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Synthesis of PTHF-Grafted PMMA Based on the Reaction of Methyl Esters with Quaternary Ammonium Salts

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ABSTRACT: A new synthetic procedure is proposed to graft polymer chains onto poly(methyl methacrylate) based on the reaction of methyl esters with quaternary ammonium salts (MEQA reaction) under nonprotic conditions. Mechanistic insight into the MEQA reaction has been given by performing model reactions, for example with methyl benzoate and the *N*-butylammonium salt of 1,4-diazabicyclo[2.2.2]octane. This reaction has been used to graft poly(tetrahydrofuran) with a 1,4-diazabicyclo[2.2.2]octane end group, synthesized from living cationic ring-opening polymerization, on poly(methyl methacrylate) by simply heating the reaction mixture of both components in 1,2-dichlorobenzene as solvent. GPC and NMR analysis demonstrated high grafting yields. The formation of the grafted structures was further evidenced by a comparative DSC study of the crystallization behavior of the starting and end products.

Introduction

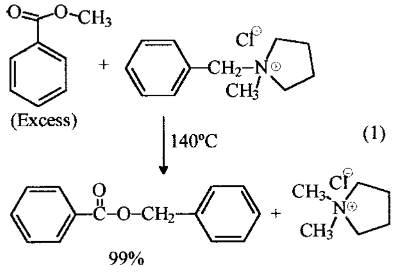
Contrary to the three-membered aziridines[1] and four-membered azetidines,[2] which can be polymerized via cationic ring-opening mechanism, the five-membered pyrrolidine and its derivatives are unpolymerizable due to the lack of ring strain. Pyrrolidine is the byproduct in the production of 1,4-diaminobutane, one of the monomers for nylon-4,6. During the exploration of the potential application of pyrrolidine and its derivatives in polymeric systems,[3−5] we found that the reaction between methyl benzoate (excess) and *N*-benzyl-*N*-methylpyrrolidinium chloride (BMPC) leads to the quantitative formation of benzyl benzoate and *N*,*N*-dimethylpyrrolidinium chloride (Scheme 1).

The transesterification reaction between methyl ester and quaternary ammonium salt (MEQA reaction) has been reported earlier by Bencivengo and San Filippo.[6] For example, the reaction of tetrabutylammonium chloride (TBAC) with methyl benzoate (1/2 molar ratio) at 140 °C after 24 h leads to 34% of butyl benzoate. It provided a synthetically satisfactory method for systems where the presence of acid-sensitive functionalities preclude classical procedures for transesterification. Mechanistically, the authors believed that the MEQA reaction occurred in a way outlined in Scheme 2. Thus, reaction 2 defines the well-known *O*-alkyl cleavage of a methyl ester by nucleophilic displacement[7,8] while reaction 3 represents the alkylation of a carboxylate anion by an onium ion.

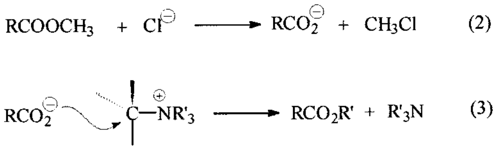
By application of this MEQA reaction onto polymeric systems, we were able to synthesize new self-cross-linkable materials based on copolymers of *N*-methyl-*N*-vinylbenzylpyrrolidinium halide and methyl methacrylate (MMA).[4] The same strategy has been followed to selectively cross-link the PMMA microdomains of triblock copolymers PMMA-*b*-poly(alkyl acrylate)-*b*-PMMA in order to improve the mechanical properties of acrylic thermoplastic elastomers.[5]

In recent years, great attention has been paid to graft copolymers because of their unique molecular architecture and morphologies and their increasing number of applications.[9] They are used to prepare compatibilizers for polymer blends,[10] as membranes for the separation of gases and liquids,[11] as drug delivery systems,[12] and as thermoplastic elastomers.[13] Most graft copolymers are synthesized by copolymerizing a monomer and macromonomers that contain polymerizable functional groups at their terminus.[14] Other techniques include irradiation-induced polymerization,[15] ring-opening metathesis polymerization,[16] polycondensation reaction,[17] iniferter-induced polymerization,[18] and combined living polymerizations.[19]

Scheme 1. Reaction between Methyl Benzoate and *N*-Benzyl-*N*-methylpyrrolidinium Chloride



Scheme 2. MEQA Reaction Pathway According to Bencivengo and San Filippo



The synthesis of PMMA-*g*-poly(tetrahydrofuran) (PTHF), obtained with the macromonomer technique, has been reported previously by Hepuzer et al.[20] Tezuka et al. also made polyTHF-containing graft copolymers using an ion-coupling reaction of monotelechelic polyTHF's, having various cyclic onium salt groups, with poly(styrene-*co*-sodium acrylate).[21] However, nothing has been reported yet on the grafting of PMMA by reaction of end group functionalized polymers with the methyl ester groups of PMMA. In this work, the MEQA reaction was applied to graft PTHF onto a PMMA backbone.

