Synthesis of well-defined poly(alkyl methacrylate)-*graft*-polylactone by sequential living polymerization

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SUMMARY: A novel combination of living polymerization reactions has been proposed for the controlled synthesis of poly(alkyl methacrylate)-*graft*-polylactones. This strategy relies upon the sequential living polymerization of alkyl methacrylates and aliphatic lactones, with an intermediate chemical transformation for shifting from the first mechanism to the second one. In the first step, an alkyl methacrylate (methyl and butyl) is copolymerized with 2-trimethylsiloxyethyl methacrylate (TMSEMA). This living anionic polymerization is initiated with diphenylhexyllithium(DPHLi) in the presence of a μ-ligand, lithium chloride, in THF at $-78\,^{\circ}$C. The trimethylsiloxy groups are then hydrolyzed with release of hydroxyl groups which are reacted with triethylaluminum in order to form a multifunctional macroinitiator of the Al alkoxide type. The second step consists of the ring opening polymerization (ROP) of aliphatic lactones (ε-caprolactone, δ-valerolactone and 1,4,8-trioxaspiro[4.6]-9-undecanone (TOSUO)) with the formation of novel graft copolymers. As a result of the livingness of both the anionic and the ROP polymerization steps, the molecular weight of both the main backbone and the grafts is predictable, the apparent polydispersity is narrow ($\overline{M}_w/\overline{M}_n$ from 1.05 to 1.30) and the grafting density can be controlled being dependent on the distribution of the hydroxyl groups within the precursor backbone.

Introduction

The controlled synthesis and thorough characterization of macromolecules of a complex although well-defined molecular structure is nowadays an important challenge in polymer science. The relevance of this issue has to be found in the strong dependence of the polymer properties not only on the size and chemical nature of the chains, but also critically on the chain topology. In addition to an academic interest, new applications have emerged for polymers and copolymers of a branched structure, e.g., viscosity modifiers for branched homopolymers and interfacial agents in emulsions, dispersions, and polymer blends for graft copolymers.

Scheme 1 illustrates the three main strategies commonly used for the synthesis of graft copolymers. The most popular strategy is the "macromonomer technique" which is based on the copolymerization of a macromonomer with vinyl or acrylic comonomers[1)]. The main advantage of this technique is the wide variety of the available macromonomers and comonomers. Since copolymerization is usually initiated by free radicals, the copolymerization yield may be limited and the branched structure is poorly controlled. This situation has however been improved in the recent past by using more extensively living anionic[2)] and group transfer polymerization[3)] and "living/controlled" radical[4)] techniques. The second strategy is the so-called "grafting-onto" technique, that requires the coupling reaction of ω-functional polymers with mutually reactive groups attached onto a preformed polymer. The limited availability of suitable pairs of reactive groups and the possibly hindered and usually unknown access of the functional groups attached to the original polymer limit the interest of this method and explain why very few well-defined branched structures have been prepared[5–6)]. In the third strategy, referred to as the "grafting-from" technique, the growth of the grafted arms from the central backbone is initiated by a multifunctional polymeric precursor[7–9)]. This method has the advantage of a limited number of reaction steps (two) and the synthesis of well-defined graft copolymers when living polymerizations are involved.

The purpose of this paper is to report on a new and general synthesis of well defined poly(alkyl methacrylate)-*graft*-polylactone copolymers by the "grafting-from" technique based on two well known living mechanisms[10, 11)], i.e., the ligated anionic polyaddition of (meth)acrylates and the coordination-insertion ring opening polymerization of lactones.

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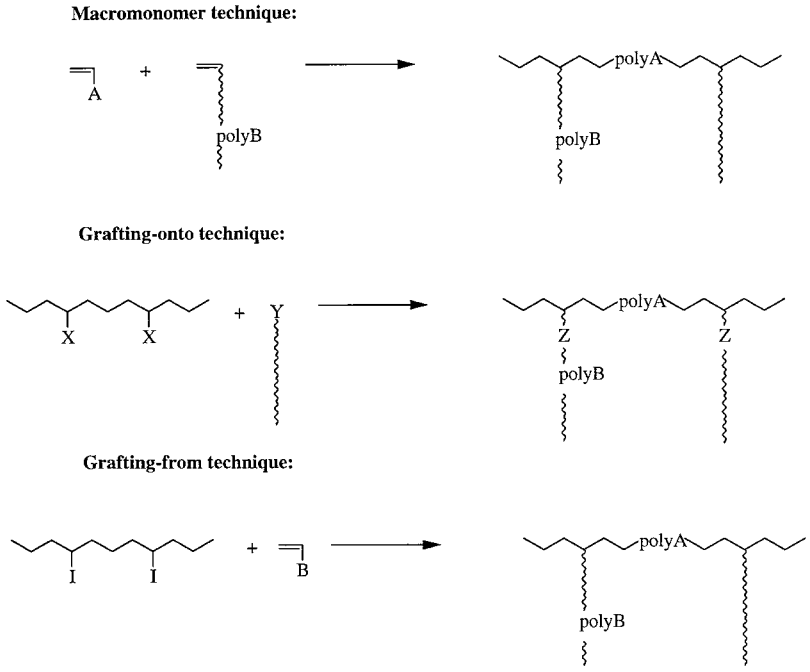
Scheme 1: Main strategies commonly used for the synthesis of graft copolymers



Experimental part

Materials

Methyl methacrylate (MMA), 2-trimethylsiloxyethyl methacrylate (TMSEMA) and butyl methacrylate (BUMA) (Aldrich) were first dried over calcium hydride for 48 h at room temperature and distilled under reduced pressure. Before polymerization, a 10 wt.-% $AlEt_3$ solution in toluene was added until a persistent yellowish green color was observed. They were then distilled under reduced pressure just before use. ε-Caprolactone (εCL) and δ-valerolactone (δVL) (Janssen) were dried over calcium hydride for 48 h and distilled just before use. 1,4,8-Trioxaspiro[4.6]-9-undecanone (TOSUO) was prepared as reported elsewhere[12] and dried by two azeotropic distillations of toluene before use. Triethylaluminium (Fluka) was dissolved in dry toluene and the concentration was measured by complexometric titration of Al with a standard solution of ethylenediaminetetraacetic acid. Toluene and tetrahydrofuran (THF) were dried by refluxing over sodium/benzophenone complex and distilled prior to use. Diphenylhexyllithium (DPHLi) was prepared at room temperature by reacting butyllithium and diphenylethylene in toluene for 24 h. Triphenylcarbenium tetrafluoroborate (Acros), sodium borohydride (Janssen) and ethanol (Riedel de Haen) were used as received.

