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Contribution of Unsymmetrical Difunctional Initiators/Monomers to the Macromolecular Engineering

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Introduction

The emerging technologies (e.g. in optics, microelectronics, medicine...) require the availability of synthetic polymers with continuously more sophisticated properties and performances. The best way for the polymer chemist to face this challenge is to tailor the molecular structure of the chains. Nowadays, the progress in the living/controlled polymerization mechanisms is such that the so-called macromolecular engineering is a vivid reality.

Historically, the chemist created new polymers by combining two or more monomers in the same chain, so leading to (more or less) statistical copolymers. With the discovery of living polyadditions, the comonomers could be polymerized in a sequential way, and the advent of microphase separated block copolymers was a revolution in polymeric materials. The range of these block copolymers was increased by using two types of initiators also in a sequential way.[1] For instance, living polyanionic chains were reacted with an electrophile, such that a radical initiator or a precursor of a Ziegler-Natta catalyst is attached as an end-group and can initiate the polymerization of families of monomers that could not be polymerized by anions. So, combinations of single initiators and single monomers (one type of polymerizable moiety) was the strategy originally used in macromolecular engineering.

Recently, a new trend emerged which consists in associating in the same molecule, either two different initiators, or two different polymerizable moieties, or, more frequently, one monomer and one initiator. These dual molecules offer new prospects not only in the search for new polymers but also in the implementation of the synthesis of multicomponent materials. These three typical strategies will be illustrated in this paper in a non exhaustive way, mainly on the basis of experiments carried out by collaborators of the author.

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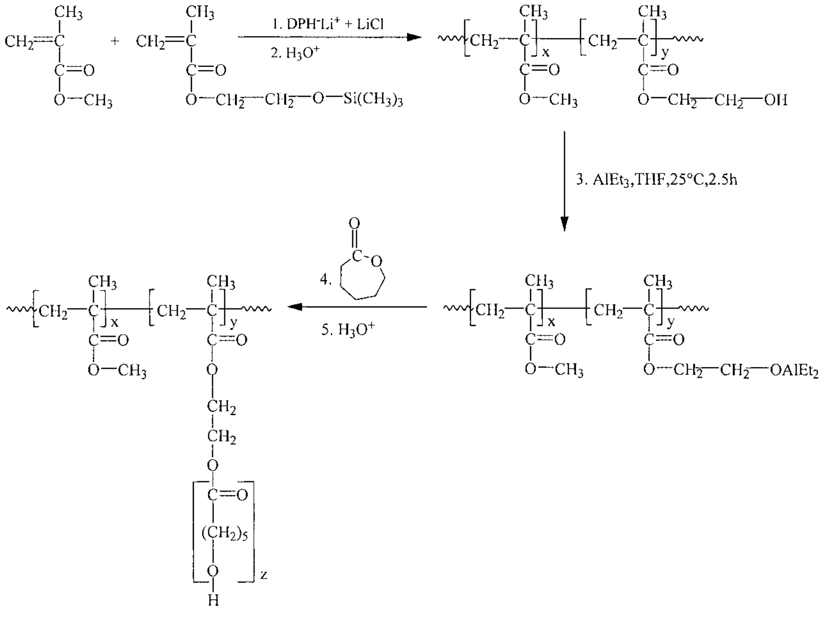
Dual Monomer/Initiator Molecules

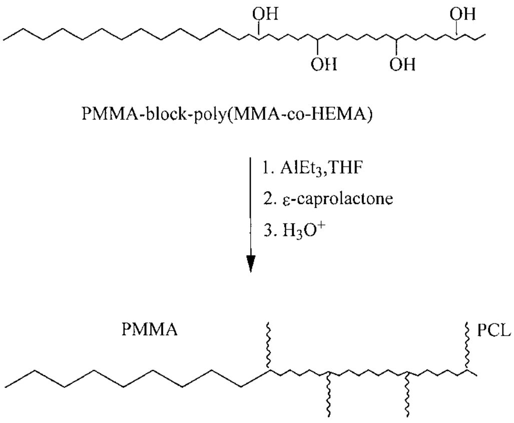
Any unsaturated and cyclic monomer substituted by a hydroxyl group (protected, if required) can be polymerized by polyaddition, and the pendant hydroxyl groups (after deprotection, if necessary) of the chains are potential initiators for the ring-opening polymerization (ROP) of lactones and lactides.

