



# Rheological characterization of multiarm star copolymers



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## ABSTRACT

Detailed rheological characterization has been performed for star-shaped graft copolymers, prepared from polycaprolactone (PCL) and hyperbranched polyester Boltorn H40 (BH40). As the reactant ratio increased from BH40:PCL = 1:1 to 1:10 the molar mass of the copolymer increased as well. Flow behavior has been determined under destructive shear conditions for the polymer melts at 75 °C, at which Cox–Merz rule has been applied for all the copolymers used. The results show that the addition of PCL to BH40 decreases the viscosity of copolymer with increasing molar mass, but only to the ratio BH40 vs. PCL = 1:4. Above that ratio a slight increase in viscosity is observed for the ratio 1:5, while viscosity significantly increases for the copolymer with the highest reactant ratio. Temperature dependence of viscoelastic properties has been performed in linear viscoelastic range at cooling/heating rate of 10 °C min<sup>-1</sup>. The results strongly coincides with the results of DSC measurements, moreover, the combination of rheological and thermal characterization provides a deeper insight into structural changes during cooling/heating process.

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## 1. Introduction

Polycaprolactone (PCL) is aliphatic, semicrystalline polyester with a broad spectrum of practical or potential applications, which is gaining an increased scientific interest in the last 10–15 years. The main property of PCL, which makes it very interesting, is its biodegradability. PCL can be degraded by microbes [1] and enzymes [2] in nature environment, whereas it cannot be degraded enzymatically in the body [3]. Therefore, it can be used in medicine (for drug delivery, as a scaffold for tissue repair, etc.) and for food packaging. Various bio-based composites and nanocomposites have been prepared with starch, cellulose, nanocellulose and other natural fibers in order to improve mechanical properties without sacrificing biocompatibility and biodegradability [4,5].

Another feature that makes PCL so interesting is its miscibility with many polymers, which makes it suitable to tailor the mechanical and physical properties of polymers [6]. The miscibility of PCL with poly(vinyl chloride) (PVC) seems to be the most interesting because PCL can be used as a replacement for phthalate-based plasticizers [7]. The stability of PVC/PCL blends have been tested for various conditions such as photodegradation [8], soil microorganism [9] and aqueous environment [10].

In recent years there has been an increasing interest in the synthesis of star-shaped [11–13] and hyperbranched (HB) [14–16] polycaprolactone polymers and copolymers, which have better solubility, lower viscosity and melting temperature as

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well as a lower degree of crystallization compared to their linear analogues. Potential applications for those polymers are diverse, from epoxy toughener, PVC plasticizer, to various biomedical applications [17–20].

Recently, we presented a simple method of grafting PCL from HB polyester Boltorn™ H40 (BH40), which does not require the addition of a catalyst, neither the extensive drying off  $\epsilon$ -caprolactone [21], because *p*-toluenesulfonic acid, which is added as a catalyst during the synthesis of BH40, acts also as a catalyst for CL grafting.

Multi-arm star-shaped copolymers based on Boltorn™ hyperbranched polyesters and PCL have already been synthesized [20–24] but with a much higher reactant ratio (up to 1:70) and different synthetic procedure as in the present article. Potential applications for such polymers were drug delivery [20] and powder coatings [23,24]. The molar mass of star copolymer was an order of magnitude higher than that of a linear PCL. The combination of high molecular weight and low viscosity is an advantage for a powder coating resin since low molecular weight resins with low viscosity could cause problems such as sagging and unwanted penetration of a porous substrate [23,24].

The rheological behavior of the polymers is the most important factor to consider when processing polymer melt, because it gives information about the internal resistance to polymer shaping and, in the case of coatings, to levelling. Numerous studies on polymer structure-properties relation can be found in literature [25–27]. Different authors have shown that branched polymers display significantly different rheological properties compared to linear polymers and polymer networks. For example, Wood-Adams et al. [28] showed that at low shear rates the viscosity of branched chains could be 100 times greater than that of linear polymers of equal molecular weight, while at high shear rates, the viscosity of the branched polymers may be lower. This is the result of the enhanced shear-thinning behavior of branched polymers. Nevertheless, in general rheological properties of polymers depend on various parameters, like the degree of branching, branch length, and chain architecture.

In the present work a systematic study of rheological behavior was performed for graft copolymers of Boltorn™ hyperbranched polyesters and PCL having various chain lengths. We focused on temperature dependent rheological properties, which were studied in the range of linear viscoelastic response (LVR). Linear properties, i.e. the storage  $G'$  and loss modulus  $G''$ , represent probably the richest source of information regarding molecular structure [28]. The techniques, used for the measurements of linear properties, offer a combination of high precision, ease of use and a broad range of time scales (frequencies). In shear mode, on the other side, large, rapid deformations appear which involve nonlinear viscoelasticity and yield data that are relatively deficient in detailed information regarding molecular structure.

## 2. Experimental

### 2.1. Materials

The details of the synthesis and characterization of BH40:PCL copolymers have already been reported [21]. Shortly, grafting of PCL from BH40 (regular type) was performed in bulk. BH40 was put in a weighted two-necked round bottom flask (100 ml) equipped with the magnetic stirrer, water condenser and rubber septum. The content of the flask was purged with nitrogen through the injection needle stabbed into rubber septum, stirred and heated to 145 °C. Then, the purging was stopped and CL was injected through the rubber septum. A weight ratio of BH40 to CL, which corresponds to molar ratio of –OH groups to CL, was from 1:1 (BH40g1) to 1:10 (BH40g10). Reaction time increased from 3 h to 24 h by increasing the reactant ratio to ensure quantitative polymerization.

Commercial linear PCLs were kindly donated by Perstorp, Sweden. Capa 6430 and Capa 6800, which were used for our study, were high molecular weight linear polyesters derived from caprolactone monomer and differed in mean molecular weight (43,000 g/mol and 80,000 g/mol, respectively) and consequently melt flow index (16.6–11.8 g/10 min and 4.03–2.01 g/10 min, respectively).

### 2.2. Rheological measurements

Rheological measurements were carried out with a rotational controlled rate rheometer (Physica MCR301, Anton Paar), equipped with a parallel plate sensor system with 1 mm gap (PP25/1 mm). The temperature of the measurements was controlled with H-PTD200 hood with Peltier heating/cooling.

All the samples were tested under rotational and oscillatory shear conditions. Rotational flow tests were performed with a triangular method by changing the shear rate from 0 to 1000 to 0 s<sup>-1</sup>. Oscillatory stress sweep tests at constant frequency of oscillation (1 Hz) were used in order to determine the linear viscoelastic range (LVR). Frequency tests were performed at constant small deformation in LVR by decreasing the frequency from 20 to 0.01 Hz. Temperature dependence of rheological properties was determined by temperature tests under the conditions of LVR at deformation small enough not to destroy the sample, which depended on the type of the sample. All tests were performed at constant frequency of oscillation 1 Hz in the temperature range from 75 °C to –15 °C and from –15 °C to 75 °C. Linear polymers were tested in the higher temperature range, i.e. from 120 °C to 50 °C to 120 °C. The rate of heating and cooling was the same as for thermal characterization, i.e. 10 °C min<sup>-1</sup>.

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