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Table 1. Molecular Weight Characteristics of the PMMA and PTHF-DABCO Samples As Measured by GPC

PMMA	$M_n \times 10^{-4}$	M_w/M_n	PTHF-DABCO[a]	$M_n \times 10^{-3}$	M_w/M_n
1	0.8	1.8	1	2.2	1.1
2	1.8	2.0	2	4.0	1.2
3	4.0	1.8	3	8.0	1.2
4	14	4.0			

[a] Details on the synthetic conditions can be found in the experimental part.

Table 2. Decomposition Temperature of Some Quaternary Ammonium Salts and Characteristics of Their Reactions with Methyl Benzoate at 145 °C (1:9 Molar Ratio)

sample	compd[a]	decomp temp (°C)[b]	MEQA reaction time (h)	MEQA reaction yield (%)[c]
1	TBAC	163	24	95
2	EMPC	254	24	0
3	BMPC	187	15	99
4	TMBAC	215	4	5
5	TEBAC	183	4	20
6	TBBAC	154	4	50
7	TBBAH	>300	24	0

[a] TBAC, tetrabutylammonium chloride; EMPC, *N*-ethyl-*N*-methylpyrrolidinium chloride; BMPC, *N*-benzyl-*N*-methylpyrrolidinium chloride; TMBAC, trimethylbenzylammonium chloride; TEBAC, triethylbenzylammonium chloride; TBBAC, tributylbenzylammonium chloride; TBBAH, tributylbenzylammonium hexafluoroantimonate. [b] Measured by TGA. [c] Calculated by ^{1}H NMR spectra of the alkyl benzoate(s) in the reaction mixture.

The cationic ring-opening polymerization (CROP) of tetrahydrofuran (THF) has been well established for decades.[22] By addition of a nucleophile to the solution of living polymers, one can easily end-cap PTHF with various functional groups.[21,23,24] We used a similar method to end-cap PTHF with 1,4-diazabicyclo[2.2.2]-octane.

The grafting reactions have been studied using model compounds, nuclear magnetic resonance, gel permeation chromatography, and differential scanning calorimetry.

Experimental Section

Materials. 1,4-Diazabicyclo[2.2.2]octane (DABCO, 98%), 1-chlorobutane (99%), methyl benzoate (99%), tributylamine (99%), 1-methylpyrrolidine (97%), chloroethane (99.7+%), benzyl chloride (97%), trimethylamine (99%), triethylamine (99%), methyl trifluoromethanesulfonate (methyl triflate, 99+%), tetrahydrofuran (THF, 99.5+%), anhydrous 1,2-dichlorobenzene (99%), anhydrous dichloromethane (99+%), and anhydrous diethyl ether (99+%) were purchased from Aldrich. Unless being mentioned, they were used as received.

THF was dried with CaH_2 under reflux for 24 h and distilled under N_2 atmosphere. It was further purified by refluxing over the deep purple sodium benzophenone complex. The dried THF was freshly distilled prior to use. DABCO was first purified by recrystallization in water. After drying under vacuum for 24 h, DABCO was further dried with molecular sieves (A4) in dried THF solution. Methyl triflate (bp 94−99 °C) was purified by distillation under argon atmosphere. PMMAs (Aldrich) with various molecular weights (Table 1) were used as received.

Synthesis of Quaternary Ammonium Salts. The quaternary ammonium salts with chloride as counteranion, e.g., *N*-butylammonium salt of DABCO, and those listed in Table 2 (TBAC, EMPC, BMPC, TEBAC, TBBAC) were synthesized from the corresponding tertiary amines and alkyl chlorides. As an example, the synthesis of the *N*-butylammonium salt of DABCO will be described in more detail. A solution of DABCO (6.72 g, 0.06 mol) was prepared in diethyl ether (30.0 mL). At room temperature, 1-chlorobutane (2.78 g, 0.03 mol) was added dropwise to the DABCO solution while stirring. After 48 h reaction, the insoluble quaternary ammonium salt (4.90 g, 80% yield) was isolated by filtration. The crude product was dissolved in anhydrous dichloromethane, precipitated in anhydrous diethyl ether, and separated by filtration. This procedure was repeated three times. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.05 (t, 3H, $-CH_3$); 1.45 (m, 2H, $-CH_2CH_3$); 1.80 (m, 2H, $-CH_2$-CH_2CH_3); 3.20 (m, 6H, $=N-CH_2-CH_2N^+\equiv$); 3.50−3.60 (m, 8H, $\equiv N^+-CH_2-$). The purified ammonium salt was stored at −18 °C. Fresh *N*-butylammonium salt of DABCO was finally dried under vacuum prior to use.

Preparation of a SbF_6^- Type Ion-Exchange Resin. A Cl^- type ion-exchange resin (Dowex 1 × 2−100, Aldrich), put in a column (300 × 25), was washed with saturated $NaSbF_6$ water solution, until no Cl^- could be detected in the eluted solution (via AgCl). The resin was further washed with deionized water to remove the excess of $NaSbF_6$.

Synthesis of Tributyl Benzylammonium Hexafluoroantimonate (TBBAH). Tributyl benzylammonium chloride solution (TBBAC, 0.1 M in H_2O) was passed through a column filled with SbF_6^- type ion-exchange resin. TBBAH was collected by removing water under reduced pressure (85% yield).

