***Star*- and *comb*-polytetrahydrofuran multimacromonomers: Synthesis and network formation**

Eric J. Goethals*, Marjorie F. Dubreuil, Leen Tanghe

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

SUMMARY: *star*- and *comb*-Polytetrahydrofuran (polyTHF) multimacromonomers have been synthesized using 4-(acryloyloxy)butyl triflate as initiator and multifunctional amines, such as diethylenetriamine, linear poly(ethylenimine) or poly(propylenimine) dendrimer, as end-capper. These reactive grafted polymers have been polymerized by photoinitiation as such or in the presence of butyl acrylate (BuA) leading to segmented networks. Elastomeric materials showing a single homogeneous amorphous phase and a strongly reduced crystallinity of the polyTHF fraction are obtained.

Introduction

Since several years, research in the field of polymer chemistry has aimed at the synthesis of sophisticated macromolecules with well-defined architecture, i.e. with a controlled molecular weight, a controlled molecular weight distribution and a well-defined end-group functionality. A way to control these different parameters is the use of living polymerizations. The cationic ring-opening polymerization of tetrahydrofuran (THF) proceeds by a living mechanism under appropriate reaction conditions. In previous articles1,2) we described the functional initiation of THF polymerization with functionalized triflate esters. Recently, well-defined star polyTHFs have been obtained by termination with multifunctional amines3). In the present work, combination of functional initiation and multifunctional termination with amines, leading to well-defined *star*- and *comb*-polyTHF multimacromonomers, will be described. These structures, which contain a controllable number of acrylate end groups, have been homopolymerized or copolymerized with butyl acrylate (BuA). Some mechanical and physicochemical properties of the thus obtained materials will be discussed.

Synthesis of *star*- and *comb*-polyTHF multimacromonomers and networks

4-(Acryloyloxy)butyl trifluoromethanesulfonate (HBAOTf) was synthesized by reaction of equimolar amounts of 4-hydroxybutyl acrylate and trifluoromethanesulfonic anhydride in dichloromethane at 20 °C1). The trifluoromethanesulfonic acid liberated by the reaction is trapped with a non-nucleophilic proton trap, 2,6-di-*tert*-butylpyridine. THF is then added and the polymerization is carried out *in situ*. Termination of the polyTHF living chains with diethylenetriamine (DETA) leads to *star*-polyTHF multimacromonomers containing up to five acrylate end groups on arms with molecular weights equal or lower than 2000.

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"Superstar" polyTHFs are obtained by grafting living polyTHF on poly(propylenimine) dendrimers[4,5)]. DAB(PA)$_{32}$, for example contains 32 primary amino functions situated in the shell of the dendrimer. This dendrimer reacts with at least 16 living polyTHF chains of molecular weight 2000, forming a 16-armed star polymer containing a polyamine core. If the living polyTHF was produced with HBAOTf as initiator, the corresponding star multimacromonomer is formed.

comb-PolyTHF multimacromonomers are obtained using linear poly(ethylenimine) (LPEI) as multifunctional end-capper. In this case, up to 60 acrylate end groups can be introduced on the polymer chain (M_n 4500) on arms with molecular weights lower or equal to 2300.

The reactive grafted structures have been crosslinked as such or in the presence of a comonomer (BuA) via photoinitiation, leading to segmented networks (Schemes 1 and 2).

Properties of *star*-polyTHF-multimacromonomer segmented networks

PolyTHF is a semicrystalline polymer with a glass transition temperature of –86 °C and a melting point around 40 °C. Depending on the molecular weight, the crystallinity of the polyTHF segments varies between 20 and 80 %. PolyBuA is an amorphous polymer with a glass transition temperature around –54 °C.

For networks based on *star*-polyTHF multimacromonomers and BuA, differential scanning calorimetry (DSC) analyses and dynamic mechanical thermal analyses (DMTA) have revealed the presence of a single homogeneous amorphous phase, whose T_g is situated between the T_g of polyTHF and that of polyBuA, and complete disappearance of crystallinity in the polyTHF segments (Fig. 1). Only networks based on 100% polyTHF show a melting peak. Even in this case, a crystallinity degree of only 10 % is recorded which is much less than the non-crosslinked *star*-polyTHFs (around 30 - 40 %) or networks based on linear polyTHF bismacromonomers (around 30 %).