Although 2-hydroxyethylmethacrylate (HEMA) is a monomer known for a long time, its use as a dual monomer/initiator compound was not widespread for a long time. HEMA is actually a precursor of graft copolymers prepared according to the so-called "grafting-from" technique. Scheme 1 illustrates the living anionic copolymerization of presilylated HEMA with methyl methacrylate (MMA), followed by deprotection of the hydroxyl groups and their conversion into dialkylaluminum alkoxides, which are commonly used to initiate the controlled ROP of lactones and lactides.[2]



Scheme 1. HEMA : Key intermediate in the synthesis of PMMA-graft-poly(ε-caprolactone) copolymers

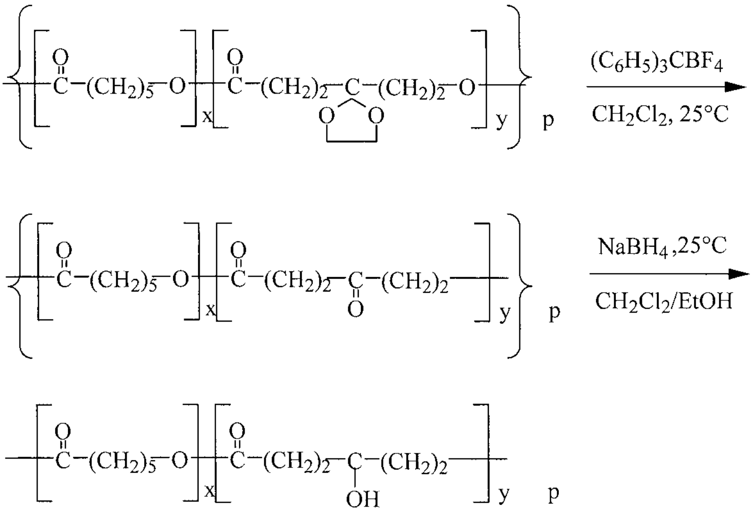
The anionic copolymerization was initiated by diphenylhexyllithium (DPH^-Li^+) in THF, at –78°C, in the presence of LiCl (10 equiv.) as a ligand. It was complete within a few hours. The livingness of the ligated polymerization allowed to control the molecular weight of the copolymer (by the comonomer/initiator molar ratio) and the grafting density (by the comonomer feed) and to trigger low polydispersity (1.05). The protecting trimethylsiloxy groups were stable towards the anions at –78°C and quantitatively deprotected at 25°C. The conversion of the hydroxyl groups into Al alkoxides was quantitative by reaction with a twofold molar excess of triethyl Al. Graft copolymers with M_n up to 2.10^5 g · mol^{-1} were prepared, that contained up to 25 grafts per molecule, M_n of the grafts being in the range from a few hundreds up to 20,000 g · mol^{-1}. The polydispersity was usually lower than 1.2. This system is very flexible because MMA can be substituted by other alkylmethacrylates and ε-caprolactone by lactides, δ-valerolactone and, better, by protected γ-hydroxyl-ε-caprolactone, which opens the way to more complex macromolecular architectures.[2] It must also be kept in mind that the hydroxyl groups of either the poly(MMA-co-HEMA) copolymers or the polyester grafts (end-group or comonomer units) are reactive in polycondensation reactions, e.g. in the sol-gel process, with the purpose to produce organic-inorganic hybrid materials.[3] HEMA is then rather a dual monomer than a dual monomer/initiator compound. This remark is valid to other hydroxyl containing monomers. Last but not least, novel palm-tree like architectures can be designed by using the poly(MMA-co-HEMA) macroinitiator as one constituent of block copolymers,[2] as schematized below.



