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# New Syntheses of Graft Copolymers Using the DPE-Technique: Cationic Graft Copolymerization

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## ABSTRACT

A new one-step synthesis of a set of macroinitiators for cationic polymerization via radical polymerization is presented. The macroinitiator consists of poly(meth)acrylate random copolymers with *p*-chloromethylstyrene. It was synthesized by controlled radical polymerization of a monomer mixture of (meth)acrylate and *p*-chloromethylstyrene in the presence of 1,1-diphenylethylene (DPE) using azobisisobutyronitrile (AIBN) as initiator. The resulting macroinitiators were used for the cationic ring-opening polymerization of cyclic ethers yielding graft copolymers which were characterized by GPC and NMR.

*Key Words:* DPE-system; Radical polymerization; Macroinitiator; Chloromethylstyrene; Block copolymers; Graft copolymers; Cyclic ether.

## INTRODUCTION

The well-defined synthesis of graft copolymers is a subject of increasing importance in polymer chemistry. Such polymers often show interesting phase properties and thus can

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be applied as amphiphiles or phase compatibilizers in polymer blends which is of high interest for tailoring properties of new polymer materials.

One of the most efficient methods for the synthesis of graft copolymers is the "grafting from" method using macroinitiators from which the synthesis of the side chains is started.

A wide range of macroinitiators for radical or ionic polymerization has been synthesized to date by nearly all available polymerization techniques. In this respect, are benzyl halides interesting and versatile initiating functions. Unfortunately, well-defined macroinitiators with benzyl halide functions can neither be synthesized by common free radical nor by anionic or metal catalyzed polymerizations in one step, due to their strong tendency to act as transfer agents and their reactivity towards anionic or transition metal catalysts so that such macroinitiators are generally synthesized by polymer analogous functionalization.[1,2]

One possibility in solving this problem is the controlled radical polymerization (CRP) of 4-vinyl benzylchloride (CMS) with TEMPO and its copolymerization with styrene.[3] 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). The atom transfer radical polymerization (ATRP) cannot be applied for this synthesis either since halogen containing compounds act as initiators in ATRP.[4,5] 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 a one-step synthesis of macroinitiators, provided that the loss of the benzyl chloride function during polymerization can be avoided. Its benzyl chloride functions can be used as initiators for cationic polymerization,[6] grafting onto[7] or ATRP.[8] 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.[9,10] This method allows for the controlled polymerization of a large variety of radically polymerizable monomers forming either random copolymers as well as block copolymers under mild conditions all of which exhibit narrow molecular weight distributions (MWD) and controlled molar mass. A major advantage of this system is that polymerization control can be achieved without the necessity to use expensive transition metal catalysts or toxic thiole compounds.

Herein, we report the synthesis of a set of (meth)acrylate macroinitiators synthesized by a one-step radical random copolymerization of (meth)acrylate monomers and CMS using the DPE-technique. The obtained macroinitiators were then applied in a "grafting from" process for the synthesis of polyether side chains by ring-opening cationic polymerization of tetrahydrofuran (THF) and dioxolane, respectively.[11,12]

## EXPERIMENTAL

### Materials

Methyl methacrylate (MMA), n-dodecyl methacrylate (DDMA), 2-ethylhexyl acrylate (EHA) 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. Tetrahydrofuran (THF), dioxolane (DXL), dichloromethane and toluene were dried for 48 h over calcium hydride and subsequently distilled before use. Silver perchlorate was used as received and stored under argon.

## Measurements

Molecular weights and molecular weight distributions were determined using a size exclusion chromatograph Waters 510 with UV (Waters 486) and RI (Waters 410) detectors and Polymer Laboratories (PL gel 10 μm MIXED B) columns calibrated with linear polystyrene standards. $CHCl_3$ was applied as eluent. $^1$H-NMR spectra were recorded with a Bruker ARX 300 at 300K in $CDCl_3$ as solvent.



## Poly(Meth)acrylate Macroinitiators

47.5 mmol (meth)acrylate (methyl methacrylate for MI1; dodecylmethacrylate for MI2; ethyl hexylacrylate for MI3) and 3 mmol CMS were dissolved in 11 mL toluene and degassed by three freeze, pump and thaw cycles. Then 24.6 mg AIBN and 26.4 μL DPE were added to the monomer solution and the mixture was stirred at 80°C for 1 d. The resulting copolymers (yields: MI1: 4.5 g, 86.3%; MI2: 10.3 g, 82.2%; MI3: 6.0 g, 65.7%) were precipitated in 500 mL methanol, reprecipitated from $CHCl_3$ in 500 mL ethanol and dried under vacuum.

