Macromol. Symp. ***153****, 209–216 (2000)*

New Polymer Architectures by Cationic Ring-opening Polymerization

E. J. Goethals*, M. Dubreuil, Y. Wang, I. De Witte, D. Christova, S. Verbrugghe, N. Yanul, L. Tanghe, G. Mynarczuk and F. Du Prez

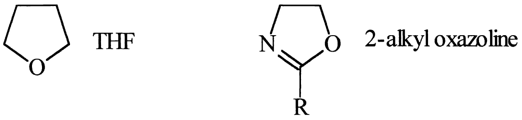
Department of Organic Chemistry, Polymer Division, University of Ghent, Ghent, Belgium.

SUMMARY: The use of the living cationic ring-opening polymerization of tetrahydrofuran (THF) and 2-alkyl oxazolines to prepare a number of new well defined polymer architectures is illustrated by three examples. Endgroup functionalized star-shaped polyTHF's were obtained by functional initiation in combination with end-capping with a multifunctional termination reagent. In this way, star-shaped and comb-shaped polyTHF multi-macromonomers were prepared.
A-B-A block-copolymers in which B is polyTHF and A poly(ethylene oxide) (PEO) or linear polyethylenimine (LPEI) were prepared. The influence of complexation of the A segments with NaSCN (specific for PEO) or with $CuCl_2$ (specific for LPEI) on the physical properties of these copolymers have been investigated.
Amphiphilic segmented polymer networks were prepared by co-polymerization of polyTHF-α,ω-bis acrylate with N-vinylcaprolactam.

Introduction

It is well known that living polymerizations are ideally suited for the design of well-defined polymer architectures. In the present chapter, the synthesis of such new polymers, with expectedly new tailored properties, based mainly on cationic ring-opening polymerizations, will be described.

Two types of cyclic monomers, known to lead to highly living polymerizations, are tetrahydrofuran (THF) and the 2-alkyl oxazolines.



CCC 1022-1360/00/$ 17.50+.50/0

PolyTHF is hydrophobic polyether with a glass transition temperature (Tg) of -80°C and a melting point (Tm) of 40°C. It is commercially available as the α,ω-dihydroxy compound of moderate molecular weight (polytetramethylene glycol, PTMG). Its main use is as starting material in the synthesis of segmented polymers such as PUR's and TPE's.

The properties of poly(alkyl oxazoline)s depend on the nature of the alkyl substituent. With R=methyl (methyl oxazoline, MeOx), the polymer is water-soluble and is amorphous with a Tg of 65°C. Poly(ethyl oxazoline) (polyEtOx) is still water-soluble but has been described to posses a lower critical solution temperature (LCST) in water. Its Tg is around 45°C. With larger alkyl groups, the corresponding polymers are water-insoluble.

Hydrolysis of poly(alkyl oxazolines) leads to linear polyethylenimine (LPEI).

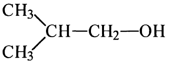
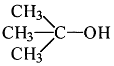
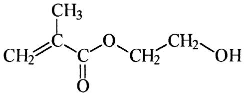
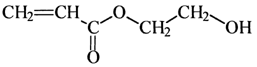
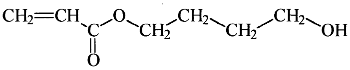
In the present work we explored the possibilities offered by these polymerizations to design a number of new polymeric architectures. For this purpose, the living polymerizations were first used to prepare well defined endgroup-reactive prepolymers (telechelic polymers and macromonomers) which were subsequently combined with other polymers. In this way, a number of new block-copolymers, star-shaped polymers, polymer networks etc. were prepared.

