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New syntheses of graft copolymers using the DPE-technique: ATRP graft copolymerization

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Summary

A new one-step synthesis of a set of macroinitiators for atom transfer radical polymerization (ATRP) via controlled radical polymerization is presented. The macroinitiators consist of methacrylate and *p*-chloromethylstyrene (CMS) and were synthesized by controlled radical polymerization in the presence of 1,1-diphenylethylene (DPE) using azobisisobutyronitrile (AIBN) as initiator. The resulting macroinitiators were used for the ATRP of different methacrylates yielding graft copolymers which were characterized by SEC and NMR.

Keywords

DPE-system, ATRP, radical polymerization, macroinitiator, *p*-chloromethylstyrene, graft copolymers, methacrylate

Introduction

The well defined synthesis of graft copolymers is a subject of increasing importance in polymer chemistry. Such polymers can be applied as amphiphiles or phase compatibilizers in polymer blends which is highly interesting for the finetuning of the properties of new polymer materials.
One of the most efficient methods for the synthesis of graft copolymers is the "grafting from" method using macroinitiators bearing functional groups that allow the initiation of side chains. [1]

A wide range of macroinitiators for radical or ionic polymerization has been synthesized to date by nearly all available polymerization techniques. In this respect, one of the most interesting and versatile initiating functional groups is benzyl halide. Unfortunately, well defined macroinitiators with benzyl halide functions cannot be synthesized by common free radical polymerization in one step, because of their strong tendency to act as transfer agents. Additionally, their reactivity towards anionic or transition metal catalysts makes an anionic or metal catalyzed polymerization of suitable monomers such as *p*-chloromethylstyrene (CMS) impossible, as well. To date, macroinitiators bearing benzyl halides are either synthesized by cationic polymerization at low temperatures or in a two step process by polymer analogous functionalization. [2, 3]

One possibility to solve this problem is the controlled radical polymerization (CRP) of CMS with TEMPO and its copolymerization with styrene [4]. Nevertheless, TEMPO is still rather limited and could not yet be applied for the polymerization or copolymerization of polar monomers such as methyl methacrylate (MMA). ATRP cannot be applied for this synthesis either since halogene containing compounds act as initiators in ATRP [5,6]. Furthermore, no polymerization of CMS via the reversible-addition-fragmentation-transfer process (RAFT) is described in the literature, yet.

CMS is an interesting comonomer for an one step synthesis of macroinitiators provided that a transformation of the benzyl chloride function during polymerization can be avoided. Its benzyl chloride function can be used as an initiator for cationic polymerization [7], grafting onto [8] or ATRP [9]. Furthermore, the monomer is commercially available and therefore interesting even for industrial applications.

Recently, we presented a new system for the controlled radical polymerization, the DPE-technique [10,11]. By this method a large variety of radically polymerizable monomers can be polymerized in a controlled way forming random copolymers as well as block copolymers under mild conditions. A major advantage of this system is that polymerization control can be achieved without the necessity to use expensive transition metal catalysts or toxic thiol compounds.

Recently, we reported the synthesis of a set of methacrylate macroinitiators by a one step radical random copolymerization of methacrylate monomers and CMS using the DPE-technique and their application for the cationic ring-opening polymerization of cyclic ethers. [12] Herein we present the application of such macroinitiators in "grafting from" polymerizations of selected methacrylates by ATRP.

Experimental

Materials

Methyl methacrylate (MMA), n-dodecyl methacrylate (DDMA), n-butyl methacrylate (BMA) and p-chloromethylstyrene (CMS) were purified via a column of basic Al_2O_3 and subsequently distilled before use. DPE was distilled before use. AIBN was recrystallized from methanol. Dichloromethane and toluene were dried for 48 hours over calcium hydride and subsequently distilled before use. Tris(triphenylphosphine)ruthenium(II) chloride (Aldrich) was stored under argon and used as received.