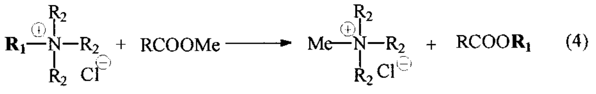
Synthesis of DABCO-Terminated PTHF. In a two-neck flask (flame-dried) fitted with a magnetic stirrer, an inlet for dry nitrogen, and a rubber septum, 40.0 mL (0.55 mol) of THF was introduced. The polymerization was initiated with 0.11 mL (0.99 mmol) of methyl triflate at 25 °C. After a polymerization time of respectively 15, 30, and 60 min at 25 °C, with respect to PTHF samples 1, 2, and 3 in Table 1, 1.05 g (9.4 mmol) of DABCO, which was dissolved in 15 mL of THF, was added for termination. The PTHF solution was first condensed to high concentration under reduced pressure and then precipitated in cold water (0 °C) saturated with sodium chloride. This procedure was repeated three times to ensure that the $CF_3SO_3^-$ anions were completely replaced by Cl^- anions. The precipitated polymers were separated by filtration and thoroughly washed with water. They were finally dried under vacuum at room temperature (yield: 60−80%). Three DABCO-terminated PTHF samples have been synthesized with M_n(GPC) in the range of (2.2−8.0) × 10^3 and M_w/M_n equal to 1.1−1.2 (Table 1).

Model Reaction of *N*-Butylammonium Salt of DABCO with Methyl Benzoate. The *N*-butylammonium salt of DABCO (0.20 g, 0.01 mol) and 12.25 g (0.09 mol) of methyl benzoate (MB) were mixed in a sealed tube under N_2 atmosphere. The reaction was carried out for 6 h at 145 °C with magnetic stirring. The reaction products and yield were obtained from the NMR analysis of the crude reaction mixture (see results section).

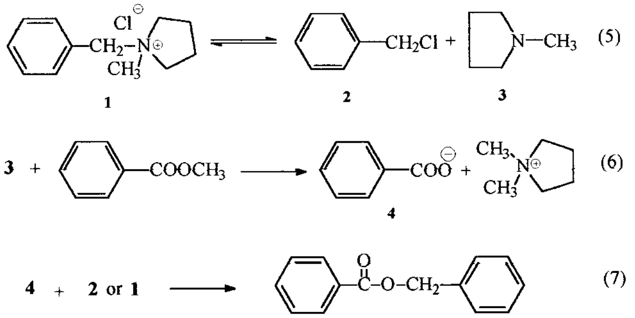
Grafting of PTHF onto PMMA. In a typical procedure, 0.6 g of DABCO-terminated PTHF ($M_n = 2.2 \times 10^3$) and 0.4 g of PMMA ($M_n = 1.8 \times 10^4$) were dissolved in 4 g of 1,2-dichlorobenzene. The grafting reaction was carried out at 170 °C under N_2 atmosphere. A grafting yield of about 60% was calculated from the comparison of the integration ratios of respectively the newly formed ester groups (2H, 4.0−4.2 ppm) and the end groups of DABCO-terminated PTHF (8H, 3.5−3.6 ppm) to the PTHF ether group (3.4 ppm) in the NMR spectra (see Figures 3 and 5).

Analysis. Molecular weight and molecular weight distribution were obtained through gel permeation chromatography (Waters apparatus) working at room temperature with chloroform as eluent at a flow rate of 1 mL min^{-1}. The apparatus was equipped with a 100, 10^3, and 10^4 Å column (Polymer Laboratories) and a differential refractive index detector (Melz). The results were analyzed by using the Waters Maxima 820 software. Universal calibration has been used for the determination of the absolute molecular weights of the PTHF samples. The molecular weights of the PMMA samples are relative to polystyrene standards. ^{1}H NMR analysis was performed on a 360 MHz Bruker FT-NMR spectrometer. DSC measurements were carried out on Perkin-Elmer DSC-7 at a heating rate of 10 °C min^{-1}. TGA analyses were performed under nitrogen atmosphere on a Polymer Laboratory TGA PL-1000 at a heating rate of 2 °C min^{-1}.

Scheme 3. Reactants and Reaction Products of MEQA Reaction



Scheme 4. New Proposal for MEQA Reaction Pathway

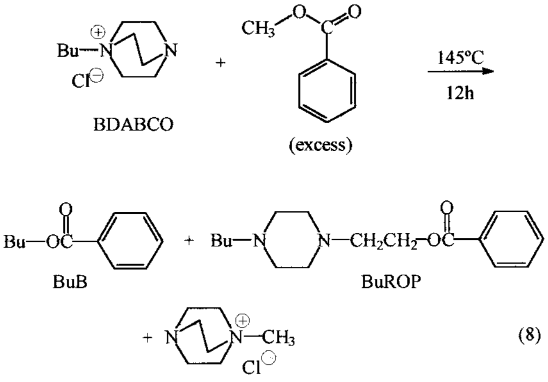


Results and Discussion

Mechanism of the MEQA Reaction and Model Reactions. The idea of using the MEQA reaction to graft PTHF onto PMMA comes from the fact that the MEQA reaction is a coupling process of a molecule carrying a quaternary ammonium salt with a methyl ester (Scheme 3). The new alkyl ester bond is usually formed with the least stable substituent (R_1), e.g., benzyl group, from the quaternary ammonium salt. A nonbenzylic substituted quaternary ammonium salt is also able to undergo the MEQA reaction as long as it has a relatively low decomposition temperature.[3,6] Table 2 reports the thermal stability of some quaternary ammonium salts with chloride and hexafluoroantimonate (SbF_6^-) counterions and the yields of the corresponding MEQA reaction with methyl benzoate at 145 °C.