Synthesis of heterotelechelic polyTHF and polyTHF (multi)macromonomers

Telechelic polyTHF can be prepared by end-capping of bifunctionally living polymer, which is obtained by polymerization initiated with trifluoromethane sulfonic acid anhydride (triflic anhydride)(1,2). This method cannot be used for the preparation of heterotelechelic polymers, i.e. polymers containing two different functional endgroups on each polymer chain. For this, a combination of functional initiation and functional termination is necessary. We found that functional initiation of THF polymerization can be achieved with functionalized triflate esters. These esters are obtained *in situ* from triflic anhydride and an alcohol that contains a second (eventually protected) functional group, in the presence of a non-nucleophilic proton trap. The synthesis of these triflate esters and their ability to initiate the polymerization of THF were investigated. Table 1 gives a survey of the efficiency of the triflate esters formation for different simple alcohols and for a number of functionalized alcohols. In some cases, the corresponding ether, formed by reaction of the triflate ester with a second molecule of alcohol, is formed as a side product. This was the case for 2-hydroxyethyl (meth)acrylate (HEA and

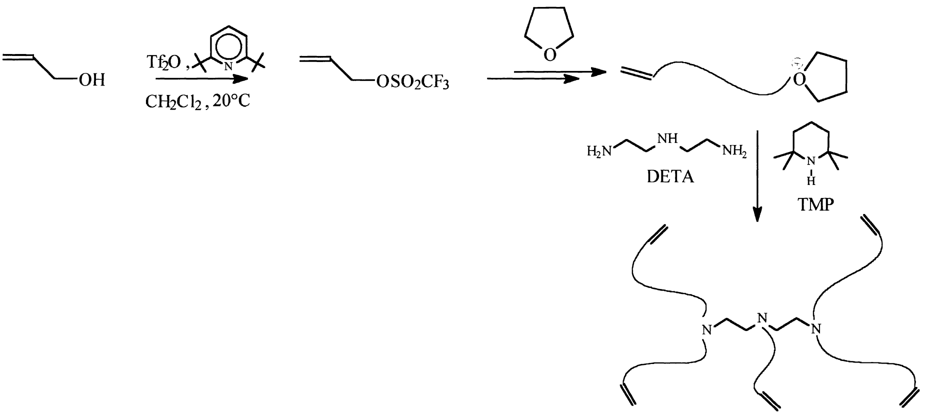
HEMA). Therefore, for the synthesis of acrylate-terminated polymer, 4-hydroxybutyl acrylate (HBA) had to be used(3).

Table 1: Synthesis of triflic esters from triflic anhydride and alcohols.

R-OH	Ester formation(%)*	Remarks
CH_3OH	100	-
$CH_3—CH_2—OH$	100	-
$CH_3—CH_2—CH_2—OH$	100	-
$CH_3—CH_2—CH_2—CH_2—OH$	100	-
	100	-
	<60	formation of isobutene
$CH_2{=}CH—CH_2—OH$	97	traces of diallylether
$CH{\equiv}C—CH_2—OH$	100	-
	<70	substantial formation of ether
	<70	substantial formation of ether
	100	-

* After 1hr. at 20°C in dichloromethane

The end-capping reaction of living polyTHF with amines is well documented(4-6). Recently, we described that, using diamines or triamines, star-shaped polyTHF is obtained(7). In these star-shaped polymers, the tendency to crystallize is strongly reduced. Functional initiation with HBA/Tf2O or allyl alcohol/Tf2O, combined with end-capping with a di- or triamine, leads to the corresponding star-shaped multi-macromonomers:



Macromonomers with a still higher functionality could be obtained by using LPEI as a terminating agent. It was observed that, for polyTHF with molecular weight of 2300, up to 70% of the amino groups of LPEI could be substituted by polyTHF chains. In this way, comb-shaped multi-macromonomers containing a variable number of acrylate endgroups were prepared.

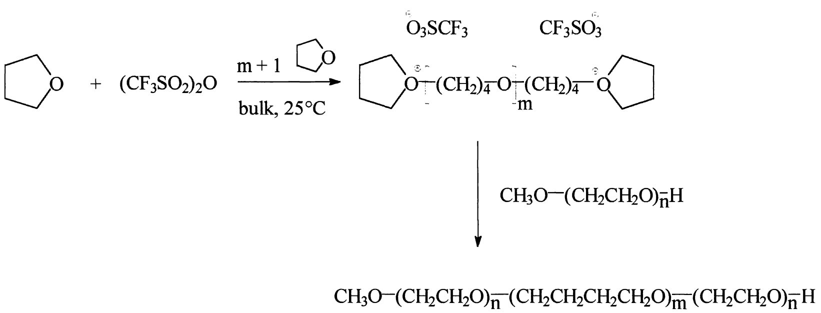
It is expected that these multi-macromoners, containing a fraction of free LPEI, will adsorb to metallic surfaces and can subsequently be polymerized or copolymerized to form stable coatings.