Measurements

Molecular weights and molecular weight distributions (MWD) of all samples were determined using a size exclusion chromatograph (SEC) Waters 510 with an RI (Waters 410) detector and Polymer Laboratories (PL gel 10 μm MIXED B) columns calibrated with linear polystyrene standards. The absolute molar mass of two samples and their molecular weight distributions were determined by using a light scattering detector (Wyatt Mini-dawn, λ = 690 nm) and Waters (Styragel HR 4E) columns. In all cases $CHCl_3$ was applied as eluent.
^{1}H-NMR spectra were recorded with a Bruker ARX 300 at 300 K in $CDCl_3$ as solvent.

Poly (methyl methacrylate-co-p-chloromethylstyrene) macroinitiator MI 1 [12]

47,5 mmol methacrylate (methyl methacrylate for MI 1; n-dodecyl methacrylate for MI 2) and 0,43 mL (3 mmol) CMS were dissolved in 11 mL toluene and degassed by three freeze, pump and thaw cycles. Then 24,6 mg (0.14 mmol) AIBN and 26,4 μL (0.14 mmol) 1,1-diphenylethylene (DPE) were added to the monomer solution and the mixture was stirred at 80 °C for 1 d. The resulting polymers (yields: MI 1: 4,5 g, 86,3 %; MI 2: 10,3 g, 82,2 %) were precipitated in 500 mL methanol, reprecipitated from $CHCl_3$ in 500 mL ethanol and dried under vacuum.

Graft copolymer GP 1

640 mg (0,41 mmol with respect to chloride content) of MI 1, 154 mg (0,16 mmol) tris(triphenylphosphine)ruthenium(II) chloride, 34 mg (0,16 mmol) aluminum(III) isopropoxide and 4,7 mL (16 mmol) DDMA were dissolved in 21 ml toluene and stirred for 1d at 80 °C. The resulting polymer (yield: 3,5 g, 72 % with respect to the conversion of DDMA) was precipitated in 500 mL methanol, reprecipitated from $CHCl_3$ in methanol and dried under vacuum.

Graft copolymer GP 2

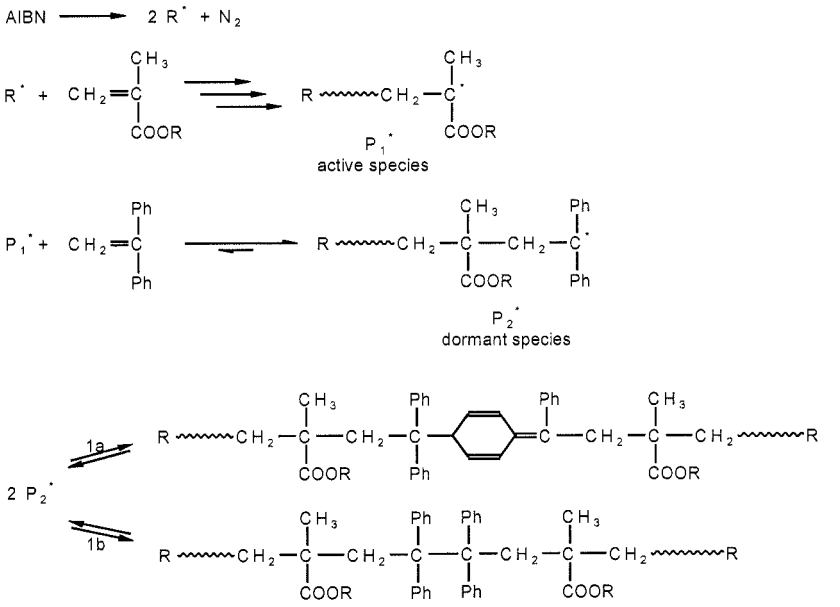
890 mg (0,56 mmol with respect to chloride content) of MI 1, 210 mg (0,22 mmol) tris(triphenylphosphine)ruthenium(II) chloride, 46 mg (0,22 mmol) aluminum(III) isopropoxide and 3,5 mL (22 mmol) BMA were dissolved in 15 ml toluene and stirred for 1d at 80 °C. The resulting polymer (yield: 3,1 g, 71 % with respect to the conversion of BMA) was precipitated in 500 mL methanol, reprecipitated from toluene in ethanol and dried under vacuum.