## Graftcopolymer GP1

160 mg (0.096 mmol with respect to chloride content) of MI1, 12 ml (148 mmol) THF and 40 mg (0.19 mmol) silver perchlorate were dissolved in 10 mL of dichloromethane and kept stirring at room temperature for 20 h. Afterwards, all volatile compounds were evaporated under vacuum. The resulting product was dissolved in 10 mL of chloroform, filtered, precipitated in 200 mL of methanol and dried under vacuum, yielding 370 mg polymer.

## Graftcopolymer GP2

260 mg (0.047 mmol with respect to chloride content) MI2, 10 mL (124 mmol) THF and 20 mg (0.096 mmol) silver perchlorate were dissolved in 10 mL of dichloromethane and kept stirring at room temperature for 22 h. Afterwards, the solution was filtered and precipitated in 200 mL of ethanol and dried under vacuum, yielding 380 mg polymer.

### Graftcopolymer GP3

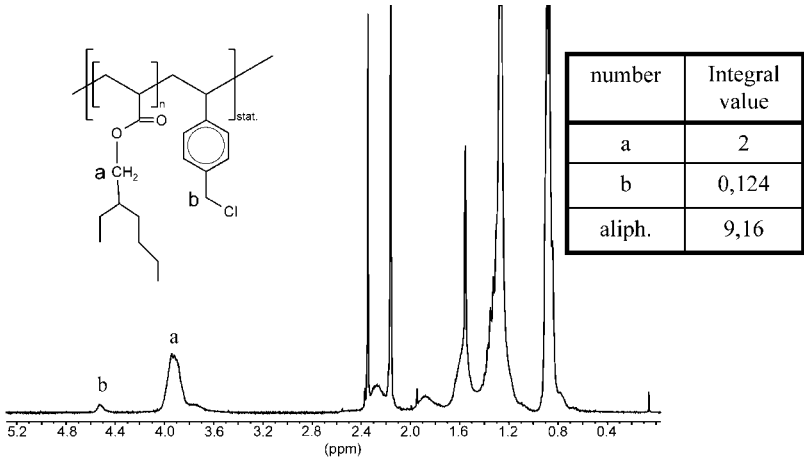
520 mg (0.095 mmol with respect to chloride content) MI2 macroinitiator, 3 mL (42.9 mmol) dioxolane (DXL) and 40 mg (0.193 mmol) silver perchlorate were dissolved in 7.5 mL of toluene and stirred at room temperature for 1 h. Afterwards, all volatile components were evaporated under vacuum. The residue was dissolved in 20 mL of chloroform, filtered, precipitated in 300 mL of ethanol and dried under vacuum, yielding 3.29 g polymer.

### Graftcopolymer GP4

480 mg (0.154 mmol with respect to chloride content) MI3 macroinitiator, 10 mL (124 mmol) THF and 60 mg (0.298 mmol) silver perchlorate were dissolved in 7.5 mL toluene and stirred at room temperature for 24 h. Afterwards all volatile compounds were evaporated under vacuum. The residue was then dissolved in 15 mL of chloroform, filtered and precipitated in 300 mL of ethanol, yielding 670 mg polymer.

### Graftcopolymer GP5

700 mg (0.224 mmol with respect to chloride content) PEHA macroinitiator, 3 mL (42.9 mmol) dioxolane (DXL) and 80 mg (0.386 mmol) silver perchlorate were dissolved in 7.5 mL toluene and stirred at room temperature for 1 h. Afterwards, all volatile components were evaporated under vacuum. The residue was dissolved in 30 mL of chloroform, filtered, precipitated in 400 mL of ethanol and dried under vacuum, yielding 2.8 g polymer.




| number | Integral value |
|---|---|
| a | 2 |
| b | 0,124 |
| aliph. | 9,16 |

***Figure 1.*** $^{1}$H-NMR spectrum of macroinitiator MI3.

*Table 1.* Characterization of the macroinitiators.

| Polymer | Yield (%) | $M_n$ | $M_w$ | MWD | Composition (NMR) |
|---|---|---|---|---|---|
| MI1 | 86.3 | 45.000 | 78.000 | 1.70 | MMA/CMS = 15 |
| MI2 | 82.2 | 69.900 | 99.900 | 1.43 | DDMA/CMS = 21 |
| MI3 | 65.7 | 38.400 | 60.400 | 1.57 | EHA/CMS = 16 |

## RESULTS AND DISCUSSION

In the first step, we synthesized a set of poly(meth)acrylate macroinitiators in the presence of DPE. According to our view[10] DPE converts the radical at the growing chain end into a dormant species and thus avoids transfer reactions with the benzyl chloride functions of CMS which has been used as a comonomer. 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 proven by $^1$H-NMR spectra, as shown for MI3 in Fig. 1.