Another type of high functionality star-shaped multi-macromonomers is obtained when the living polymerization is end-capped with amino-dendrimers. The 3rd generation propylenimine dendrimer, containing 16 primary amino functions, could be grafted with 16 living polyTHFs.

ABA-triblock-copolymers with polyTHF as B-block and complexing polymers as A-blocks

Two types of these block-copolymers were synthesized. In the first series, the A-blocks were poly(ethylene oxide) (PEO) and in the second series, the A-blocks were LPEI.

The PEO-polyTHF-PEO copolymers were prepared by polymerization of THF initiated with triflic anhydride, followed by end-capping of the polymers with polyethylene glycol monomethyl ether:



It is known that PEO forms complexes with salts such as sodium thiocyanate(8). The melting points of these complexes are at appr. 175°C. Addition of sodium thiocyanate to the block-copolymers, transforms the low-melting materials into high melting thermoplastic elastomers(9).

LPEI-polyTHF-LPEI block-copolymers were obtained by adding MeOx to bifunctionally living polyTHF, and subsequent polymerization of the MeOx at 70°C in acetonitrile, which leads to the polyMeOx-polyTHF-polyMeOx triblock copolymers(10), followed by hydrolysis. These block-copolymers are semi-crystalline with Tm's at appr. 30°C due to the polyTHF segments. At room temperature, these materials are brittle and it is not possible to make films of them. Above the melting temperature, they directly turn into viscous liquids. When copper(II) chloride is added, the mechanical properties change dramatically due to the formation of complexes between the LPEI segments and $CuCl_2$. The mechanical properties depend on the length of the LPEI blocks and on the [N]/[Cu] ratio. As an example, Fig. 1 shows the shear modulus of the complexed materials as a function of temperature for a block copolymer LPEI-polyTHF-LPEI with molar ratio of [N]/[Cu] form 16/1 to 4/1. It is clear that the increase of the concentration of copper ions leads to an increase in intermolecular interactions, resulting in an increase of the rubbery phase temperature region.

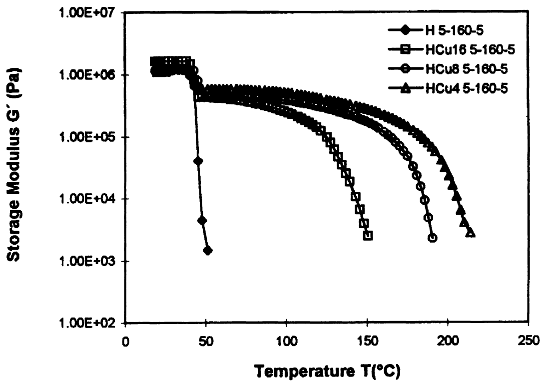


Fig. 1 Temperature dependence of shear storage modulus for LPEI-polyTHF-LPEI (H 5-160-5: block copolymer with MW ca. 500-15600-500) and its Cu-complexes with molar ratio of [N]/[Cu] = 16, 8 and 4.

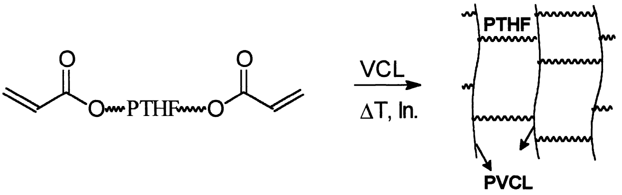
Synthesis of amphiphilic segmented polymer networks (ASPN's)

ASPN's are networks in which one polymer chain is crosslinked by means of another polymer chain of opposite phylicity. These polymers lead to materials with interesting physical properties(11-14). One striking property is the fact that the surface of these materials adopts itself to the phylicity of the material with which it is in contact.

One appropriate method for the synthesis of ASPN's is the copolymerization of a "bis-macromonomer", i.e. a polymer containing two (co)polymerizable endgroups, with a monomer of opposite phylicity.