Graft copolymer GP 3

380 mg (0,07 mmol with respect to chloride content) of MI 2, 66 mg (0,07 mmol) tris(triphenylphosphine)ruthenium(II) chloride, 14 mg (0,07 mmol) aluminum(III) isopropoxide and 0,75 mL (7 mmol) MMA were dissolved in 10 ml toluene and stirred for 1d at 80 °C. The resulting polymer (yield: 720 mg, 49 % with respect to the conversion of MMA) was precipitated in 500 mL methanol, reprecipitated from $CHCl_3$ in methanol and dried under vacuum.

Results and discussion

In the first step, we synthesized a set of polymethacrylate macroinitiators in the presence of DPE. According to our view [11] DPE reacts with the growing chains (active species), deactivates them (dormant species) and by this protects them from transfer reactions with the benzyl chloride functions of the polymer and unreacted CMS. Termination by combination of two $P_2^{\bullet}$ via route 1a is favored over route 1b (Scheme 1) [13].



Scheme 1. Reaction of DPE with the growing chain end exemplified for the polymerization of CH_2=C(CH_3)(COOR).

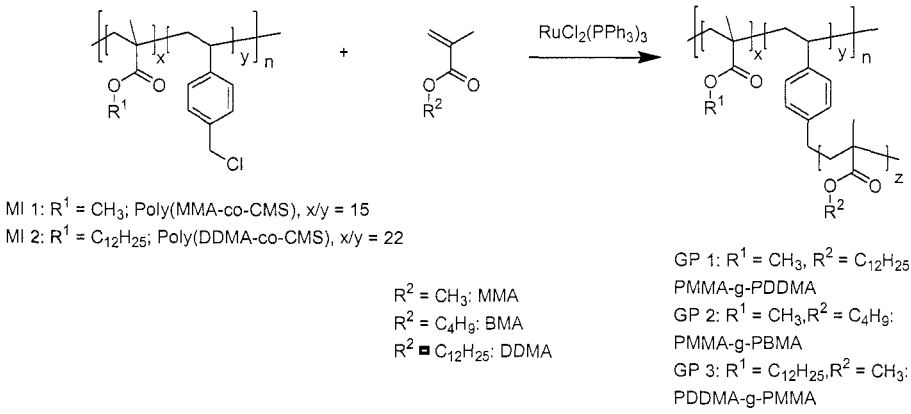
By this, macroinitiators bearing benzyl chloride functions could be synthesized in a simple one step radical random copolymerization. The incorporation of CMS into the polymer was proved by ^{1}H-NMR spectra (cf. figure 2).
The molar masses and benzyl chloride content of the macroinitiators synthesized is shown in table 1.

Table 1. Characterization of the macroinitiators

Polymer	Yield	M_n	M_w	MWD	Composition (NMR)
MI 1	86,3 %	45.000	78.000	1,70	MMA/CMS = 15
MI 2	82,2 %	69.900	99.900	1,43	DDMA/CMS = 22

All macroinitiators synthesized proved active as initiators for the ATRP polymerization of another methacrylate monomer for the synthesis of the side chains. As ATRP catalyst tris(triphenylphosphine)ruthenium(II) dichloride was applied, a

widely used standard system and one of the first catalysts applied for ATRP [14]. In most cases the macroinitiator was applied in a two fold excess. The initiator efficiency calculated by ^{1}H-NMR ranged between 18 and 47 % with respect to benzyl chloride conversion (cf. table 2).
The grafting from polymerization is displayed in scheme 2.