General procedure for the anionic copolymerization of alkyl methacrylates

The anionic copolymerization of mixtures of TMSEMA and MMA or BUMA were carried out in a previously flamed and nitrogen-purged glass reactor under a nitrogen atmosphere. LiCl (10 equivalents with respect to the initiator) was first introduced and dried under high vacuum at 80 °C for 16 h. THF and the initiator were transferred into the glass reactor through a rubber septum with a stainless steel capillary and a syringe, respectively. The initiator solution was added dropwise at −78 °C to LiCl containing THF until the initiator red color persisted. The required amount of initiator was then added, followed by the comonomers mixture. Copolymerization was carried out for 5 h at −78 °C. The reaction medium was then added with an excess of acidic methanol and stirred at room temperature for 18 h in order to deprotect the trimethylsiloxy groups into the desired hydroxyl functions. The copolymer was precipitated into cold hexane, and dried under vacuum at 60 °C for 48 h.

General procedure for the graft ring opening polymerization

The required amount of methacrylic copolymer was added to a previously flamed and nitrogen-purged glass reactor under nitrogen flux. It was dried by two azeotropic distillations of toluene, and then dissolved in dry THF. This solution was cooled down to −78 °C, and 2 equivalents of $AlEt_3$ (with respect to the hydroxyl pendant groups) were added with a syringe and reacted at room temperature for 150 min and then at 50 °C for extra 30 min. Finally, the selected lactone was added to the reaction mixture and let to polymerize under vigorous stirring at room temperature. After addition of an HCl excess with respect to the initiator (0.1 M HCl solution), THF was partly distilled off and the polymer was precipitated into cold heptane. The crude copolymer was dried under vacuum at 40 °C until constant weight. The TOSUO comonomer units were derivatized into ketones and finally into hydroxyl groups as reported elsewhere[12]. The hydroxyl end groups of the polyester grafts were reacted with 2 equivalents of 3-triethoxysilylpropyl isocyanate in

dry toluene at 50 °C for 48 h, and the final copolymer was precipitated in dry heptane.

Characterization

Size exclusion chromatography (SEC) was carried out by using a Hewlett-Packard 1090 Liquid Chromatogram equipped with four columns (10^5, 10^3, 500 and 100 Å) and a Hewlett-Packard 1037A refractive index detector. Polystyrene or poly(methyl methacrylate) standards were used for calibration, and the number ($\overline{M}_n$) and weight average ($\overline{M}_w$) molecular weights and the polydispersity index ($\overline{M}_w/\overline{M}_n$) were calculated. Nuclear magnetic resonance spectroscopy was performed with a Bruker AM400 spectrometer using deuterated chloroform as solvent and tetramethylsilane as internal reference. Differential scanning calorimetry (DSC) was carried out with a Mettler-Toledo TA8000 apparatus.

Results and discussion

Synthesis of graft copolymers by the "grafting-from" technique requires the preliminary synthesis of (co)polymers containing initiator sites for the graft formation, protected or not and randomly distributed along the chain. In this study (Scheme 2), hydroxyl groups have been attached along a methacrylic backbone by living anionic copolymerization of 2-trimethylsiloxyethyl methacrylate (TMSEMA) with methyl methacrylate (MMA). The trimethylsiloxy groups of the TMSEMA units are very convenient precursors of the desired hydroxyl groups due to their stability towards anions at low temperature and their propensity to hydrolysis under acidic conditions. Tab. 1 lists the copolymethacrylates that have been prepared with molecular weight, polydispersity, and 2-hydroxyethyl methacrylate (HEMA) content. This OH content has been calculated by ^{1}H NMR from the relative intensity of the methylene protons of HEMA at 4.11 and 3.84 ppm and the methyl ester of MMA at 3.60 ppm. There is a good agreement with the expected values based on the theoretical TMSEMA comonomer content. Consistently with the use of LiCl as a ligand for the active species, the polydispersity is very narrow. The copolymethacrylate chains prepared in THF contain ca. 80% syndiotactic triads. It is worth pointing out that the TMSEMA and thus the HEMA contents have been deliberately maintained low in order to prepare graft copolymers with a low branching density. The experimental data reported in Tab. 1 confirm that the ligated anionic copolymerization of at least the MMA/TMSEMA pair allows to control the molecular weight of the copolymer backbone by the monomer to initiator mole ratio and to predict the grafting density by the TMSEMA content of the comonomer feed. How the grafts are distributed along the polymethacrylate backbone remains, however, a pending question, since the reactivity ratios characteristic of the anionic copolymerization of the MMA/TMSEMA and BUMA/TMSEMA pairs are unknown in the scientific literature and their very time consuming determination was out of the scope of this study. It is however reasonable to assume that these reactivity ratios are not equal to unity, so that a composition drift of the copolymer formed might take place and result in a heterogeneous distribution of the hydroxyl groups and ultimately of the grafts. The best way to limit this possible heterogeneity is to keep the copolymerization yield low enough.