Scheme 2. Synthesis of "palm-tree" shaped block copolymers

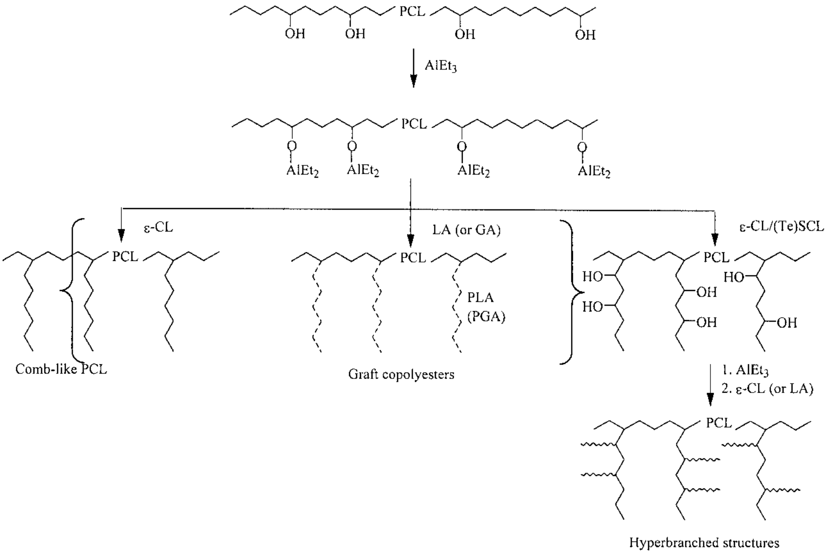
Finally, controlled radical polymerization (CRP) could be carried out instead of living anionic polymerization in the first step of scheme 1, such that combinations of anionic/ROP and CRP/ROP can be envisioned.

As an answer to the urgent need to functionalize biodegradable and biocompatible aliphatic polyesters, γ-functional ε-caprolactones have been recently synthesized, particularly monomers γ-substituted by a protected hydroxyl group.[4,5] The acetal group attached to ε-caprolactone in γ-position in 1,4,8-trioxaspiro-[4,6]-9-undecanone (TOSUO) can be quantitatively derivatized into a hydroxyl group when part of a poly(ε-CL-co-polyTOSUO) copolymer. The 2-step derivatization is shown in scheme 3. Better, γ-(t-butyldimethylsilyloxy) ε-caprolactone (SCL) or triethylsilyloxy ε-caprolactone (TeSCL) can be copolymerized with ε-CL in a controlled way, and the one-step deprotection of the (Te)SCL comonomer units is straightforward. These deprotection reactions leave the polyester chains unaffected.



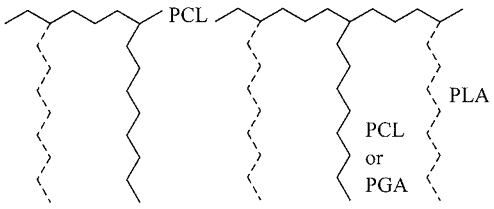
Scheme 3. Deprotection of γ-acetal pendant groups

The reaction of the hydroxyl pendant groups with $AlEt_3$ leads to the macroinitiator for the ROP of ε-CL, γ-substituted ε-CL, lactides, etc. Therefore, comb-like polyesters, graft copolymers and hyperbranched (dendritic) (co)polyesters can be prepared,[6,7] as illustrated by scheme 4.



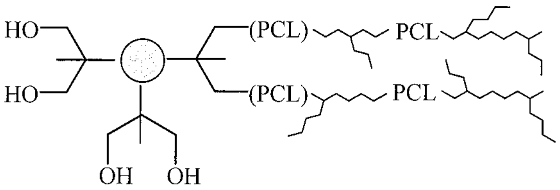
Scheme 4. Synthesis of comb-like, graft and hyperbranched (co)polyesters

In order to go a step further in the macromolecular engineering, ε-CL was copolymerized with TOSUO and (Te)SCL. An interesting characteristic of these terpolymers is the difference in stability of the protected hydroxyl groups. Indeed, the hydrolysis of the silanolate groups is selective in the presence of the acetal protecting groups. Therefore, the sequential deprotection of the hydroxyl groups followed by their conversion into Al alkoxides is an efficient strategy to prepare hetero-graft copolymers (scheme 5).