The reactivity of the MEQA reaction is indeed related to the thermal stability of the quaternary ammonium salt in the sense that a lower decomposition temperature of the quaternary ammonium salt results in a higher yield of the MEQA reaction. The thermal stability of the quaternary ammonium salt is influenced by the alkyl substituents and counteranions (Table 2). The decomposition temperature (T) decreases with the bulkiness of the alkyl groups (e.g., $T_{\mathrm{MBAC}} > T_{\mathrm{TEBAC}} > T_{\mathrm{TBBAC}}$) and with the nucleophilicity of the counteranion ($T_{\mathrm{TBBAH}} > T_{\mathrm{TBBAC}}$). If a tertiary amine (e.g., 1 equiv of tributylamine) is added to the nonreactive quaternary ammonium salt tributylbenzylammonium hexafluoroantimonate (T_{BBAH}) (run 7 in Table 2), 99% of benzyl benzoate is found after 12 h at 145 °C, which indicates that the tertiary amine is a nucleophile for ester cleavage. Similarly, Miles and Parish reported earlier that hindered methyl esters could be cleaved in 94% yield by reaction with 1,5-diazabicyclo[4.3.0]non-5-ene after 6 h in boiling xylene.[25,26] Therefore, we propose the mechanism in Scheme 4 for the MEQA reaction without disregarding the possibility of Bencivengo and San Filippo's explanation (Scheme 2). In this example, the MEQA reaction starts from the decomposition of the quaternary ammonium salt *N*-benzyl-*N*-methylpyrrolidinium chloride (BMPC, 1) into the tertiary amine (step 5), which in turn cleaves the methyl ester (benzyl benzoate) with the intermediate formation of an ammonium benzoate salt (step 6). The benzoate anion then attacks the benzylic carbon of either benzyl chloride or BMPC and eventually leads to benzyl benzoate (step 7).

Scheme 5. Model Reaction Reaction of the *N*-Butylammonium Salt of DABCO (BDABCO) with Methyl Benzoate



In the polymeric system, R_1 (Scheme 3) is the PTHF chain and R is the PMMA backbone; one would desire the $\mathrm{PTHF{-}N^+{\equiv}}$ bond to be the less stable one in the $\mathrm{(PTHF)N^+(R_3)}$ quaternary ammonium salt in order to favor the grafting reaction. On the other hand, one would also desire a reasonable temperature (e.g., < 200 °C) for the grafting reaction in order to avoid decomposition of the PTHF grafts. These two requirements conflict in the selection of the R_2 group. Because R_1 is a PTHF chain (similar to butyl group) instead of a benzyl group, bulky R_2 groups would be necessary to lower the decomposition temperature of the end group of the quaternary ammonium salt, which however makes R_1 and R_2 indistinguishable and would lead to uncontrollable coupling reactions with all the R groups. To circumvent this problem, we selected 1,4-diazabicyclo[2.2.2]octane (DABCO) as the end-capper for living PTHF, because in that case the coupling reaction with the R_2 group (thus the ring-opening reaction) will also result in a grafted polymer. We started our investigation with the model reaction of the *N*-butylammonium salt of DABCO (BDABCO) with methyl benzoate (Scheme 5). BDABCO was chosen because its butyl group is similar to the PTHF unit. Methyl benzoate was selected because of its high boiling point (198 °C) suitable for the MEQA reaction (>140 °C) and its simple structure that facilitates NMR analysis. After heating BDABCO in the presence of an excess of methyl benzoate at 145 °C for 6 h, two new ester compounds ($\mathrm{COOC}H_2$ at 4.3 and 4.4 ppm) were found by ^{1}H NMR (Figure 1) besides the original methyl benzoate ($\mathrm{COOC}H_3$, 3.9 ppm).

Butyl benzoate (BuB), as one of the products, is formed by the attack of the benzoate anion on the butyl carbon of either BDABCO or butyl chloride (cf. step 7, Scheme 4). The other one, a ring-opening product (BuROP), is generated by attack of the benzoate anion on the ethylene carbon adjacent to the cation.

After acidification of the liquid part of the reaction mixture with diluted HCl solution, methyl benzoate and BuB were removed by extraction with diethyl ether. Pure BuROP was recovered by the deprotonation of the ammonium salt with K_2CO_3 (Figure 2).

Using ^{1}H NMR, 42% of BuB and 49% of BuROP were formed with respect to the original BDABCO and methyl benzoate. Thus, the MEQA reaction is suitable for the coupling reaction of a methyl ester with a molecule carrying a BDABCO unit.