Tab. 1. Anionic copolymerization of mixtures of TMSEMA and MMA (BUMA) initiated by diphenylhexyllithium in THF at –78 °C in the presence of 10 equivalents of LiCl[a)]

Code	Alkyl methacrylate	f_{TMSEMA}[b)]	F_{HEMA}[c)]	$\overline{M}_{n,calc}$[d)]	$\overline{M}_{n,SEC}$[e)]	$\overline{M}_w/\overline{M}_n$
1a	MMA	0.08	0.08	20000	20000	1.01
1b	MMA	0.04	0.03	60000	61000	1.04
1c	MMA	0.04	0.03	30000	28000	1.02
1d	BUMA	0.08	0.07	15000	11000	1.01

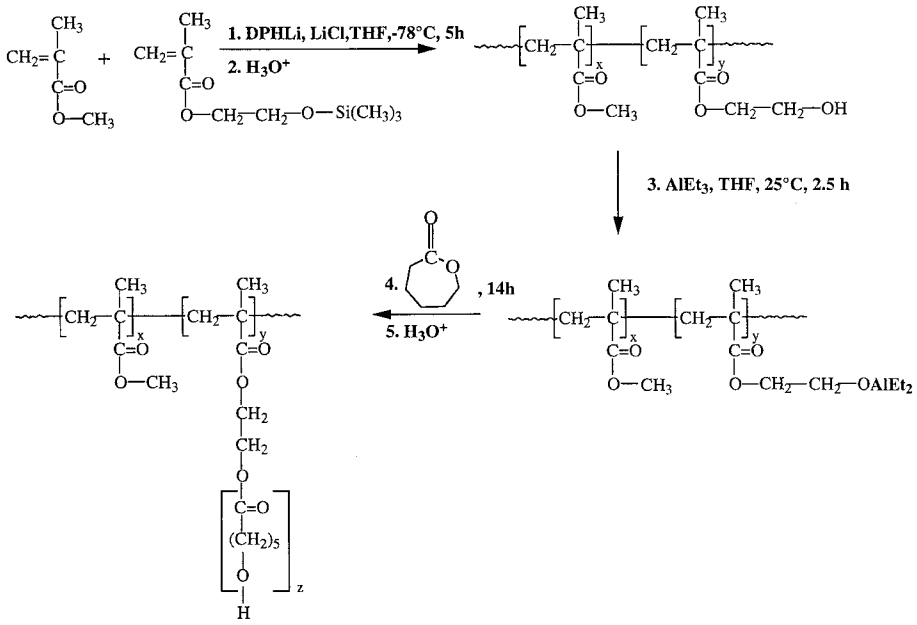
a) Copolymerization was complete within 5 h.
b) Mole fraction in the comonomer feed.
c) Mole fraction in the copolymer measured by ^{1}H NMR.
d) Theoretical number average molecular weight = Σ comonomer mass/mole initiator.
e) Experimental number average molecular weight measured by SEC (PMMA standards).

The second step of the grafting reaction is the conversion of the HEMA containing polymethacrylate into a multifunctional macroinitiator for the ROP of lactones. The hydroxyl groups have thus been reacted with a twofold molar excess of $AlEt_3$ (with respect to Al) using dilute solutions (ca. $2 \cdot 10^{-3}$ M hydroxyl and $4 \cdot 10^{-3}$ M $AlEt_3$). Under these conditions, the reaction is driven to completion, aggregation of the formed diethylaluminium monoalkoxides[13)] and formation of monoalkylaluminium dialkoxides[14)] are minimized. Tab. 2 lists the main experimental conditions and the molecular characteristics of the synthesized graft copolymers. This strategy has been extended to several methacrylic monomers (MMA and BUMA) and lactones (εCL, δVL, and TOSUO). The copolymerization yield is usually high, and the copolymer composition is in good agreement with values expected from the initial OH/lactone mole ratios. $\overline{M}_n$ of the graft copolymers has been calculated according to Eq. (1):

$$\overline{M}_n = \overline{M}_{n,macro} + (W_{lact}/W_{ma}) \cdot \overline{M}_{n,macro} \quad (1)$$

where $\overline{M}_{n,macro}$ is the molecular weight of the macroinitiator (determined by SEC) and W_{lact} and W_{ma} are the weight compositions in lactone and methacrylate, respectively. The average number of branches per chain (N_{br}) is supposed to be the average number of hydroxyl groups per chain. It is calculated as the product of the number average degree of polymerization (DP_n) of the polymethacryl-

Scheme 2: Application of the "grafting-from" technique to the synthesis of poly(methyl methacrylate)-*graft*-poly(ε-caprolactone) copolymers



Tab. 2. Molecular characterization of polymethacrylate-*graft*-polylactone copolymers[a)]