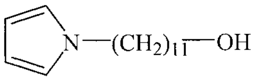
Scheme 5. Heterograft copolymers synthesized from ε-CL/TOSUO/(Te)SCL terpolymers

A variation on the theme may be found in the initiation of the ring-opening copolymerization of the ε-CL/TOSUO (or (Te)SCL) mixture by a multifunctional compound, which may lead to novel architectures in which block and graft structures, or dendrimeric and graft structures coexist (scheme 6).[8]

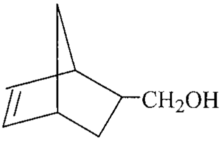


Scheme 6. Possible architectures from multifunctional ROP initiators

Additional examples of hydroxyl substituted monomers have been studied, including N-pyrrole-11-undecanol (Py-OH)[9] and 2-hydroxymethyl-5-norbornene (NBE-OH).[10]



Py-OH

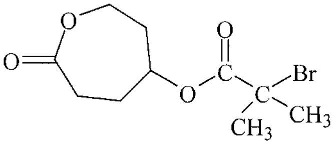


NBE-OH

These molecules are precursors of polyester macromonomers bearing a pyrrole or a norbornene polymerizable group.[9,10] The Py-PCL macromonomer was copolymerized with pyrrole (Py) by chemical or electrochemical oxidation leading to graft copolymers with improved film forming and mechanical properties compared to polyPy.[9] α-Norbornenyl PCL was also copolymerized with norbornene and norbornene acetate by the [$RuCl_2$(p-cymene)]$_2$ PCy_3/(trimethylsilyl)diazomethane complex (Grubbs catalyst)]. The metathesis copolymerization is better controlled in case of the norbornene acetate comonomer which is less reactive than norbornene and decreases the extent of side reactions.[10] It must be noted that the macromonomer can be homopolymerized into high molecular weight comb-like chains of low polydispersity (M_w/M_n = 1.10) within high yields (90%).[10] Finally, random copolymers of norbornene and norbornene acetate are macroinitiators for the graft copolymerization of lactones and lactides after deprotection of the hydroxyl groups (n-BuLi in THF).[11]

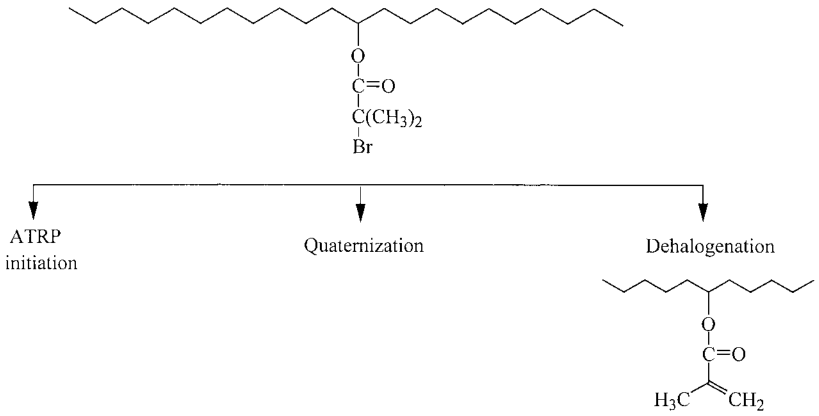
p-Chloromethylstyrene is a known styrene derivative which associates a polymerizable vinyl group and a benzyl chloride in the same molecule. The nitroxide-mediated controlled radical polymerization of styrene is very well-known and it proved to be tolerant for reactive derivatives including p-chloromethylstyrene and other functional monomers, such as HEMA.[12] Benzyl chloride is a potential initiator for the controlled radical polymerization by ATRP. Therefore, p-chloromethylstyrene is a dual molecule which allows two different CRP processes to be combined in one synthesis scheme. Either α-styryl macromonomers can be synthesized or macroinitiators for the "grafting-from" technique based on ATRP can be made available.

Similarly to p-chloromethylstyrene, γ-(2-bromo-2-methylpropionate)-ε-caprolactone (BMPCL) is an interesting combination of a cyclic monomer and an initiator for ATRP polymerization.