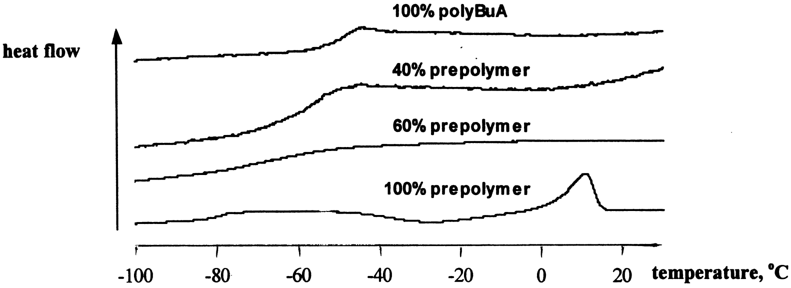
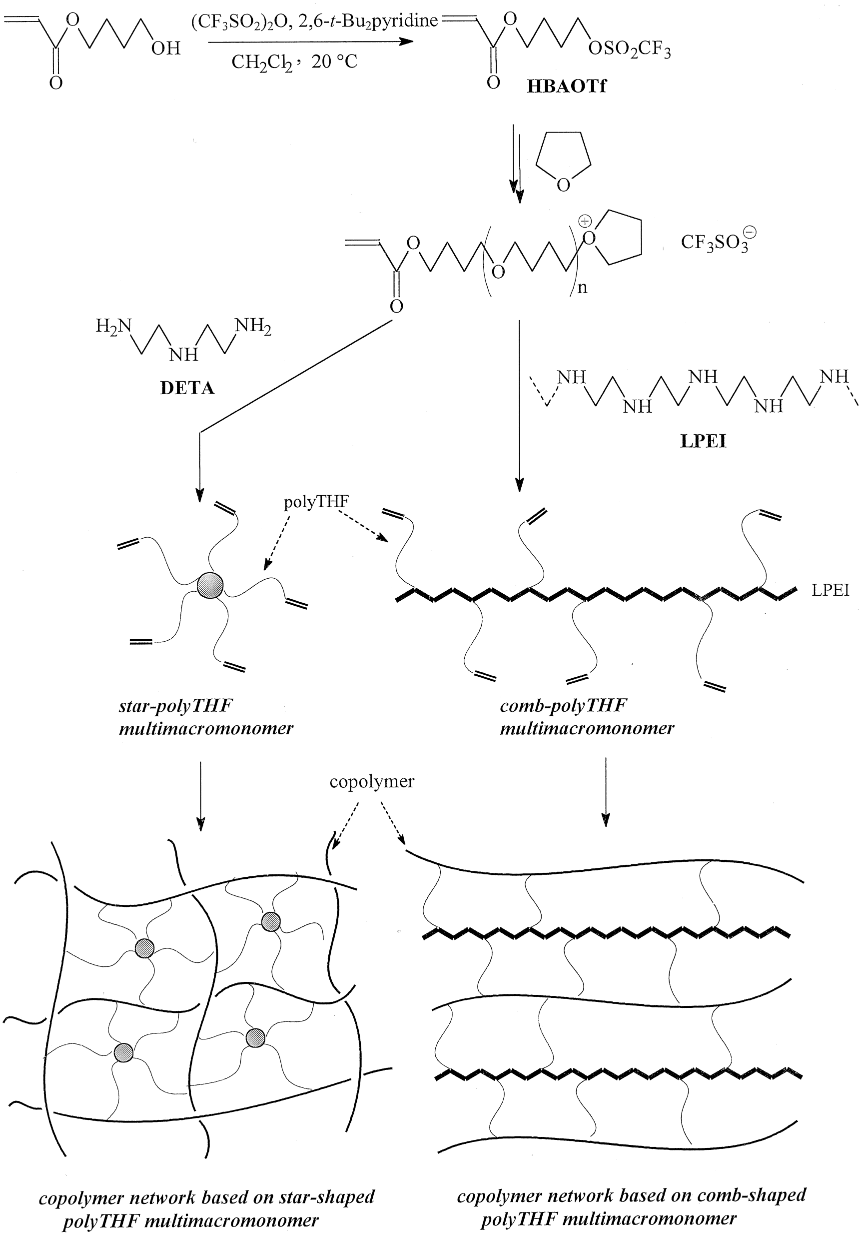