Code	Macro-initiator	Lactone	Polym. time / h	Yield / wt.-%	f_{lact}[b)]	F_{lact}[c)]	$\overline{M}_n$[d)]	$\overline{M}_{n,SEC}$[e)]	$\overline{M}_w/\overline{M}_n$	N_{br}[f)]	$\overline{M}_{n,bg}$[g)]	$\overline{M}_{n,graft}$[h)]
2a	**1a**	εCL	15	85	0.30	0.20	25000	20000	1.08	24.3	1300	400
2b	**1a**	εCL	15	85	0.46	0.30	29000	24000	1.11	24.3	1300	700
2c	**1a**	εCL	17	90	0.60	0.52	44000	38000	1.26	24.3	1300	2000
2d	**1a**	εCL	15	90	0.72	0.66	64000	50000	1.19	24.3	1300	3100
2e[i)]	**1a**	εCL	16	98	0.78	0.80	111000	90000	1.17	24.3	1300	6400
2f	**1b**	εCL	15	85	0.47	0.33	94000	88000	1.05	19.8	3000	1700
2g[i)]	**1b**	εCL	24	98	0.47	0.47	122000	108000	1.08	19.8	3000	3100
2h[i)]	**1b**	εCL	16	99	0.72	0.71	232000	216000	1.09	19.8	3000	8700
2i	**1b**	δVL	16	85	0.80	0.55	135000	88000	1.05	19.8	3000	3700
2j	**1b**	εCL/TOSUO[j)]	24	50	0.62	0.33[k)]	97000	80000	1.05	19.8	3000	1700
2k	**1b**	εCL/TOSUO[j)]	39	75	0.80	0.58[k)]	164000	180000	1.09	19.8	3000	4200
2l	**1c**	εCL	18	80	0.72	0.54	65000	60000	1.30	9.2	3000	4100
2m	**1c**	εCL	21	85	0.87	0.74	118000	133000	1.14	9.2	3000	9700
2n[i)]	**1d**	εCL	20	95	0.49	0.44	18000	21000	1.13	7.7	2000	1400
2p[i)]	**1d**	εCL	20	98	0.60	0.60	27000	32000	1.17	7.7	2000	2700
2q	**1d**	εCL	40	95	0.77	0.72	35000	45000	1.22	7.7	2000	4600
2r[i)]	**1d**	εCL	16	97	0.83	0.80	48000	52000	1.16	7.7	2000	7200
2s[i)]	**1d**	εCL	21	98	0.91	0.91	114000	114000	1.10	7.7	2000	18000

a) Synthesis in THF at 25 °C with an Al alkoxide concentration of $2 \cdot 10^{-3}$ mol l^{-1}.
b) Lactone mole fraction in the comonomer feed.
c) Lactone mole fraction in the copolymer measured by ^{1}H NMR.
d) Cf. Eq. (1).
e) $\overline{M}_n$ determined by SEC (polystyrene standards).
f) N_{br} = average number of branches per molecule.
g) $\overline{M}_{n,bg}$ = number average molecular weight between the nearest grafting points.
h) $\overline{M}_{n,graft}$ = number average molecular weight of grafted polylactone chains.
i) The polymerization mixture turned into a gel.
j) εCL/TOSUO mole ratio = 0.8/0.2.
k) Graft composition εCL/TOSUO = 0.16/0.86 (mol/mol).

ate backbone (determined by SEC) and the mole fraction of HEMA in the graft copolymer (determined by ^{1}H NMR), Eq. (2):

$$N_{br} = DP_n \cdot F_{HEMA} \quad (2)$$

The average molecular weight between the nearest grafting points has been calculated as the ratio of the number average molecular weight of the macroinitiator (determined by SEC) to the average number of branches per chain, Eq. (3):

$$\overline{M}_{n,bg} = \overline{M}_{n,macro}/N_{br} \quad (3)$$

Finally, the number average molecular weight of the polylactone grafts ($\overline{M}_{n,graft}$) is the average molecular weight between the nearest grafting sites multiplied by the weight fraction of lactone in the graft copolymer, Eq (4):

$$\overline{M}_{n,graft} = \overline{M}_{n,bg} \cdot F_{lact} \cdot MW_{lact}/(F_{lact} \cdot MW_{lact} + (1 - F_{lact}) \cdot MW_{ma}) \quad (4)$$

where F_{lact} is the mole fraction of lactone in the graft copolymer (calculated by ^{1}H NMR) and MW_{lact} and MW_{ma} are the molecular weights for the lactone and the methacrylate repeating units, respectively. Fig. 1 compares the SEC chromatograms for the macroinitiator **1b** and the final graft copolymer **2g**. The molecular weight of the macroinitiator is shifted toward higher values in close agreement with the theoretical value. Very importantly, no trace of unreacted macroinitiator is observed, and the apparent molecular weight distribution ($\overline{M}_w/\overline{M}_n$ = 1.08) is very narrow for a graft copolymer. The MWD of the graft copolymers tends however to broaden with the number of

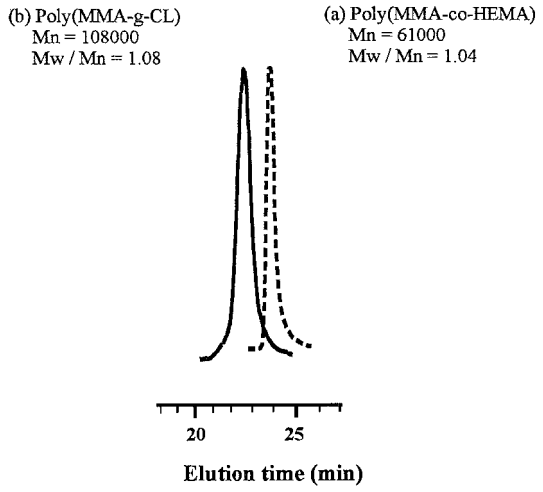
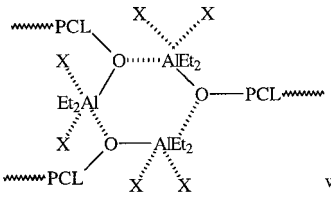


Fig. 1. Comparison of the SEC traces for the poly(MMA-*co*-HEMA) macroinitiator **1b** (a) and the final polyMMA-*graft*-polyCL copolymer **2g** (b)

Scheme 3: Cyclic trimer formed by diethylaluminium alkoxide species



branches per chain (a comparison of the copolymers prepared from macroinitiators **1a** and **1b** is given in Tab. 2). Fig. 2 compares the ^{1}H NMR spectra of the macroinitiator **1b** and the graft copolymer **2d**. The proton signals characteristic of the MMA units (resonances at 3.60, 1.81, 1.02, and 0.85 ppm) and the εCL units (resonances at 4.06, 2.29, 1.62, and 1.38 ppm) are clearly observed. Furthermore, the downfield shift of the methylene protons of the HEMA units in the copolymethacrylate from 4.11 and 3.84 ppm (H_d and H_e, upper spectrum) to 4.27 ppm in the graft copolymer (H_{d+e}, lower spectrum) is evidence for the alcohol esterification and thus for the efficiency of the grafting reaction. As a rule, the agreement is good between the lactone mole fraction in the final copolymers (^{1}H NMR analysis) and the molar composition of the comonomer feed corrected for the copolymerization yield (see yield and F_{lact} in Tab. 2). The mole fraction of εCL in the copolymers has been calculated from the relative intensities of the signals at 3.60 ppm for MMA and at 4.06 ppm for the εCL units.