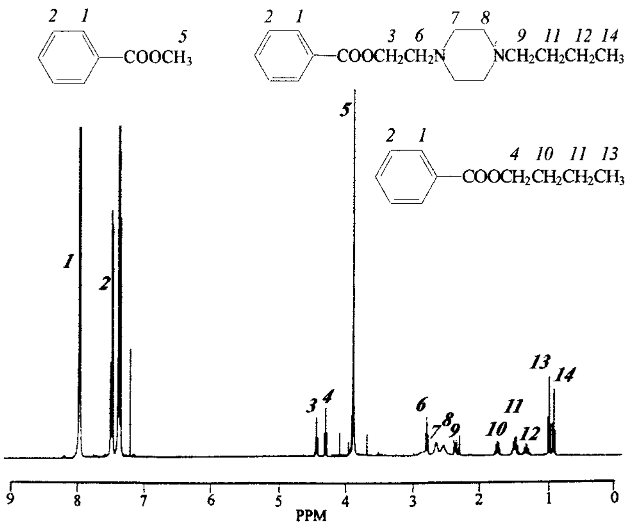


Figure 1. ^{1}H NMR spectrum of the reaction mixture (liquid part) of BDABCO and methyl benzoate after 12 h at 145 °C.

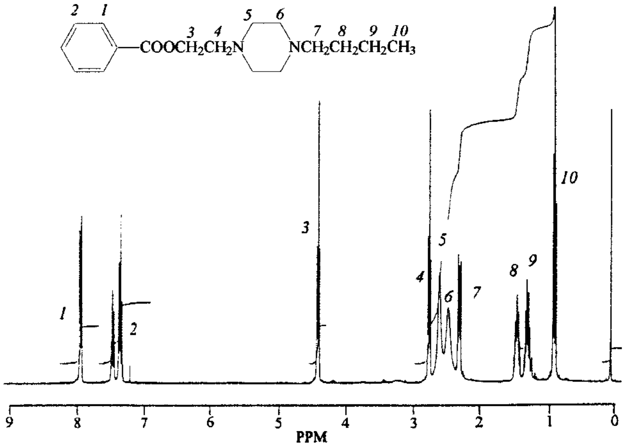
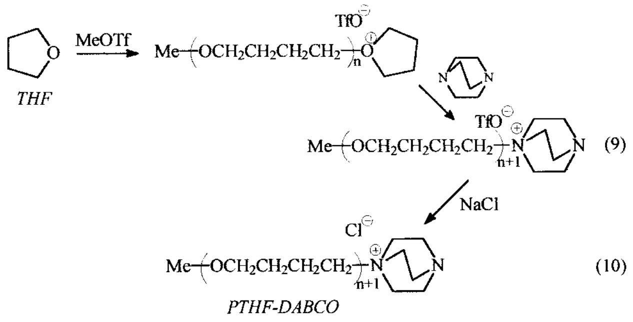


Figure 2. ^{1}H NMR spectrum of BuROP.

Synthesis of DABCO-Functionalized PTHF. The monofunctionalized PTHFs used in this work were synthesized by the cationic ring-opening polymerization (CROP) of THF, which leads to polymers with low polydispersity and predictable molecular weights if the polymerization is carried out in bulk and if the monomer to initiator concentration ratio is properly chosen.[27] Methyl triflate was used as the initiator and DABCO as the end-capping agent. It should be noted that the CROP of DABCO is only possible under more drastic conditions, which means that the reaction of living PTHF with the excess amount of DABCO at room temperature only leads to DABCO-terminated PTHF.[28] It is also interesting to note that no chain coupling of PTHF with the difunctional BDABCO was observed from the GPC traces (not shown here). In addition to the use of the excess of DABCO, we believe that the second quaternization of PTHF-DABCO should be more difficult. Finally, the triflate counterions were replaced by chloride anions (Scheme 6).

Figure 3 shows the ^{1}H NMR spectrum of a DABCO-terminated PTHF (PTHF-DABCO). The signals corresponding to the end groups and to the initiator groups are clearly visible for low molecular weights of the polymers. A molecular weight (M_n) of 2×10^3 g mol^{-1} was calculated from the integration ratio of the signals 1 and 5. This is in good agreement with the molecular weight obtained by GPC ($M_n = 2.2 \times 10^3$ g mol^{-1}).