In the present work, we have used polyTHF-bis-macromonomer as a hydrophobic segment to be copolymerized with a hydrophilic comonomer, and polyMeOx bis-macromonomer as hydrophilic segment, to be copolymerized with a hydrophobic comonomer.

One of the potential uses of these materials is in membrane technology, more specifically for the separation of aqueous mixtures(12). In this case it seems to be of importance that the hydrophylic-hydrophobic balance of the materials can be adjusted or be changed eventually during the process. Therefore, we chose a component which shows a LCST behavior in water, i.e. that becomes insoluble above a certain critical temperature so that the hydrophilicity can be changed by increasing the temperature. As an example, segmented networks of polyTHF with poly(N-vinyl caprolactam) (PVCL), which is reported to have a LCST at appr. 36°C, were prepared(15):



Bis-macromonomers derived from MeOx have been prepared by end-capping of bifunctionally propagating living polyMeOx with acrylate salts(16). The copolymerization of these bis-acrylates with methyl methacrylate (MMA), leads to the corresponding ASPN's. However, the physical properties of the obtained materials were poor. ASPN's made from polyEtOx and MMA, have better mechanical properties and due to the fact that polyEtOx has LCST properties in water, materials with temperature-controllable hydrophilicity are expected to be obtained.

Conclusions

Based on the living character of the CROP of THF and 2-alkyl oxazolines, a number of well-defined functional polymers have been prepared. The properties of the new materials can be varied over a wide range thanks to the control of the structure of the polymers, which are in turn due to the high level of knowledge of the mechanisms governing these polymerization systems. This allows the polymer chemist to perform precise "macromolecular engineering".

References

1. S. Smith, A. Hubin, *J. Macromol. Sci. – Chem.*, **A7**, 1399 (1973)
2. F. D'Haese, E.J. Goethals, *Br. Polym. J.*, **20**, 103 (1988)
3. M. Dubreuil, E.J. Goethals, *Macromol. Chem. Phys.*, **198**, 3077 (1997)
4. A. Cunliffe, D. Richards, F. Robertson, *Polymer*, **22**, 108 (1981)
5. D. Hartley, M. Hayes, D. Richards, *Polymer*, **22**, 1081 (1981)

6. P. Cohen, M. Abadie, F. Schué, D. Richards, *Polymer*, **23**, 108 (1982)
7. P. Van Caeter, E.J. Goethals, *Macromol. Rapid Commun.*, **18**, 393 (1997)
8. B. Bogdanov, Chr. Uzov, M. Michailov, *Acta Polym.*, **43**, 202 (1992)
9. I. De Witte, E. Goethals, *Polym. Adv. Technol.*, **10**, 1 (1999)
10. S. Kobayashi, K. Hiroishi, M. Tokunoh, T. Saegusa, *Macromolecules*, **20**, 1496 (1987)
11. F. Du Prez, D. Christova, E.J. Goethals, "Amphiphilic multicomponent polymer networks: design, evaluation and applications", in: *the Wiley Polymer Networks Group Review Series*, vol. **2**, B. Stokke, A. Elgsaeter, Eds., John Wiley & Sons, West Sussex, UK, in press 1999
12. F. Du Prez, E.J. Goethals, R. Schué, H. Qariouh, F. Schué, *Polym. Int.*, **46**, 117 (1998)
13. Y. Tezuka, Y. Murakami, T. Shiomi, *Polymer*, **39**, 2973 (1998)
14. F. Du Prez, E.J. Goethals, "Segmented polymer networks by cationic polymerization: design and applications", in: *Cationic Polymerization and Related Processes*, J. Puskas, Ed., NATO-ASI Series, Series E, Kluwer Academic Publisher, Dordrecht, Nederland, 1999
15. N. Yanul, S. Verbrugghe, E.J. Goethals, Y. Kirsh, F. Du Prez, *Macromol. Rapid Commun.*, submitted (1999)
16. D. Christova, R. Velichkova, E.J. Goethals, *Macromol. Rapid Commun.*, **18**, 1067 (1997)

Acknowledgements

The Belgian Programme on Interuniversity Attraction Poles (IUAP P4/11) initiated by the Belgian State, Prime Minister's office, is acknowledged for financial support.