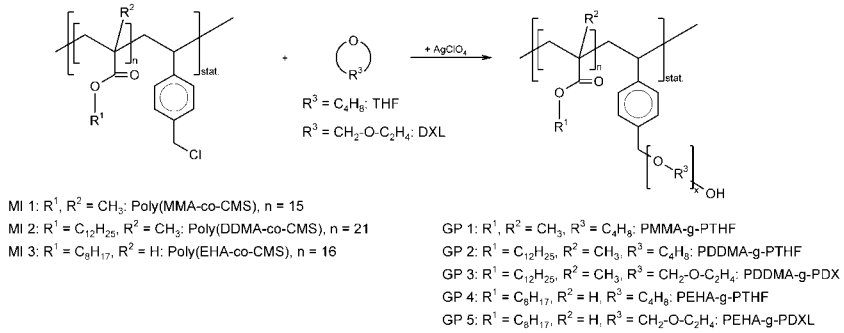
The molar masses and benzyl chloride content of these macroinitiators are shown in Table 1.

All macroinitiators synthesized proved active in the following initiation step for the ring-opening cationic polymerization of cyclic ethers using a two fold excess of silver perchlorate as the coinitiator. The initiator efficiency calculated by $^1$H-NMR ranged between 30 and 100% with respect to benzyl chloride conversion (cf. Table 2). The grafting from polymerization (cf. Sch. 1) was performed using a large excess of the cyclic ether monomer and was stopped at low conversions to avoid the formation of homo-polyethers which took place in the case of THF.

In the case of dioxolane as a monomer, the formation of homo-poly(dioxolane) could not be avoided completely, due to the very fast polymerization kinetics and the high tendency of acetal groups to act as transition agents.[13–15] However, the clear increase of molar masses observed by size exclusion chromatography prove that the graft copolymerization was successful and graft copolymers bearing PTHF and PDXL side chains, respectively could be synthesized as described. This is exemplified by the SEC curves of macroinitiator MI2 and both of its resulting grafting products are shown in Fig. 2.

*Table 2.* Characterization of the graft copolymers.

| Polymer | Initiator efficiency (%) | $M_n$ | $M_w$ | MWD | Composition (NMR) | Composition (gravimetry) |
|---|---|---|---|---|---|---|
| GP1 | 60.1 | 184.000 | 310.000 | 1.70 | MMA/THF 1/1.5 | MMA/THF 1/1.8 |
| GP2 | 100 | 105.000 | 207.000 | 1.98 | DDMA/THF 1/1.1 | DDMA/THF 1/1.6 |
| GP3 | 100 | 73.500 | 134.400 | 1.83 | DDMA/THF 1/16.8 | DDMA/DXL 1/18.4 |
| GP4 | 100 | 40.400 | 103.000 | 2.55 | EHA/THF 1/0.9 | EHA/THF 1/1.4 |
| GP5 | 30.0 | 46.100 | 72.200 | 1.59 | EHA/DXL 1/6.7 | EHA/DXL 1/7.5 |




***Scheme 1.*** Cationic grafting from polymerization.



The $^1$H-NMR spectra of MI2 and its grafting products are presented in Fig. 3.

The characterization by SEC and $^1$H-NMR of all herein described graft copolymers is summarized in Table 2.

In all cases, the composition calculated from gravimetry indicates a higher polyether content compared with the composition calculated from $^1$H-NMR spectra. All graft copolymers are of elastomeric type which makes it difficult to dry them completely. Thus, the overestimation of the conversion is most likely due to residual solvent in the polymers.

All graft copolymers show a certain increase of molar mass compared with the molar masses of the respective macroinitiators. As the SEC was only calibrated by linear polystyrene the resulting molar masses were not used to calculate chain lengths of side chains. It is well known that the random coils formed by branched polymers are more compact than the ones of linear polymers and thus, the molar masses of branched polymers are generally underestimated by such SEC. By this, the increase in molar mass can only regarded as a qualitative prove for the formation of graft copolymers.