Scheme 6. Synthesis of Monofunctionalized PTHF with DABCO End Group



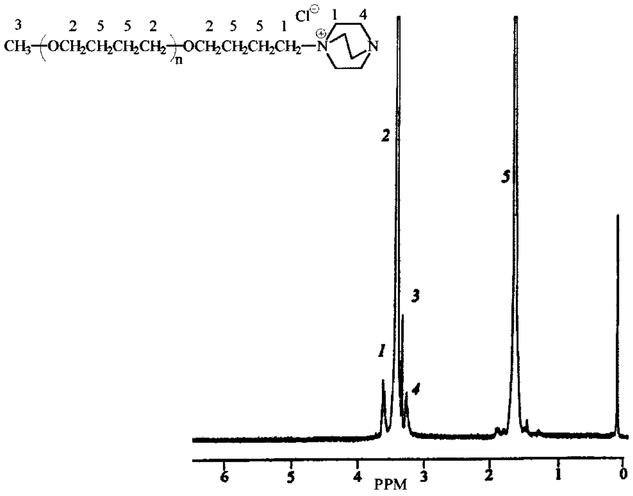
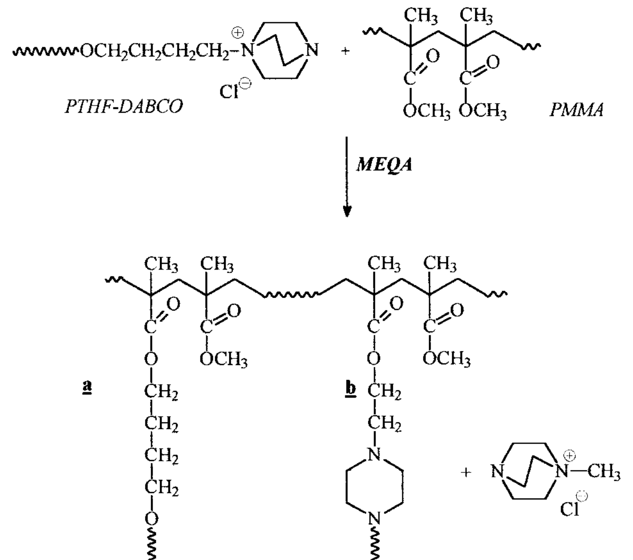


Figure 3. ^{1}H NMR spectrum of PTHF-DABCO1.

Scheme 7. Schematic Presentation of Grafting Reaction of PTHF-DABCO onto PMMA by Means of MEQA Reaction



The anion-exchange procedure from triflate to chloride was accomplished by precipitating the polymer solution into NaCl saturated water. In this study, three PTHF-DABCOs were synthesized with molecular weights ranging from 2.2×10^3 to 8.0×10^3 g mol^{-1} and with M_w/M_n equal to 1.1−1.2.

Grafting of PTHF-DABCO onto PMMA by MEQA Reaction. Scheme 7 outlines the grafting reaction of PTHF-DABCO onto PMMA. The first attempt of the

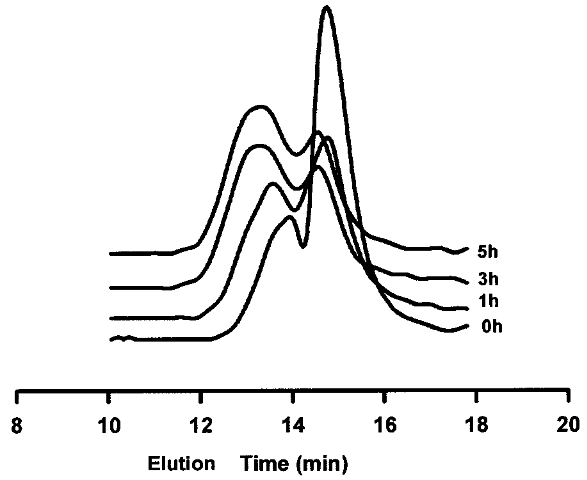


Figure 4. GPC traces at different reaction times for the grafting reaction of PTHF1/PMMA1 in 1,2-dichlorobenzene (12/8/80) at 155 °C.

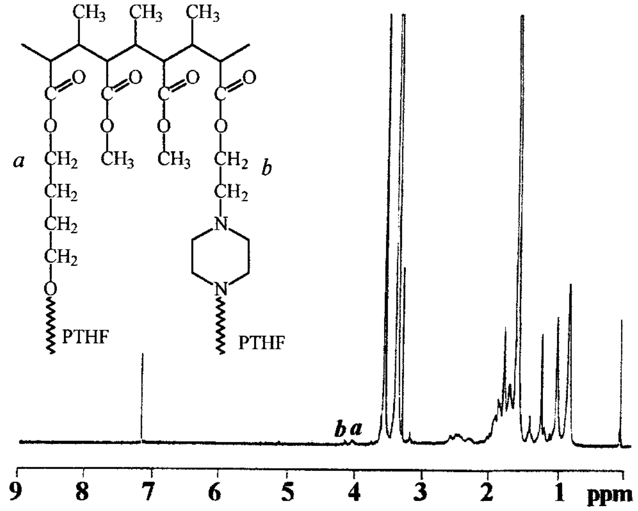


Figure 5. ^{1}H NMR spectrum of PMMA1-*g*-PTHF1.

grafting reaction was carried out in bulk with a solvent-cast film (from CH_2Cl_2) of PTHF-DABCO1 and PMMA3 (6/4). After 8 h at 150 °C, no molecular weight changes (GPC) or additional NMR signals were detected in the reaction mixture, which indicated the absence of the MEQA reaction. This could be explained either by the poor miscibility of PTHF with PMMA or by the self-association of the polar ionic end groups in the apolar PTHF matrix. Such a microphase separation of the PTHF-DABCO itself would make the DABCO groups inaccessible to the ester functions of PMMA. Therefore, further attempts were performed in a homogeneous system with 1,2-dichlorobenzene as solvent. Figure 4 shows the GPC traces of the reaction mixture of PTHF-DABCO1/PMMA1/solvent (12/8/80) at different reaction stages.