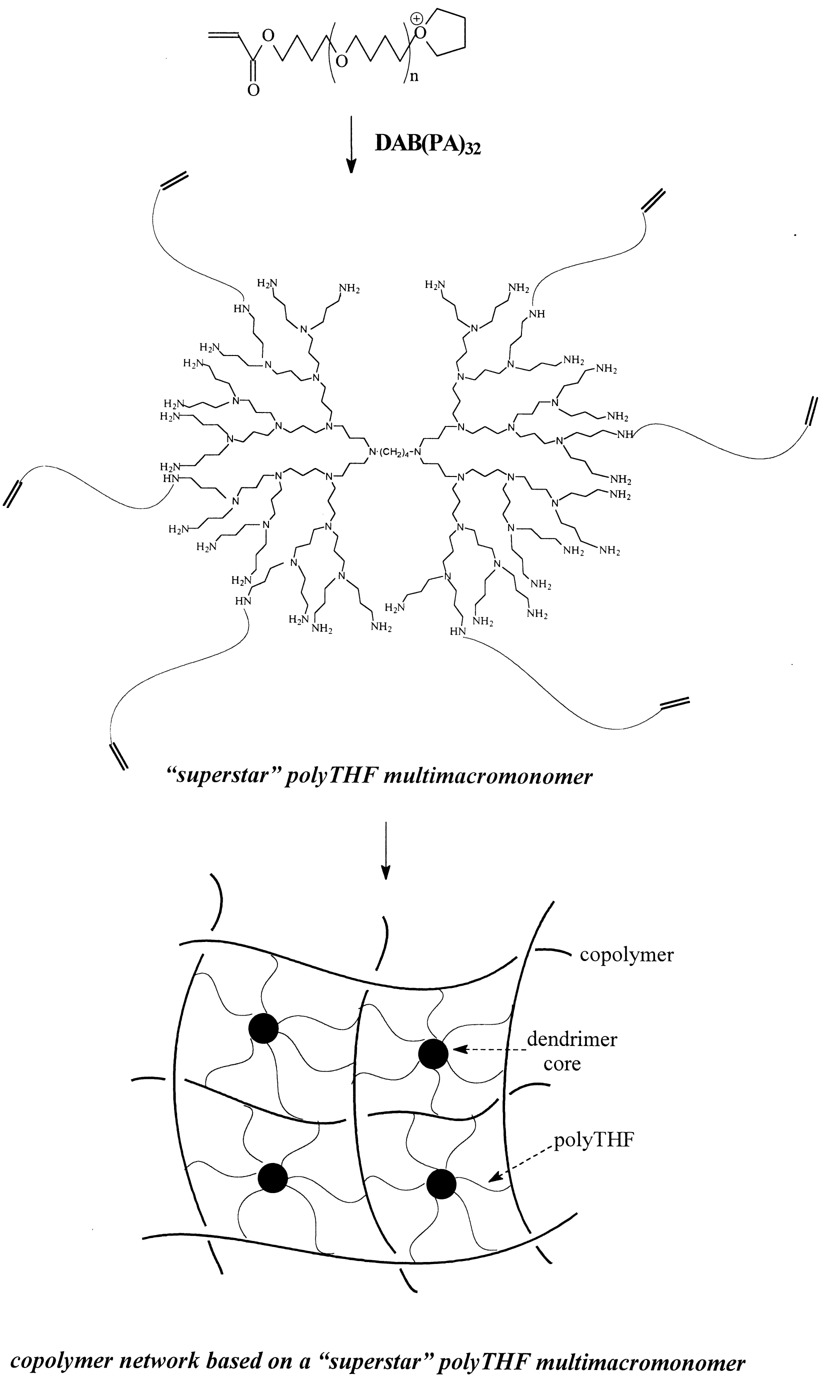