BMPCL

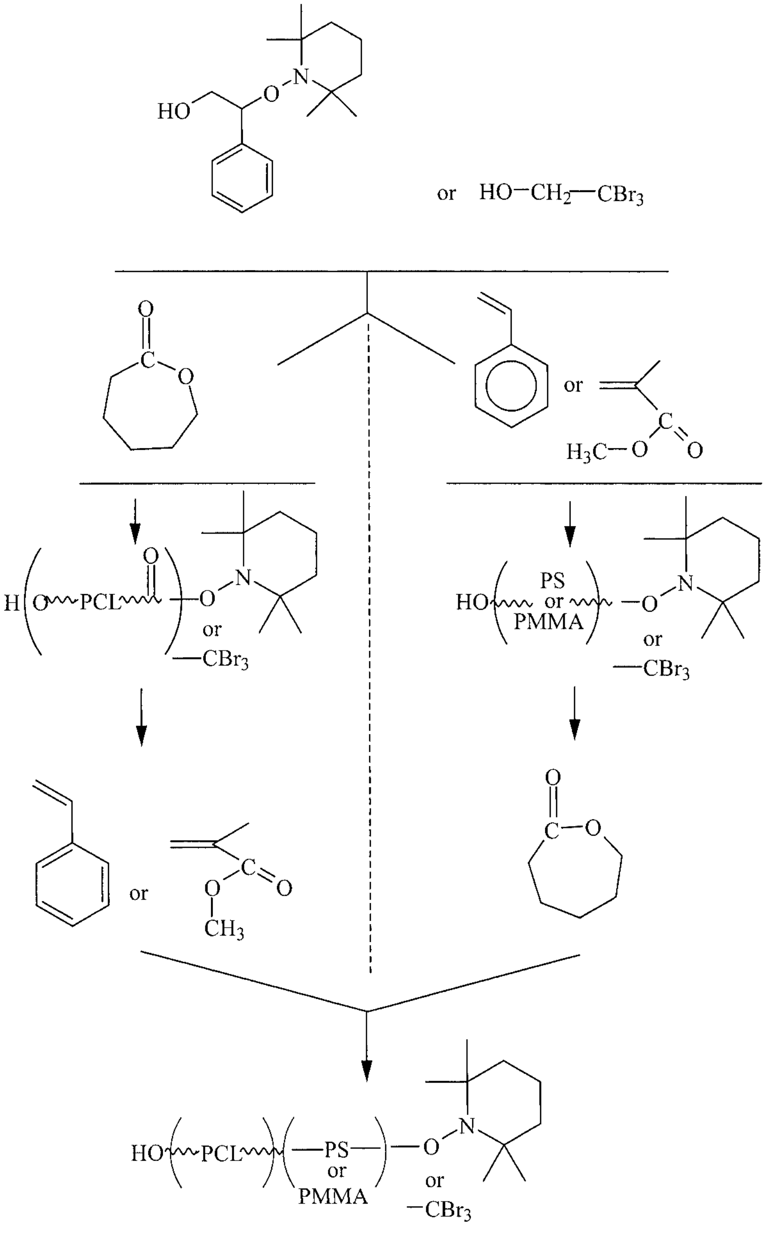
Chains end-capped by a polymerizable ε-caprolactone unit can thus be prepared by CRP and copolymerized by ROP with formation of graft copolymers. Moreover, copolyesters of ε-CL and BMPCL are easily synthesized and the pendant activated bromides can either initiate a "grafting-from" reaction by ATRP, or be dehydrohalogenated into acrylic-type double bonds (making the chains crosslinkable) or be quaternized (making the chains amphiphilic or water-soluble) as shown in scheme 7.[13]