Usually, when the εCL conversion is high (>95%) the reaction medium turns into a gel (Tab. 2), which however disappears as soon as a few drops of a 0.1 M HCl solution are added. This observation is consistent with the coordinative aggregation of the diethylaluminium alkoxides responsible for the εCL polymerization. As long as the monomer is available, it is known to coordinate onto the Al atom of the active species. Nevertheless, in the specific case of diethylaluminium monoalkoxides the active species have been reported to form cyclic trimers in THF and to remain associated all along the εCL polymerization[15], that proceeds through the fast reversible dissociation of these monomer (and THF) solvated trimers. These observations have been reported for the εCL homopolymerization. In this study, the polyester chains are growing from a common backbone, which might perturb the association of the growing Al alkoxides into trimers connecting all the copolymer chains in a three-dimensional network. When most εCL is consumed, this situation starts to dominate.

A series of graft copolymers have been prepared from the same macroinitiator, while changing the lactone composition. It may be noted that a graft copolymer with a very high εCL content (copolymer **2s** in Tab. 2, F_{lact} = 0.91) looks like a multistar-like polycaprolactone. The use of macroinitiators of different HEMA content leads to

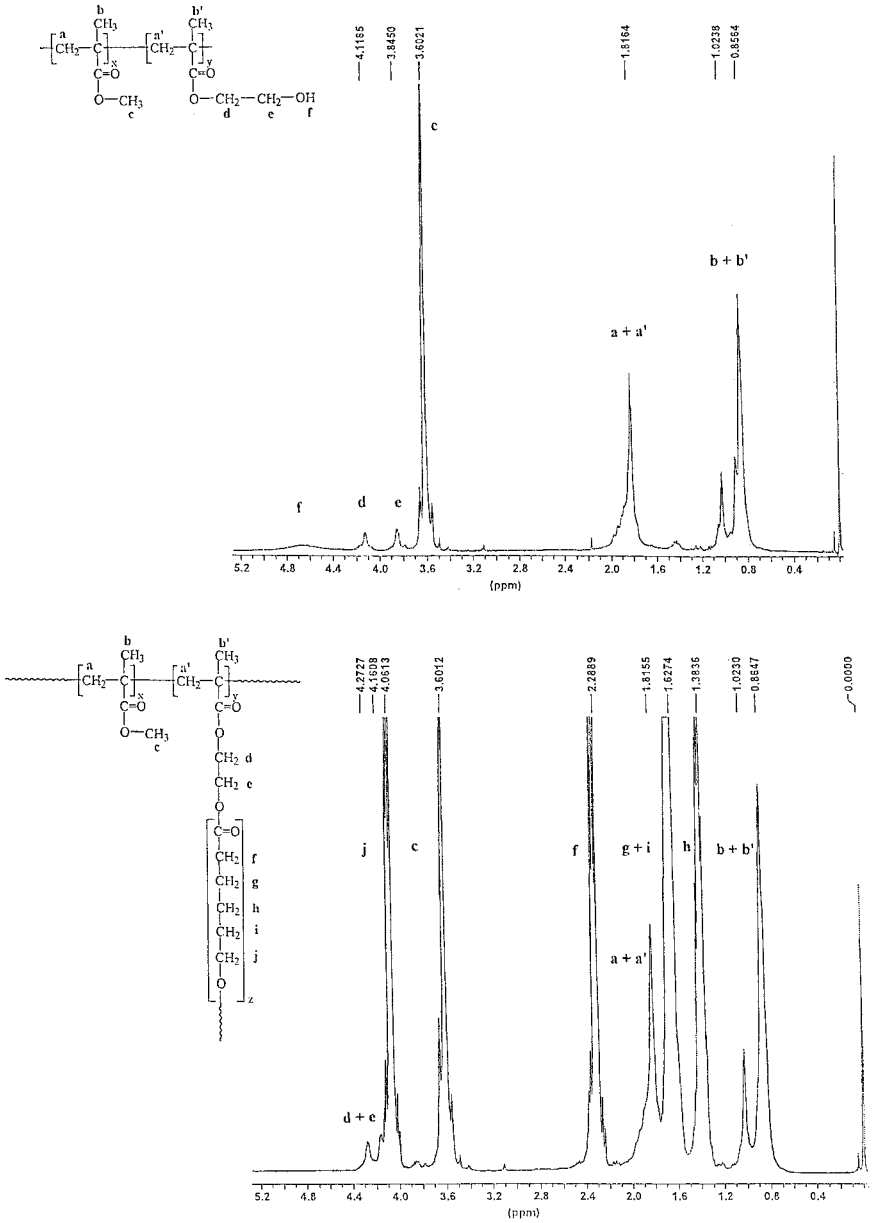


Fig. 2. 400 MHz ^{1}H NMR spectra for the poly(MMA-*co*-HEMA) macroinitiator **1a** (upper spectrum) and the final polyMMA-*graft*-polyCL copolymer **2d** (lower spectrum)

graft copolymers with a large range of weight composition, grafting density and relative molecular weight of the polymeric backbone and the grafts. Fig. 3 compares the DSC trace (first scan) for the copolymers **2a**, **2b**, **2c**, **2d**, and **2e** prepared from the same PMMA backbone but with an increasing PCL content. The melting endotherm of the PCL component is observed for contents exceeding 30 mol-% (F_{CL}). However, the glass transition temperature(s) of the graft copolymer are not detected even after the fast cooling of the melt in the second scan. The solid-state morphology of these PMMA-*graft*-PCL copolymers is under current investigation by more sensitive techniques such as dielectric spectroscopy and it will be the topic of a forthcoming publication.