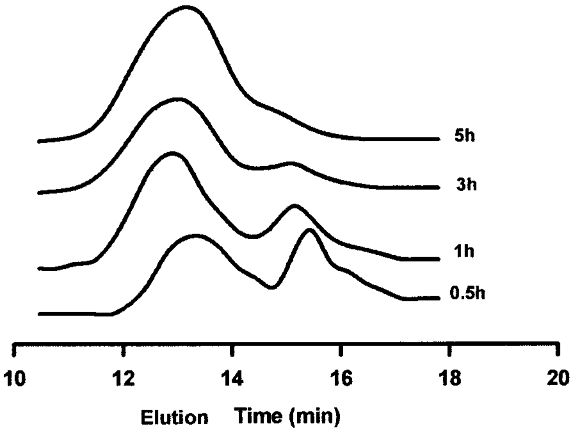


Figure 6. GPC traces at different reaction times for the grafting reaction of PTHF1/PMMA2 in 1,2-dichlorobenzene (12/8/80) at 155 °C.

The starting trace was a combination of narrow disperse PTHF-DABCO and polydisperse homo-PMMA. During the reaction, the PMMA peak shifted to the high molecular weight region, whereas the PTHF peak remained essentially unchanged. Furthermore, the ratio of the peak areas respectively covered by PMMA and PTHF-DABCO was increasing. Finally, the ^{1}H NMR spectrum (Figure 5) reveals two additional signals, appearing at 4.1 and 4.2 ppm, and a significant reduction of the peak at 3.3 ppm $(-\mathit{CH}_2\mathrm{N}{=})$ after 5 h reaction time.

On the basis of the model reaction of BDABCO with methyl benzoate (Scheme 5, Figure 1), these two new signals were assigned to the ester bonds attached to the grafted PTHF chains. The reduction of the peak at 3.3 ppm is an evidence for the consumption of the DABCO end group on the functionalized PTHF chains. The NMR analysis revealed that the total grafting yield was about 60%.

Influence of the MW on the Grafting Reaction. Figure 6 shows the GPC traces of the grafting reaction for PTHF-DABCO1/PMMA2/solvent (12/8/80) at 155 °C. In the first hour of the reaction, the PMMA trace shifted to high molecular weight region, which indicated the formation of the grafted polymers. However, longer reaction times resulted again in an increase of the retention time of the PMMA signal, i.e., lower molecular weights, although in the meantime the PTHF was still being consumed (evidenced by the peak area ratio). As this observation could be due to the degradation of the PTHF grafts, the thermal stability of PTHF-DABCO, PMMA, and PMMA-*g*-PTHF (purified product of PMMA1-*g*-PTHF1) has been investigated by means of TGA and GPC. Below 300 °C, no degradation reaction was detected, which excluded the degradation hypothesis. On the other hand, the apparent molecular weight of a branched polymer, as measured by GPC, may be significantly different from its absolute value, owing to the lower hydrodynamic volume. When the nature of the branched polymer is unlike the backbone polymer, the hydrodynamic volume of the grafted polymer vary with the solution medium and branch number. In the reaction of PTHF-DABCO1 with various PMMAs, the grafting yields, calculated from the NMR spectra, were essentially the same (50−70%), which results in a higher number of branches per PMMA chain for increasing molecular weights. Therefore, we speculate that the highly branched PMMA-*g*-PTHF copolymer may exist in a condensed coil structure in chloroform (GPC eluent), leading to a decrease in hydrodynamic volume. During the grafting reaction with the high molecular weight PMMA sample (PMMA4), the apparent molecular weight decreased immediately after the start of the reaction (curve 4, Figure 7).

The grafting yield depends much on the molecular weight of the PTHF-DABCO chains. Higher molecular weights of the PTHF result in lower concentrations of

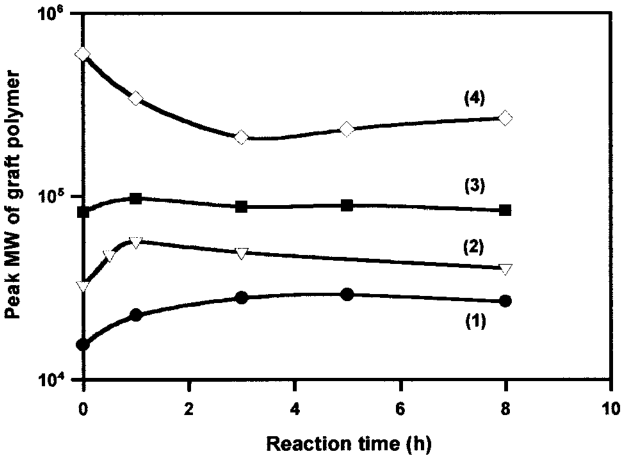


Figure 7. Influence of the molecular weight of PMMA on the apparent molecular weight (left peak maximum in GPC spectrum) of the graft copolymers poly(MMA-*g*-THF1) as a function of reaction time: (1) poly(MMA1-*g*-THF1); (2) poly(MMA2-*g*-THF1); (3) poly(MMA3-*g*-THF1); (4) poly(MMA4-*g*-THF1).