Scheme 7. Possible derivatizations of ε-CL/BMPCL copolyesters

Unsymmetrical difunctional initiators

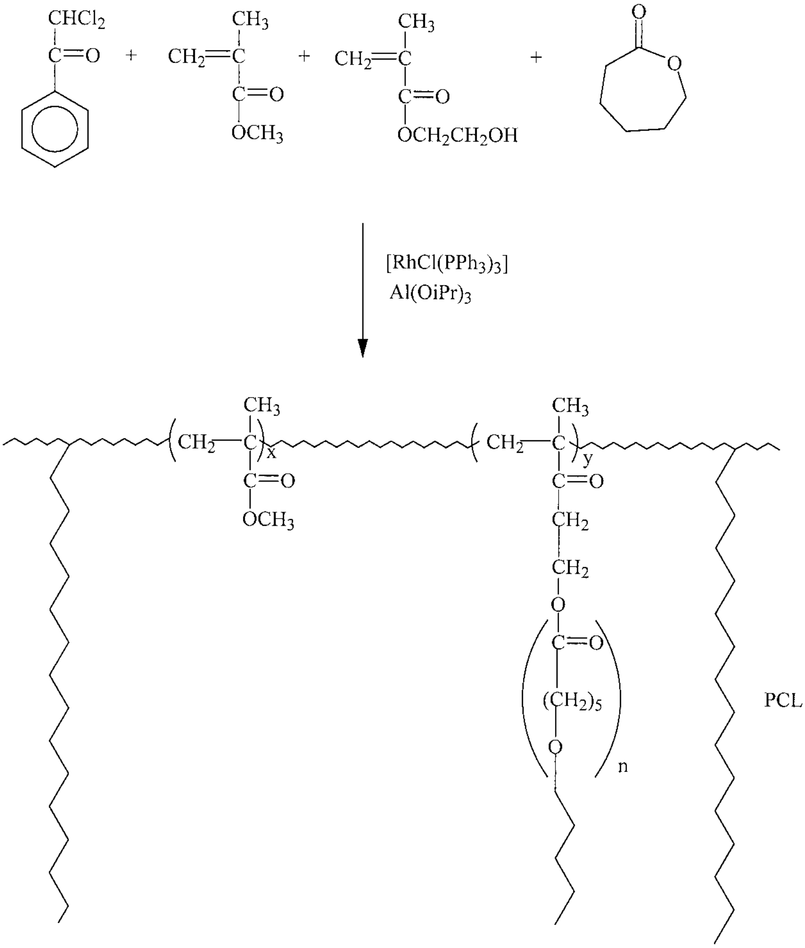
A substantial improvement of the concept of performing dual living/controlled polymerization from a single molecule was improved by C.J. Hawker and J.L. Hedrick who proposed to use a dual initiator for the living/controlled polymerization of dissimilar monomers without the need of intermediate activation or transformation steps.[14] Coexistence of hydroxyl groups with either alkoxyamine or tribromo initiating groups was found to be compatible with the experimental conditions for both the living ROP of ε-caprolactone and nitroxide-mediated or atom transfer controlled radical polymerizations (scheme 8).



Scheme 8. Synthesis of diblocks from a dual initiatior active in CRP and ROP

The possible synthesis of a variety of well-defined block copolymers was demonstrated. For instance, from a hydroxyl-functionalized alkoxyamine, either the living ROP of ε-caprolactone (lactides, γ-functional ε-CL, glycolide, cyclic anhydrides...), or the CRP of styrene (other vinyl monomers) can be carried out with formation of low polydispersity macroinitiators. These polymeric initiators can then be used to initiate the living/controlled polymerization of the other monomer system without the need for intermediate steps. When an activated bromide is used instead of an alkoxyamine, the copolymerization can be extended to (meth)acrylate monomers. Therefore, this strategy allows novel well-defined block copolymers to be readily synthesized under nondemanding experimental conditions.

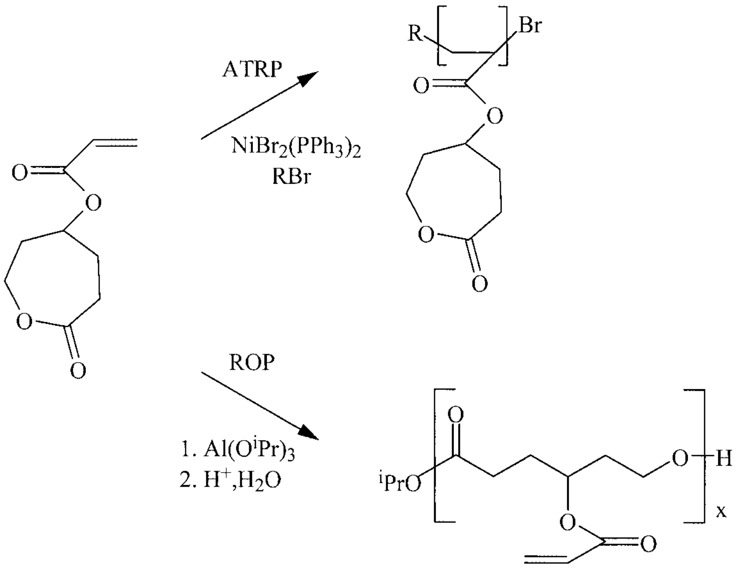
Last but not least, the sequential two-step method discussed above can be turned into a one-step process whenever the two monomers and initiating/catalytic systems are compatible and tolerate each other, and the kinetics of the two simultaneously occurring reactions is comparable at the selected temperature. This unusual one-step block copolymerization was successfully carried out in bulk, in the cases illustrated in scheme 8.[15] This one-step approach was also extended to the synthesis of graft copolymers, particularly of poly(MMA-graft-polyε-CL) (scheme 9). The simultaneous CRP of a mixture of MMA and HEMA was initiated by 2,2-dichloroacetophenone and catalyzed by $RhCl(PPh_3)_3$, and the ROP of ε-CL was promoted by the hydroxyl group from HEMA and Al isopropoxide as catalyst. The reaction was conducted at 50°C, in bulk conditions, and the molecular weight of the PMMA backbone (after complete hydrolysis of the polyester grafts) was the value expected from the monomer-to-initiator molar ratio.