The versatility of the new grafting route reported in this paper has been illustrated by substituting BUMA for MMA and εCL for δVL and TOSUO. These examples are not restrictive. A special mention should be made to the polyMMA-*graft*-poly(CL-*co*-TOSUO) copolymers **2j** and **2k**. Some of us have previously reported[12] that ethylene ketal pendant groups of poly(CL-*co*-TOSUO) copolymers could be completely deacetalized with the formation of ketone pendant groups. These ketone groups have also been quantitatively and selectively reduced into hydroxyl

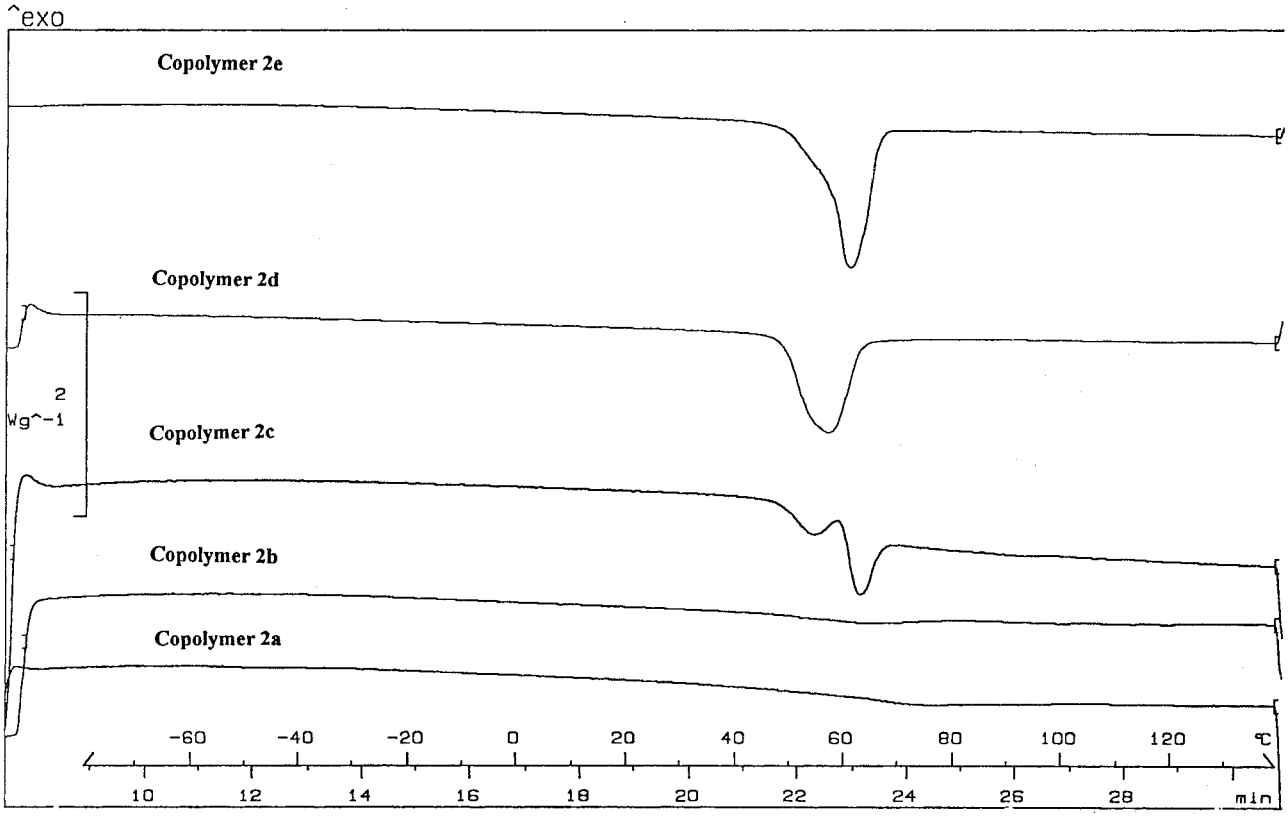


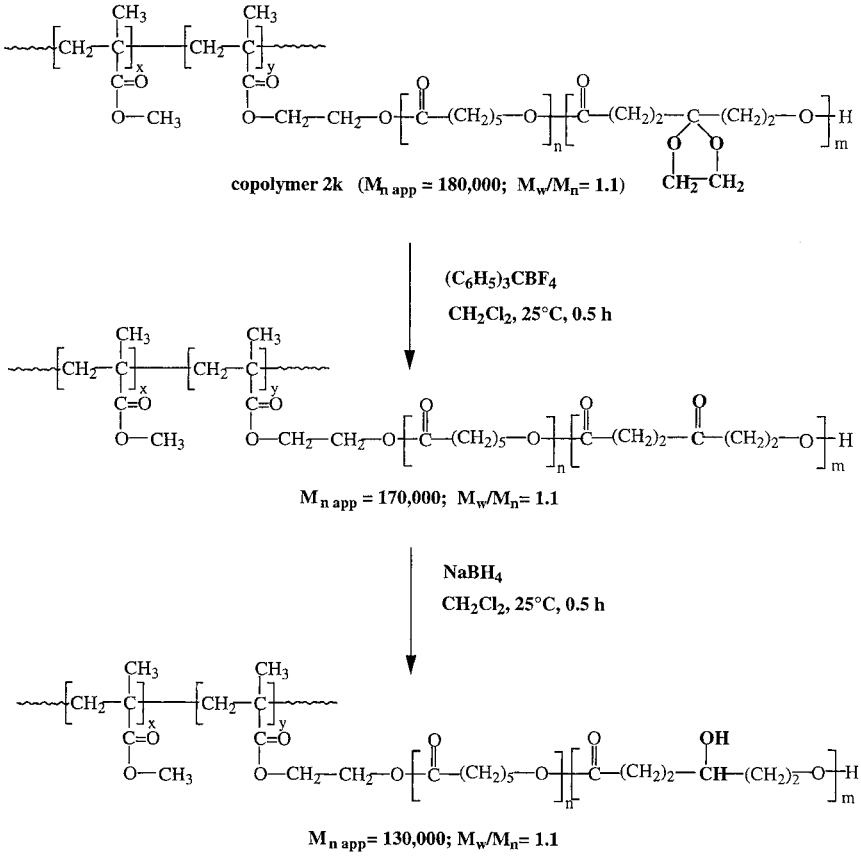
Fig. 3. DSC curves for the polyMMA-*graft*-polyCL copolymers **2a**, **2b**, **2c**, **2d**, and **2e** (first scan, 20 °C/min)

