpropane (**DDP**) is formed, which is a symmetrical molecule (Eq. 5). The two chlorine atoms are in identical chemical environment which, in addition, is similar to a growing polystyrene chain end. From kinetic measurements, the bidirectional chain growth was proved for styrene as the monomer. For methyl methacrylate as the monomer, the situation is different. Upon addition of the first MMA monomer to **2**, an asymmetric dichloride (**DMPB**) is obtained (Eq. 6), one end representing a polystyrene chain end and the other one a PMMA chain end. Kinetic measurements for this system suggest a prevailing monodirectional chain growth by the PMMA-like species[4].

Atom transfer radical polymerization of MMA in butyl acetate in the presence of allyl alcohol using the monofunctional initiator **1** results in a polymer with 91% yield. The molecular weight of the expected hydroxy-telechelic product is $M_n \approx 1200$. The functionality of the telechelic product was determined by titration to be 90%. By assuming that 50% of the OH groups were introduced with the initiator, a 40% conversion for the atom transfer radical addition has to be considered.

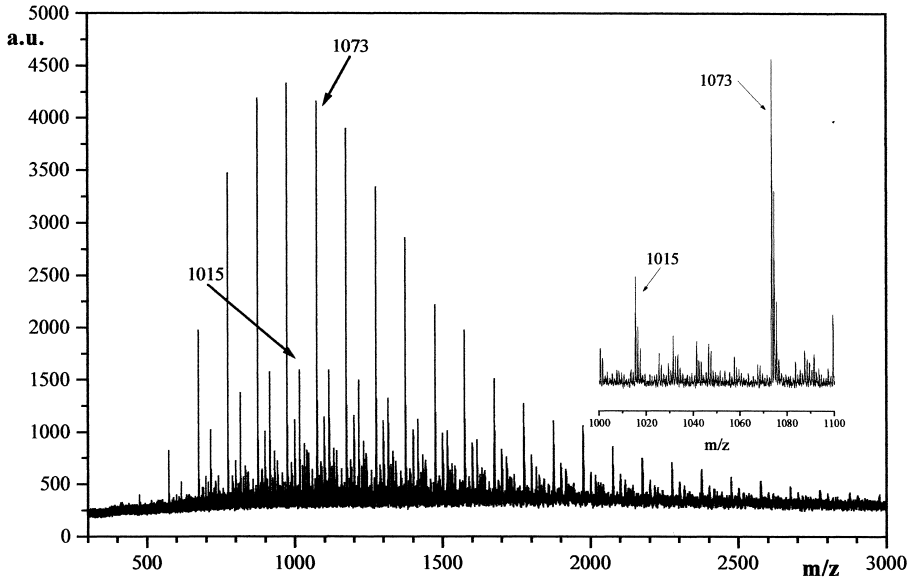


Fig. 2 MALDI-TOF-MS of hydroxy-telechelic oligomers prepared with the hydroxy-functional initiator **1** and end-capping with allyl alcohol

Analysis of the product by MALDI-TOF-MS (Fig. 2) reveals a major peak series besides a minor peak series with the mass difference of 58 corresponding to the mass of allyl alcohol. This means that the major product is end-capped with allyl alcohol and some unreacted product is still present. It must be mentioned, however, that the observed mass of the hydroxy-telechelic product is by 28 units smaller than the calculated value for both the functionalized and unfunctionalized product. This difference of 28 units was found also for other initiators, other end-capping agents and for polystyrene prepared by ATRP[5]. We assume that in the MALDI spectrometer, a reaction takes place leading to the deviation from the observed molecular weight.

In order to obtain some information on the kinetics of the end-capping reaction, carbamate end-cappers were used which are suitable for the determination of the end group

concentration by ^{1}H NMR spectroscopy. The singlet of the CH_3 end group at $\delta \sim 2.3$ ppm is related to the OCH_3 singlet of the MMA repeating units. The results obtained for the end-capping at a ratio of end-capper to dormant species of 3 is shown in Fig. 3.