Scheme 2 grafting from polymerization by ATRP

The clear increase of molar masses observed by size exclusion chromatography (SEC) proves the formation of polymers with high molar masses. In all cases, no formation of low molar mass homopolymers was observed as it can be seen in the SEC curves (RI detector) of MI 1, GP 1 and GP 2 presented in figure 1.

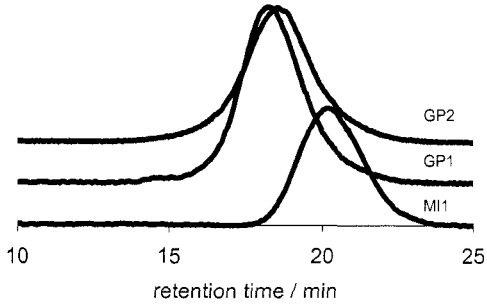


Figure 1. SEC curves of MI 1, GP 1 and GP 2.

The transformation of benzyl chloride initiating functions was measured by integration of the ^{1}H-NMR spectra. Figure 2 shows the ^{1}H-NMR spectra of MI 1 and GP 2.

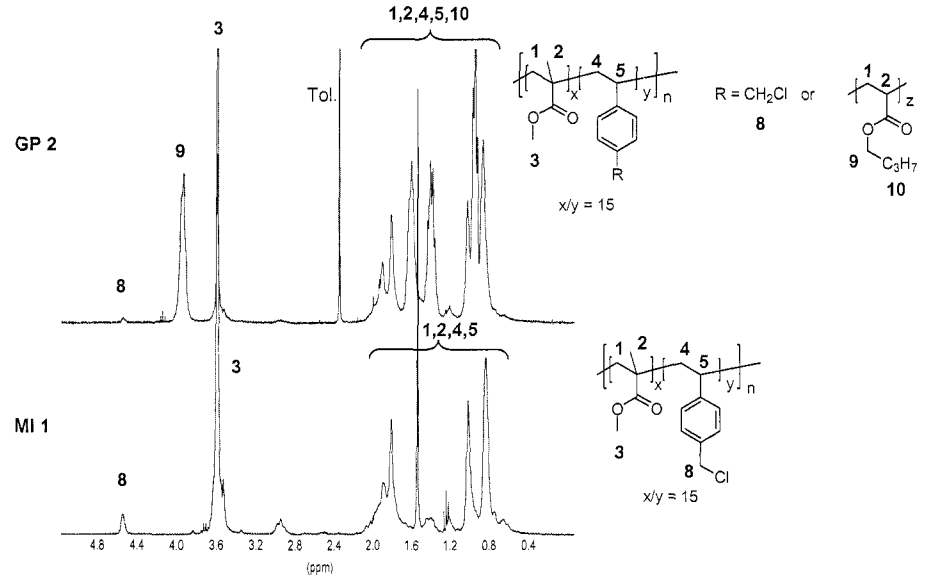


Figure 2. [1]H-NMR spectra of MI 1 and GP 2.

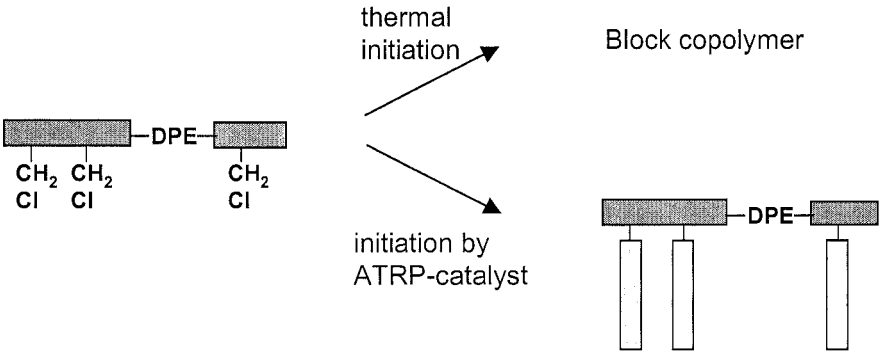
The complete set of experimental data for all graft copolymers is presented in table 2.