groups without scission of the polyester backbone. These experimental conditions have been successfully used for the treatment of the polyMMA-*graft*-poly(CL-*co*-TOSUO) copolymer **2k** (Scheme 4). Indeed, the ^{1}H NMR analysis of the original graft copolymers has confirmed the observation of the signals characteristic of the MMA units (resonances at 3.60, 1.81, 1.02, and 0.85 ppm), the εCL units (resonances at 4.06, 2.29, 1.62, and 1.38 ppm) and the TOSUO units (resonances at 4.18, 3.94, 2.38, and 2.0 ppm). Upon deacetalization, the acetal protons of the TOSUO units at 3.94 ppm completely disappear, whereas the other signals are shifted to lower fields (new resonances at 2.61, 2.76, 2.81, and 4.35 ppm). The ketone pendant groups are also completely reduced to hydroxyl pendant groups by sodium borohydride in a dichloromethane/ethanol mixture at 25 °C. The previous signals for the ketone-containing units are indeed shifted back to higher fields, which results in some overlapping with signals of the PCL protons. The molecular weight distribution remains narrow ($\bar{M}_w/\bar{M}_n < 1.10$), which is in favor of the absence of chain scission. Expectedly, the chemical modification of the TOSUO-containing grafts is responsible for changes in the polymer-solvent interaction and particularly in the elution volume and apparent molecular weight of the derivatized graft copolymers. Ketone and hydroxyl groups attached to the grafts can serve for the anchoring of molecules of interest such as drugs, non-linear optical chromophores, liquid crystals, etc. Furthermore, the well known interfacial activity of graft copolymers in polymer blends could be used for improving the interfacial adhesion by reaction of one phase with the reactive sites of the grafts.

An additional benefit of this grafting route has to be found in the hydroxyl end-capping of the polyester grafts. These functional groups can be used for labeling the copolymer with chromophores (UV and fluorescence)[16] or they can be derivatized into, e.g., carboxylic acids, aromatic amines, and triethoxysilane groups[13, 17, 18]. For instance, the copolymer **2d** has been reacted with 3-triethoxysilylpropyl isocyanate as detailed elsewhere[17]. Fig. 4 shows the ^{1}H NMR spectrum of the triethoxysilane containing copolymer, which confirms the conversion of the PCL hydroxyl end groups into triethoxysilane ones (resonances at 3.83, 3.17, 1.24, and 0.64 ppm). From the relative intensity of those signals with respect to the signal at 4.27 ppm for the methylene (e + d) units, a 93% yield was found for this conversion. The potential of these macromolecules as templates in the production of organic-inorganic hybrids by the sol-gel process is currently investigated.

In addition to the synthesis of the novel comb-like graft copolymers reported in this study, the structure of the polymethacrylate macroinitiators can be designed in such a way that different macromolecular architectures can be

Scheme 4: Chemical modification of PMMA-*graft*-polyester copolymers that contain TOSUO units in the polyester grafts.