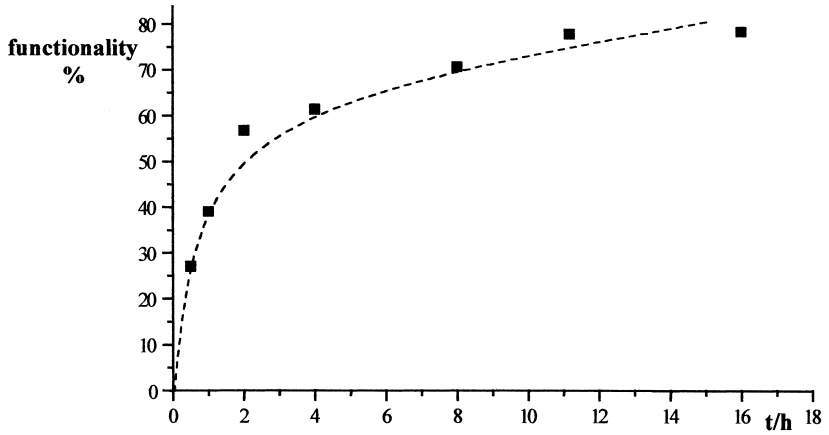


Fig. 3 Time dependence of concentration of functional end groups as determined by ^{1}H NMR spectroscopy. (Polymerization conditions: CuCl (1), bpy (2.5), **2** (1), MMA (20), **5** (6) in butyl acetate (30), 110 °C.)

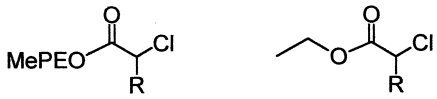
The course of end-capping can be divided into two regimes, the first, high-rate end-capping and the second regime with a lower rate of end-capping. This observation is in accordance with our assumption of monodirectional chain growth in the polymerization of MMA with **2** as the initiator resulting in a chain with two different dormant species and, hence, different reactivities in the atom transfer radical addition.

At this point it should be mentioned that the presence of allyl alcohol during polymerization has no major effect on the molecular weight or the polydispersity index of the resulting polymer. This means that the rate of polymerization is much higher than the rate of end-capping.

Poly(ethylene oxide)-block-poly(methyl methacrylate)

The second purpose of this study was the preparation of A-B block copolymers with poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA) blocks by ATRP. For this purpose, the macroinitiators **6a-c** were prepared by a chain-analogous reaction starting from methoxy-hydroxy-telechelic PEO-1900 and the corresponding 2-chloroacyl chlorides. The macroinitiators were analysed by ^{1}H NMR spectroscopy and MALDI-TOF-MS. From these data, the high purity of the macroinitiators employed was confirmed, showing that the

chain-analogous transformation necessary for the synthesis of the macroinitiator occurred quantitatively[6].



6a-c **7a-c**

a R = C_6H_5, b R = CH_3, c R = H

The MALDI-TOF spectrum (Fig. 4) for the macroinitiator **6a** shows a single major peak series with a peak difference of 44.1 (CH_2CH_2O), confirming the proposed structure and the purity of this initiator. The experimentally obtained mass of 2160.15 corresponds to the mass of the proposed structure **6a** $CH_3O(CH_2CH_2O)_{44}COCHClPh/K$ (2161.92). At 2190.14 and at 2184.12, the respective sodium and silver adducts of **6a** $CH_3O(CH_2CH_2O)_{45}COCHClPh/Na$ (2189.86) and $CH_3O(CH_2CH_2O)_{43}COCHClPh/Ag$ (2186.64) are detected. A minor peak series with a mass difference of about 10 units (2170.2) to the major peak series is found to correspond with the structure $CH_3O(CH_2CH_2O)_{45}COCH_2Ph/K$ (2171.52), indicating that the chlorine atom is substituted by an H atom in the MALDI spectrometer.