Table 2. Characterization of the graft copolymers

Polymer	GP 1	GP 2	GP 3
Macroinitiator used for grafting	MI 1	MI 1	MI 2
Initiator efficiency	18,2 %	47,0 %	18,8 %
Approx. number of side chains	5	13	2
M_n (SEC, RI-Det.[1])	120.000	135.500	112.000
MWD (SEC, RI-Det.[1])	1,99	1,78	1,87
M_n (SEC, LS-Det.[2])	720.000	1.500.000	-
MWD (SEC, LS-Det.[2])	1,55	1,13	-
Composition (NMR)	MMA/DDMA	MMA/BMA	DDMA/MMA
	1 : 2,7	1 : 2,5	1 : 1,8
[corresponding M_n]	[340.000 g/mol]	[204.000 g/mol]	[121.000 g/mol]
Composition (Gravimetry)	MMA/DDMA	MMA/BMA	DDMA/MMA
	1 : 1,8	1 : 1,8	1 : 2,3
[corresponding M_n]	[240.000 g/mol]	[160.000 g/mol]	[135.000 g/mol]

1) RI-Det. = refraction index detector; 2) LS-Det. = light scattering detector

The experimental data proves the formation of high molar mass copolymers. In all cases an increase of the molar mass distribution (MWD) was observed. This is most probably due to the fact that not all benzyl chloride functions were transformed during the initiation and thus graft copolymers with different numbers of side chains were formed.
In a previous publication, the synthesis of block copolymers using the DPE technique under similar conditions was described, however in the absence of an ATRP catalyst system. [15] Thus, the increase of molar mass might also be interpreted as formation of block copolymers.



Scheme 3. Possible reaction pathways of block and graft copolymerization

Nevertheless, the experimental data collected herein can only be interpreted as to prove the formation of graft copolymers rather than simple block copolymers in this case.
A strong hint for this interpretation is the fact, that all molar masses of graft copolymers observed by SEC, which was calibrated by linear standards, using an RI detector only, are significantly lower than the molar masses that would be expected from the composition observed by ^{1}H-NMR for the respective block copolymers. In general, the random coils formed by branched polymers in solution are more compact than the ones formed by linear polymers of the same molar mass. As by this SEC method only the hydrodynamic diameter of the random coils is measured, branched polymers will exhibit lower molar mass in SEC than linear polymers of the same molar mass.
The molar masses and MWDs of the graft copolymers GP 1 and GP 2 were also measured by SEC using a light scattering detector (LS-Det.), which allows the measurement of absolute molar masses. However, the high number is either an indication for aggregates or for the fact that light scattering can not be applied for for the determination of molar masses of graft copolymers without additional information like the specific *dn/dc*.

Conclusion

In this paper we presented a facile one step synthesis of a set of macroinitiators bearing benzyl chloride groups applying the DPE-technique for the controlled radical polymerization. By this technique we synthesized in one step a set of macroinitiators

using MMA, DDMA and CMS as monomers, which is not published via TEMPO, ATRP or RAFT yet. The resulting polymers are macroinitiators that can be used to initiate the ATRP polymerization of methacrylates. By this, an easy synthesis of graft copolymers with different polymethacrylate backbones and side chains is realized. The large variety of commercially available methacrylates makes it an interesting method for the controlled synthesis of such functional copolymers. In all cases the polymerizations did not result in any formation of homopolymer thus suggesting a highly controlled polymerization free of transfer reactions. The observation that all molar masses observed by SEC, calibrated by linear standards, are lower than the ones calculated from ^{1}H-NMR and from increase of masses strongly suggests the formation of graft copolymers.

The large variety of monomers polymerizable by the DPE-technique and ATRP allows the synthesis of many other graft copolymers with interesting macroscopic properties by this simple two step procedure.

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