Fig. 1. DSC curves for a series of networks based on three-arm *star*-polyTHF multimacromonomers ($M_{n(arm)}$ 2500) and BuA



Scheme 1. Synthesis of copolymer networks based on *star*- and *comb*-polyTHF multimacromonomers



Scheme 2. Synthesis of copolymer networks based on "superstar" polyTHF multimacromonomers

In DMTA, only one peak in tan δ could be observed corresponding to the T_g of the copolymer network (Fig. 2). No transition due to melting could be recorded.

These materials are transparent and flexible for all compositions. Stress-strain measurements have shown low Young moduli (lower than 3 MPa), and elongations at break up to 100 %.

The properties of networks based on "superstar" multimacromonomers derived from the dendrimer are still under investigation.

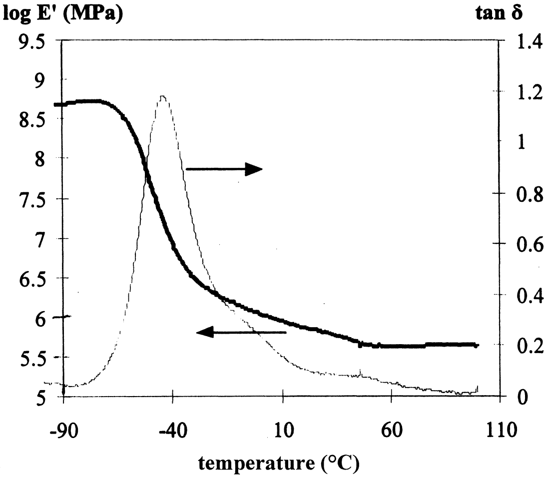


Fig. 2. Storage modulus and tan δ as functions of temperature for a network based on 60% three-arm *star*-polyTHF multimacromonomer ($M_{n(arm)}$ 2400) and 40 % of BuA

Properties of *comb*-polyTHF-multimacromonomer segmented networks

Materials based on *comb*-polyTHF multimacromonomers and BuA show – like the *star*-polyTHFs - only a single homogeneous amorphous phase. Some crystallinity could be recorded for the polyTHF segments at high polyTHF contents (Fig. 3). However, this crystallinity is strongly reduced compared with non-crosslinked *comb*-polyTHFs (around 40 %) or networks based on linear polyTHF bismacromonomers.

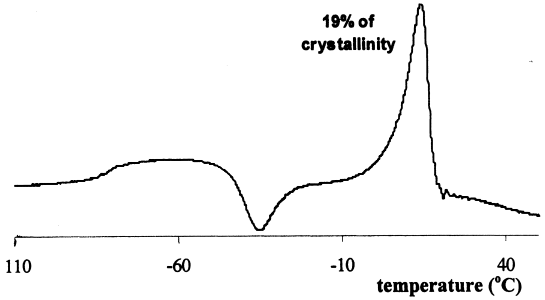


Fig.3.
DSC curve for a network based on 80 % of *comb*-polyTHF multimacromonomer ($M_{n(arm)}$ 2000, grafting degree 25 %) and 20% of BuA

In DMTA, several transitions can be observed (Fig. 4). The broad peak in tan δ at low temperatures corresponds to the amorphous phase. An increase in the E modulus is then observed which is attributed to a partial crystallization of the polyTHF segments. Finally, a second peak in tan δ is observed around 25 °C corresponding to the melting process of the crystalline polyTHF segments.

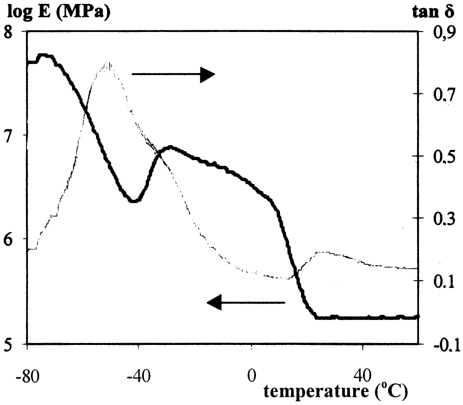


Fig.4.
Storage modulus and tan δ as functions of temperature for a network based on 80 % of *comb*-polyTHF multimacromonomer ($M_{n(arm)}$ 2000, grafting degree 50 %) and 20 % of BuA

Although these materials clearly show some degree of phase separation (as evidenced by the presence of some crystalline polyTHF), they are transparent and flexible for all compositions. This is attributed to a small size of crystalline domains. They have low Young moduli (lower than 2 MPa) and elongations at break up to 370 %, increasing with the comonomer content.

Conclusions

Copolymer networks based on *star*-polyTHF or *comb*-polyTHF multimacromonomers and BuA have been synthesized. In these complex structures, the molecular weight and grafting degree of polyTHF and, therefore, the concentration of reactive end groups can be controlled. The structure of the polyTHF precursor has a strong influence on the presence or absence of crystallinity in the polyTHF segments, on the crosslinking density, and hence on mechanical properties of the resulting materials.

References

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