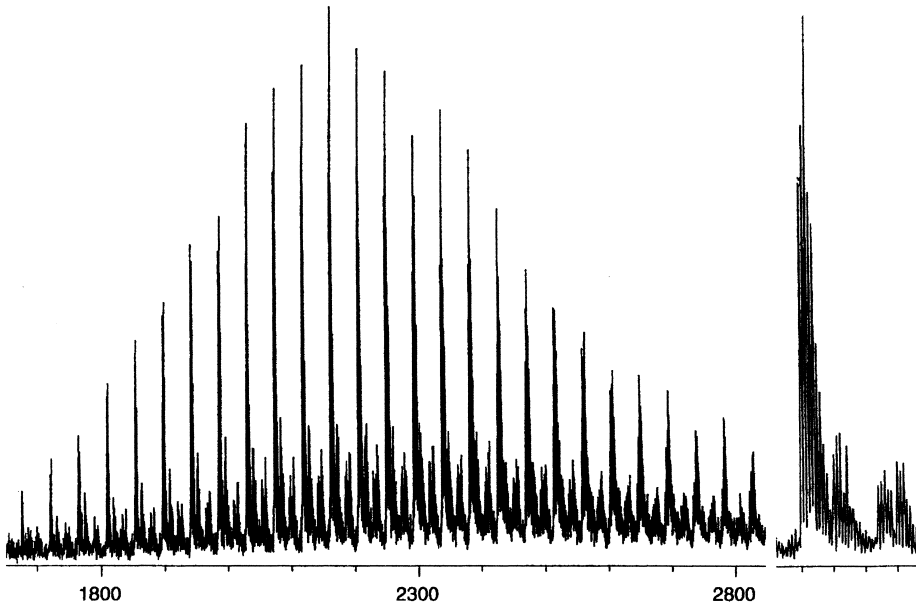


Fig. 4 MALDI-TOF-MS of the macroinitiator **6a**

GPC measurements in DMAc (PMMA standards) of the macroinitiators revealed an average molecular weight of 4000 and a narrow MWD. These results have to be considered when block copolymers are analysed by means of GPC.

Polymerization of MMA with the macroinitiators **6a-c** was performed in bulk in a heterogeneous system with a monomer/initiator ratio of about 200 at 130 °C for 2 h. Macroscopically, the system remains clear up to the end of the polymerization suggesting that the macroinitiator or the PEO block is soluble in MMA/PMMA under polymerization conditions. The reaction mixture was precipitated into methanol/aqueous HCl in order to remove unreacted PEO macroinitiator and the catalyst. The polymer yield was about 90% for all the macroinitiators used. GPC analysis of the PEO-PMMA block copolymer obtained with **6a** reveals a good agreement of the theoretical and experimental number-average molecular weight and a narrow MWD. For the polymers obtained with **6b** and **6c,** the experimentally observed molecular weights are higher than those theoretically expected. Furthermore, the polydispersity indices are higher than the one found for the polymer obtained with **6a** (Table 1).

Table 1 Polymerization of methyl methacrylate with the macroinitiators **6a-c** and the model initiators **7a-c** in the presence of CuBr/2,2′-bipyridine[a]

No.	I	$[M]_0/[I]_0$	x_p / %[b]	$\overline{M}_{n,th}$[c] / $\overline{M}_{n,exp}$[d]	Q[d]	$[EO]_0/[M]_0$[e]	$[EO]_p/[M]_p$[f]
1	**6a**	216.8	91	20 700 / 20 700	1.15	0.22	0.17
2	**6b**	199.1	87	17 300 / 33 900	1.38	0.23	0.06
3	**6c**	216.1	90	19 400 / 50 100	1.28	0.21	0.03
4	**7a**	212.6	86	18 300 / 16 700	1.15	-	-
5	**7b**	196,9	90	17 700 / 41 400	1.38	-	-
6	**7c**	247.0	25	6 200 / 59 800	1.28	-	-

[a] Molar ratio of initiator/CuBr/bpy = 1/1/3; T = 130 °C, t = 2 h; [b] gravimetrically; [c] calculated from $\overline{M}_{n,th} = [M]/[I]\ x_p M_{mon}$; [d] by GPC (elution with LiCl in DMAC (1.22 g/L), 80 °C, calibration with PMMA standards); [e] introduced in the feed; [f] by ^{1}H NMR spectroscopy

From ^{1}H NMR data of the polymers prepared with macroinitiators **6a-6c**, the ratio of EO/MMA repeating units in the copolymer is determined (Table 1). Only for the polymer obtained with **6a**, the ratio of repeating units corresponds to the ratio introduced into the feed indicating that the macroinitiator is incorporated in the copolymer. For **6b** and **6c** as initiators, however, a large discrepancy between the the EO/MMA ratio in the feed and that in the polymer was found due to a low initiation efficiency as already suggested by the GPC data.