Scheme 9. One-step synthesis of poly(MMA-graft-poly ε-caprolactone)

Unsymmetrical Difunctional Monomers

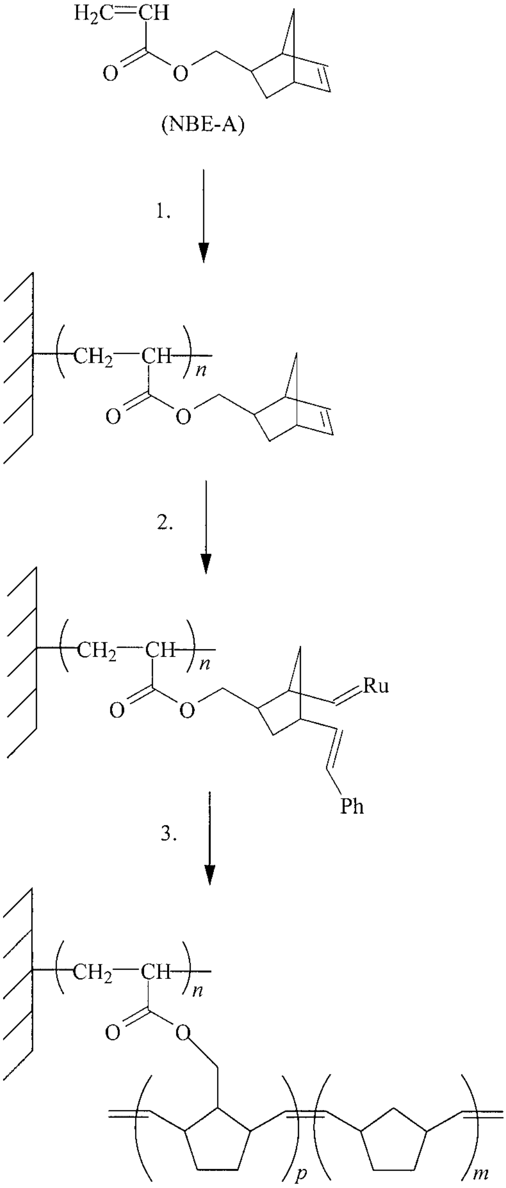
4-(acryloyloxy)-ε-caprolactone (AOCL) is a novel difunctional acrylate-lactone monomer which can be selectively polymerized in a living/controlled way by two different polymerization mechanisms, i.e., ATRP and ROP (scheme 10).[16]



Scheme 10. Alternative polymerization routes for 4-(acryloyloxy)-ε-caprolactone

This scheme illustrates that the ATRP of AOCL leads to new polyacrylates containing pendant caprolactone groups. The molecular weight is controlled and the polydispersity is low ($M_w/M_n \sim 1.1$ in the range of 10-25000 M_n). Alternatively, ROP of AOCL makes new functional aliphatic polyesters available with a good control of the molecular parameters. The pendant acrylate groups in the copolyester chains are sensitive to thermally or photochemically generated radicals, which opens the way to cross-linkable biodegradable materials.

Norbornenylmethylene acrylate (NBE-A) is another example of unsymmetrical difunctional monomer, that has been recently electropolymerized (through the acrylate double bond) and polymerized by ring-opening metathesis (ROMP).[17] It must be pointed out that the electroreduction of monomers of the (meth)acrylate type at an appropriate potential leads to the chemisorption of a thin polymer film onto the cathode.[18,19] Moreover, well-defined and highly active catalysts in ROMP of cycloolefins were recently reported by Schrock[20] and Grubbs.[21] Therefore, the electrografting process was combined with living ROMP in order to overcome the intrinsic limitations of electrochemistry, i.e. very low thickness of the "electrografted-from" film (< 100 μm) due to the rapid passivation of the electrode and restriction to (meth)acrylates that contain no protic functions. Scheme 11 illustrates the strategy that was worked out.