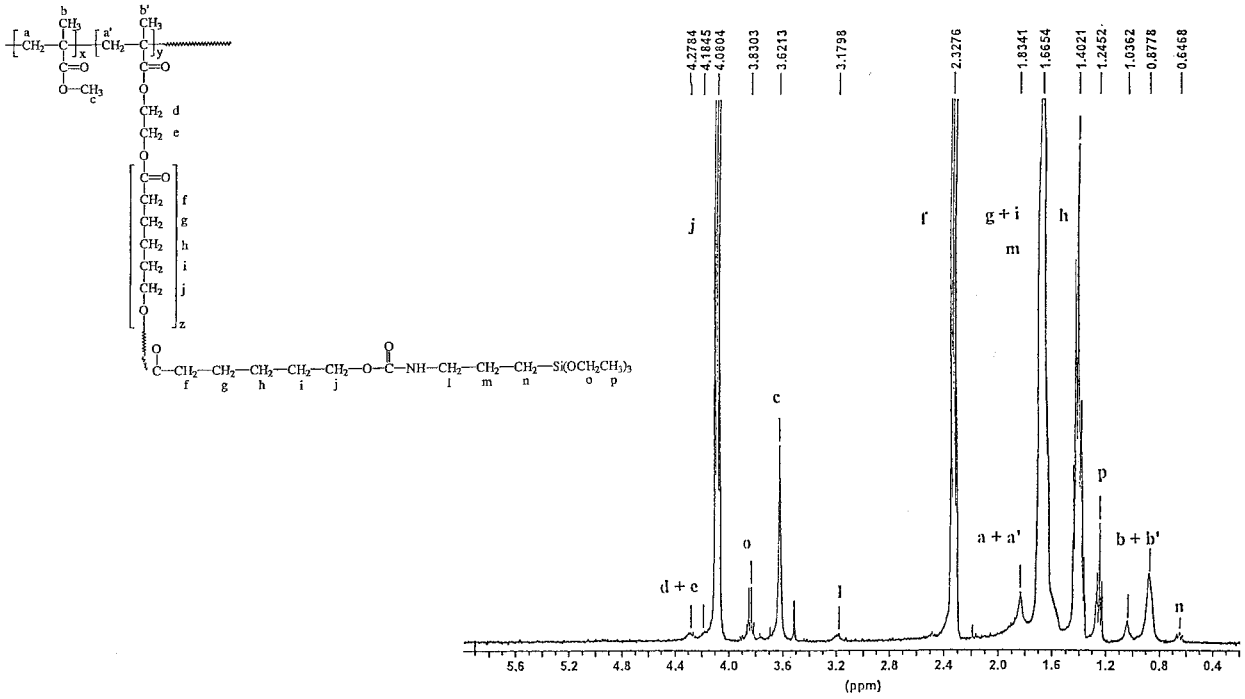
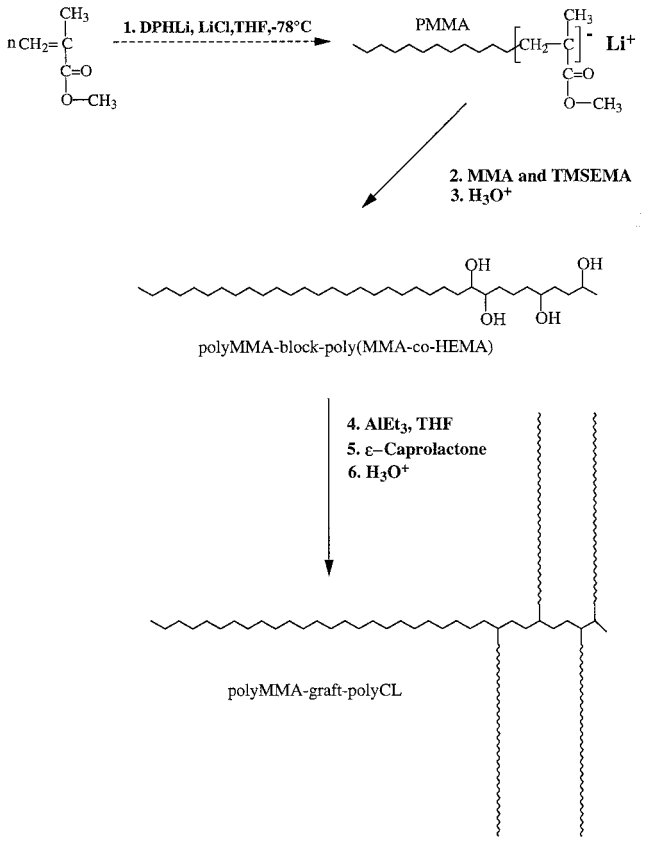


Fig. 4. 400 MHz ^{1}H NMR spectrum of the polyMMA-*graft*-polyCL copolymer **2 d**, after modification of the hydroxyl end groups by reaction with 3-triethoxysilylpropyl isocyanate (at 50 °C in toluene in the presence of DABCO (1,4-diazabicyclo[2.2.2]octane) for 48 h

Scheme 5: Synthetic pathway to "palm-tree shaped" copolymers.



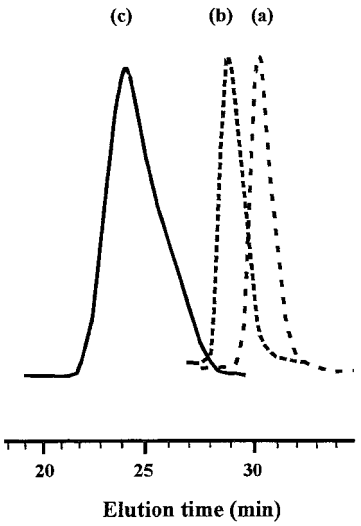


Fig. 5. Comparison of the SEC traces for (a) the first polyMMA block ($\overline{M}_{n,SEC}$ = 3300, $\overline{M}_w/\overline{M}_n$ = 1.06); (b) the polyMMA-*block*-poly(MMA-*co*-HEMA) macroinitiator ($\overline{M}_{n,SEC}$ = 6000, $\overline{M}_w/\overline{M}_n$ = 1.06, F_{HEMA} = 0.10); and (c) the final palm-tree like graft copolymer polyMMA-*graft*-PCL ($\overline{M}_{n,SEC}$ = 29000, $\overline{M}_w/\overline{M}_n$ = .35, F_{CL} = 0.85)

made available. As an example, a polyMMA-*block*-poly(MMA-*co*-HEMA) copolymer has been synthesized by the sequential anionic polymerization of MMA and a mixture of MMA and TMSEMA. This copolymer has been used as discussed in this paper for promoting the ring opening polymerization of εCL (Scheme 5). Fig. 5 compares the SEC traces for the PMMA first block, the polyMMA-*block*-poly(MMA-*co*-HEMA) macroinitiator and the resulting PMMA-*graft*-PCL copolymer. The shift of each elution curve toward smaller volumes confirms that the reaction of each intermediate compound is close to completion and leads to a PMMA-*graft*-PCL copolymer of a palm-tree like architecture with a significantly increased polydispersity compared to the macroinitiator.

In conclusion, well-defined poly(alkyl methacrylate)-*graft*-polylactone copolymers of a wide range of composition and molecular weight and of different molecular architectures (comb-like, palm-tree like structures) have been successfully synthesized. The key for the success has to be found in the coupling of two living polymerizations, i.e., the ligated anionic polymerization of methacrylates and the coordination-insertion ring opening polymerization of aliphatic lactones. These novel copolymers have the unique feature of being reactive, since each polyester graft is end-capped by a hydroxyl end group which can be easily derivatized into other organic functionalities, such as triethoxysilanes. They can thus be used as such or as intermediates for the design of more complex macromolecular systems.

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