In order to evaluate the influence of the PEO moiety on the course of the polymerization, the corresponding model initiators **7a-7c** were used for the polymerization of MMA. The polymers obtained with the model initiators show the same polydispersity indices as the

corresponding block copolymers thus proving no effect of the PEO moiety on the polymerization course. It should be noted, however, that the obtained molecular weights of the polymers prepared with the macroinitiators at similar conversions are lower than those of the PMMAs obtained with the model initiators. This may be due to a higher viscosity on the one hand and, on the other, to the dilution caused by the PEO moiety in the critical pre-equilibrium phase of the polymerization during which combination of initiating radicals can take place. However, the exact role of the PEO moiety and the deviating behaviour of model initiator **7c** during polymerization must be further investigated.

Investigation of the initiation efficiency of the model initiators **7a-7c** was performed in a heterogeneous system with the initiator/CuBr/bpy/MMA ratio of 1/1/3/15 for various times t (t_{max} = 10 min). From first-order kinetic plots, the apparent rate constants $k_{app} = k_p \cdot [P\bullet]$ were determined, where k_p is the rate constant of propagation and [P•] the radical concentration. The highest value for the apparent rate constant was observed for the phenyl-substituted initiator **7a** (k_{app}(**7a**) = $41.8 \cdot 10^{-4}$ s^{-1}, k_{app}(**7b**) = $10.0 \cdot 10^{-4}$ s^{-1}, k_{app}(**7c**) = $1.3 \cdot 10^{-4}$ s^{-1}), the lowest for initiator **7c**. Since the rate constant of propagation k_p is a monomer-specific constant, the different k_{app} values must result from different radical concentrations introduced into the system by the initiators. This proves **7a** and, consequently, also **6a** to be efficient initiators for the polymerization of MMA. According to Szwarc[7], a fast and efficient initiation reaction is a prerequisite for the preparation of well defined homopolymers and block copolymers.

Experimental part

Materials: Methyl methacrylate, butyl acetate (both from Bayer AG) and the initiators used for polymerizations were of high purity. CuCl (98%, Aldrich) and 2,2'-bipyridine (bpy) (ABCR) were used as received without purification.

Measurements: NMR, MALDI and GPC analyses were performed as described in Ref.[4,6].

Polymerization of methyl methacrylate in butyl acetate as a solvent (general procedure): Initiator, CuCl, and bpy in a molar ratio of 1:1:3 were introduced into a Schlenk glass tube. Monomer and butyl acetate (1:1 vol.) were added and the heterogeneous mixture was degassed (3 times), filled with nitrogen and immersed into an oil bath at 110 or 130 °C. After a certain time, the polymerization was terminated by cooling to room temperature. The product was dissolved in CH_2Cl_2 and washed with 5% aqueous HCl. The organic phase was separated, dried and the solvent removed by distillation. The polymer was dried to constant weight and analyzed by GPC (Fig. 1).

(a) $[\mathbf{2}]_0/[MMA]_0$ = 1/3, T = 130 °C, t = 65 h, yield 91 %; (b) $[\mathbf{3}]_0/[MMA]_0$ = 1/5, T = 130 °C, t = 24 h, yield 93 %; (c) $[\mathbf{1}]_0/[MMA]_0$ = 1/10, T = 130 °C, t = 20 h, yield 92 %.

Polymerization of methyl methacrylate in butyl acetate in the presence of allyl alcohol (**4**).
The general procedure was followed. To obtain the polymer as a powder, a concentrated solution of the polymer in CH_2Cl_2 was precipitated in hexane. $[\mathbf{1}]_0/[MMA]_0/[\mathbf{4}]_0$ = 1/10/10, T = 130 °C, t = 63 h, yield 91%.

Polymerization of methyl methacrylate in butyl acetate in the presence of allyl N-(4-tolyl)carbamate (**5**).
The general procedure was followed. To obtain the polymer as a powder, a concentrated solution of the polymer in CH_2Cl_2 was precipitated in hexane. $[\mathbf{2}]_0/[MMA]_0/[\mathbf{5}]_0$ = 1/20/6, T = 110 °C.

t (h)	0.5	1.0	2.0	4.0	8.0	11.2	16
M_a	3000	3600	3800	3950	4100	3400	3700
M_w/M_n	1.19	1.25	1.31	1.31	1.31	1.36	1.28

Polymerization of methyl methacrylate with macroinitiators **6a-6c** *and model initiators* **7a-7c**
The general procedure was followed. To obtain the polymer as a powder, a concentrated solution of the polymer in CH_2Cl_2 was precipitated in methanol containing aqueous HCl. The results are summarized in Table 1.

ACKNOWLEDGEMENT

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