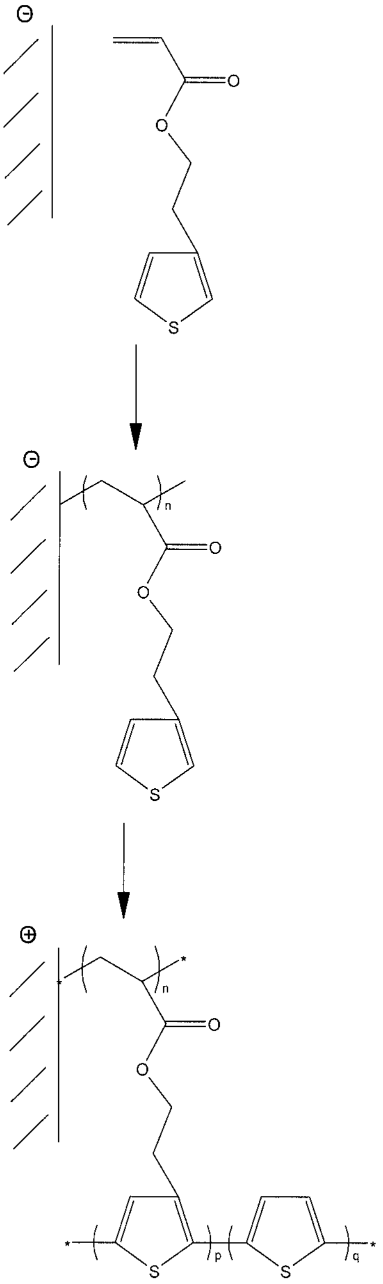


Scheme 11. Combination of electrografting and ROMP for the dual NBE-A monomer

Upon cathodic electropolymerization of NBE-A at a well-defined potential, the cathode is passivated within a few seconds. The analysis of the insulating film by X-ray Photoelectron Spectroscopy (XPS) confirms a chemical structure that fits the expectedly grafted poly(NBE-A). The Grubbs ROMP catalyst was then attached to the poly(NBE-A) coated surface by dipping the modified electrode into a solution of this Ru containing catalyst. After careful washing off of the excess catalyst, the substrate was exposed to a solution of NBE and the "grafting from" polymerization occurred. The film thickness is easily controlled by the monomer concentration and the polymerization time. This mixed electropolymerization/ROMP technique is very versatile, e.g., it can be carried out on metallic (steel, copper...) plates and wires, and on carbon plates and fibers. The brush (of polyNBE, in scheme 11) which is grafted from the primary polyacrylate coating can be changed depending on the pendant "monomer" attached to this polyacrylate coating and the chemistry worked out for the implementation of the "grafting from" step. The adhering top coating can thus be designed for imparting specific functionality to the surface, e.g. for sensor development.

The unsymmetrical 3-(2-acryloyloxyethyl)thiophene and N-(2-acryloylethyl(pyrrole)) monomers were recently synthesized with the purpose to prepare electrically conducting polymers strongly adhering to metallic surfaces by the aforementioned electrochemical technique.[22] Scheme 12 shows the two-step procedure which consists of the cathodic electrografting of polyacrylate chains bearing a precursor of the conducting polymer in the ester group (thiophene, in scheme 12), followed by the anodic polymerization of this precursor (in the presence or not of additional monomer (i.e. thiophene) in solution). The strongly adhering two-component film is conducting and electroactive, as shown by cyclic voltammetry (reversible doping and dedoping).

The unusual electrografting of acrylate containing dual monomers is thus a very promising technique to provide an organic coating with strong adhesion to inorganic (conducting) substrates with the additional flexibility in the choice of the chemical properties via the second polymerizable moiety of the monomer.



Scheme 12. Two-step electropolymerization of 3-(2-acryloyloxyethylthiophene)

Conclusion

The few examples discussed in this paper point out that single difunctional molecules which associate two different initiators or two different monomers or one monomer and one initiator have a remarkable potential in macromolecular engineering. Novel two-component (and usually multiphase) materials can accordingly be tailored, and the surface properties of inorganic substrates can be modified by strongly adhering organic coatings with various chemical properties.

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