With all graft copolymers a slight increase in the molecular weight distribution as compared with the respective macroinitiator is observed. However, with one exception

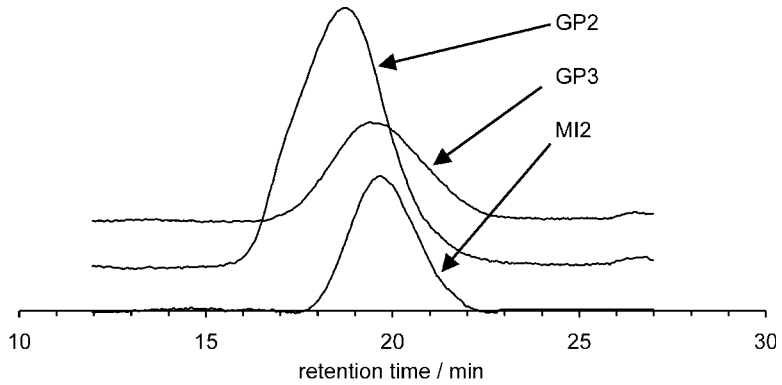



***Figure 2.*** SEC curves of macroinitiator MI2, GP2, and GP3.

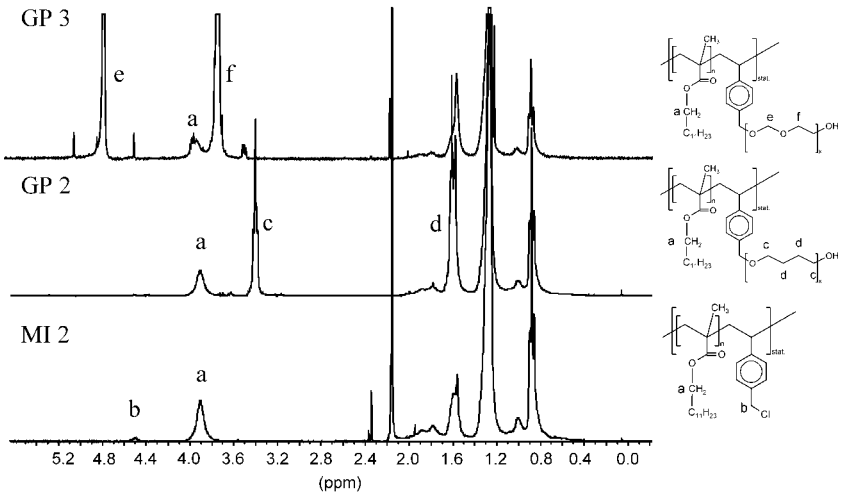



***Figure 3.*** $^{1}$H-NMR spectra of macroinitiator MI2, GP2, and GP3.

the MWDs are all below 2.0 and thus, rather narrow. Together with the observation that in the case of the polymerization of THF no homo-PTHF was detected by SEC, this indicates that the polymerization occurs in a controlled manner. One possible reason for this could be that the ester groups in the (meth)acrylate backbone polymer could act as a kind of controlling agent stabilizing the cation at the growing chain end.[16,17]

In the case of dioxolane as monomer, the loss of control of the polymerization is due to the acetal groups acting as transfer agents.[13] The amounts of homo-PDXL and graft copolymer could not be specified because of similar solubility of both products most likely due to the PDXL side chains of the graft copolymer. However, the SEC indicates only small amounts of homo-PDXL as the signal of the graft copolymer is the most intensive one. A more precise characterization of the composition of the polymerization product requires the use of preparative SEC and will be performed soon.

## CONCLUSION

In this paper we presented a facile one step synthesis 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, EHA 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 ring-opening cationic polymerization of cyclic ethers such as THF and dioxolane. By this, it is possible to prepare graft copolymers having (meth)acrylate backbones and polyether side chains by combining cationic and radical polymerization. In the case of THF, the formation of homo-PTHF could be avoided indicating the absence of transition reactions. This polymerization control is likely to be due to the ester groups in

the (meth)acrylate backbone which can stabilize the cation at the growing chain end and has been observed in the cationic polymerization of isobutylene, before.[16,17] The MWDs observed are low indicating good polymerization control, even in the case of dioxolane as the monomer, where the formation of homo-PDXL could not be avoided completely.

We were able to show a new facile two step polymerization process leading to graft copolymers having (meth)acrylate backbones and polyether side chains. Further experiments will focus on improving the control of the polymerization of dioxolane. For further investigations on the structure of the resulting graft copolymers, light scattering methods will be applied to identify the absolute molar masses, degree of branching and the length of the side chains. Furthermore, the synthesis of graft copolymers of well-defined composition needs a more detailed investigation of the polymerization kinetics, which still has to be undertaken.



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