

## The Effect of Polycaprolactone Grafting on Temperature Dependent Rheological Properties of Multiarm Star copolymers

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The rheological properties of the polymers are one of the most important factors when processing polymer melt since they provide information about the internal resistance to polymer shaping and, in the case of coatings, to levelling. In general, rheological properties of polymers depend on various parameters, like the degree of branching, branch length, and chain architecture. It is well known that branched polymers display significantly different rheological properties compared to linear polymers and polymer networks. Some authors have already reported 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<sup>1</sup>. This is the result of the enhanced shear-thinning behaviour of branched polymers. In recent years there has been an increasing interest in the synthesis of star-shaped and hyperbranched (HB) polycaprolactone polymers and copolymers, which have better solubility, lower viscosity and melting temperature as well as a lower degree of crystallization compared to their linear analogues<sup>2,3</sup>. Potential applications for those polymers are diverse, from epoxy toughener, PVC plasticizer, to various biomedical applications.

In the present work a Polycaprolactone was used with hyperbranched polyester Boltorn H40 in order to prepare star-shaped graft copolymers with improved mechanical properties. Various reactant ratios were used for a systematic thermal and rheological characterization. In addition, the same rheological characterization was performed for two linear polymers, which exhibited similar number average molecular weight ( $M_n$ ) as above mentioned star-shaped copolymers. For all samples the complex viscosities, obtained in linear viscoelastic range, were at 75°C correlated to molar mass. The results showed that as the reactant ratio increased from BH40:PCL=1:1 to 1:5 the complex viscosity exponentially decreased with the increasing molecular weight. However, as the reactant ratio was increased above 1:5 the complex viscosity significantly increased. In order to evaluate structural changes that occurred during heating and cooling the rheological properties of all samples were determined as a function of temperature. The temperature dependence of the rheological properties of copolymers was followed in LVR and compared to thermal characterization, obtained with differential scanning calorimetry (DSC) measurements. The rate of cooling/heating strongly influences the crystallization process and consequently also the rheological properties of the

polymers. Various rates of heating/cooling were therefore applied to the copolymers. The present study showed that the results of rheological characterization strongly coincided with the results of thermal characterization. New information about structural changes that occur during cooling/heating process of the studied copolymers are also presented.

## REFERENCES

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