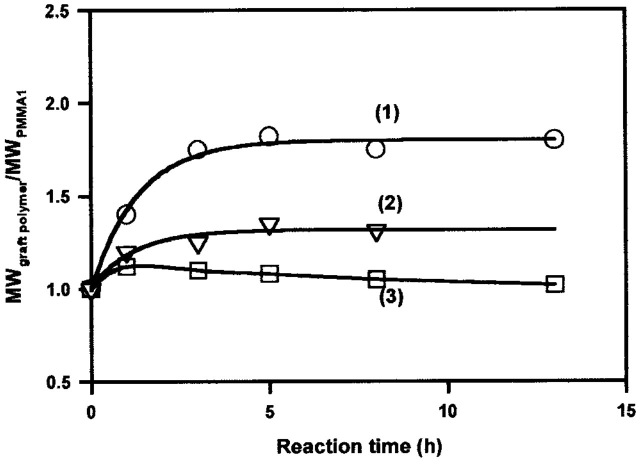


Figure 8. Influence of the molecular weight of PTHF on the normalized apparent molecular weight (GPC) of the graft copolymers poly(MMA1-*g*-THF) as a function of reaction time: (1) poly(MMA1-*g*-THF1); (2) poly(MMA1-*g*-THF2); (3) poly(MMA1-*g*-THF3).

end groups, which lowered the grafting efficiency. In Figure 8, the molecular weight increase of PMMA1-*g*-PTHF, as measured by GPC, is plotted as a function of reaction time for different molecular weights of the PTHF-DABCO chains.

Additional Evidence for Grafting from DSC Measurements. The copolymer PMMA2-*g*-PTHF1 has been fractionated by preparative GPC from the mixture after 5 h at 155 °C (ca. 45 wt % PTHF by NMR). A transition at −78 °C was found by DSC analysis, which is assigned to the glass transition temperature (T_g) of the amorphous PTHF domains. At temperatures above the melting point of the crystalline PTHF fraction and below the T_g of PMMA (105 °C), another broad transition (45−100 °C) was observed. The presence of this transition can be explained by the fact that the PTHF (with low MW) above its melting point is weakly miscible with PMMA, thus broadening the T_g of the PMMA-rich domains.

The melting behavior of the PTHF segments in the graft copolymer (sample 5) has been compared to several other references (Table 3). As reported in Table 3, PTHF1-DABCO has a melting point at 29 °C and a degree of crystallinity equal to 50%. Sample 2 is the same compound after heating at 155 °C for 8 h. Its melting behavior is identical to that of sample 1, revealing that the reaction conditions of the MEQA reaction do not affect the PTHF-DABCO chains. Blends of samples 1 or 2 with PMMA2 (PMMA/PTHF = 4/6) (samples 3 and 4) showed slight decreases of the PTHF heat of fusion, which can be ascribed to the retarded crystallinity process of PTHF in the PMMA matrix. In sharp contrast, the crystallinity of PMMA2-*g*-PTHF1 (sample 5) was negligible. The formation of a grafted structure, which results in the anchorage of the PTHF chains onto the PMMA backbones, clearly prevents the PTHF domains from crystallizing.

Table 3. Melting Point and Heat of Fusion of PTHF Segments in DABCO-Functionalized Polymer, PMMA/PTHF Polymer Blends, and PMMA-*g*-PTHF Graft Copolymer[a]

run	sample name	melting temp (°C)	heat of fusion (J/g)[b]	degree of crystallinity (%)[c]
1	PTHF1	29	84	50
2	PTHF1 after heating 8 h	29	81	49
3	PTHF1 + PMMA2	27	68	41
4	sample 2 + PMMA2	27	71	43
5	PMMA2-*g*-PTHF1	27	0.1	0.1

[a] All the samples were preheated at 120 °C for 5 min, cooled to 10 °C (crystallization temperature) at 10 °C/min, kept at that temperature for 5 min, and then cooled to −10 °C. The second heating was from −10 to 50 °C with a heat rate of 10 °C/min. The polymer blends were prepared via solvent-casting from CH_2Cl_2. [b] Heat of fusion per gram of PTHF. [c] Enthalpy of melting of 100% crystalline PTHF = 167 J/g according to: Kretz, M.; Meurer B.; Lotz, B.; Weill, G. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1671.

Conclusion

The reaction of *N*-butylammonium salt of DABCO with methyl benzoate has been used as a model for the grafting reaction of DABCO-terminated PTHF onto PMMA chains. This reaction was efficient in the coupling with a methyl ester at temperatures above 145 °C (MEQA reaction). DABCO-functionalized PTHF has been prepared by living cationic ring-opening polymerization and grafted to PMMA in high yields based on the MEQA reaction. The hydrodynamic volume of the graft copolymers was found to be sensitive to the molecular weight of PMMA and PTHF and to the degree of branching. In the grafted copolymers, the crystallization of the PTHF segments is completely inhibited.

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