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RHEOLOGICAL AND THERMAL PROPERTIES OF BOLTORN® HYPERBRANCHED POLYESTERS

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Abstract

Rheological (in solution and in melt) and thermal properties of aliphatic hydroxy-functional Boltorn® hyperbranched polyesters of different pseudo generation were investigated in this work. The obtained results show that 40 wt.% solutions of Boltorn® samples in N-methyl-2-pyrrolidinon exhibit Newtonian behaviour at 30 °C and that zero shear viscosity increases with increase of the generation number, i.e. molar mass. On the other side, vales of the T_g show only slight increase with increase of the molar mass. Thermal stability of investigated samples increases with increase of the number of generation.

Introduction

The scientific importance of hyperbranched polymers (HBPs) has been proved through numerous publications [1-3]. The reasons for such attention are interesting and unique properties of these polymers, similar to those of dendrimers, which enable their use in applications where tedious synthesis of dendrimers can be avoided. Because of the relationship between rheological, thermal and processing properties, characterization of the rheological flow behaviour and thermal stability of HBPs is very important. Therefore, the aim of this work was investigation of three Boltorn® aliphatic HBPs of the second (BH-20), third (BH-30) and fourth (BH-40) pseudo generation. The influence of the number of the pseudo generation on the rheological and thermal properties of these polymers was examined.

Experimental

Boltorn® samples are aliphatic hydroxy-functional hyperbranched polyesters supplied by Perstorp (Specialty Chemicals AB, Sweden). According to the supplier's data, these polymers were synthesized in a acid-catalyzed polyesterification reaction from the 2,2-bis(hydroxymethyl)propionic acid as AB_2 monomer and a tetrafunctional ethoxylated pentaerythrytol core, using pseudo one-step procedure.

Vapour pressure osmometry (VPO) was carried out in N,N-dimethylformamide as a solvent, at 90 °C, using a Knauer vapour pressure

osmometer. For the calibration benzil was used. Rheological properties of Boltorn® samples in solution (solvent - N-methyl-2-pyrrolidinon (NMP)) and in melt were determined by Carri-Med CSL-100 stress controlled cone and plate rheometer (TA Instruments), fitted with a 2 cm diameter cone of 2° cone angle. The thermal stability of HB polyesters was determined by thermogravimetric (TG) analysis, using a NETZSCH TG 209 instrument in nitrogen atmosphere, at heating rate of 10 °C/min (flow rate of N_2 was 25 cm^3/min).

Results and Discussion

Some important properties of investigated Boltorn® samples are listed in Table 1. From these results and results presented in Fig. 1a it can be seen that viscosity of 40 wt.% solutions of Boltorn® samples in NMP, determined at 30 °C, is independent of the shear rate and approaches a constant value, i.e. zero shear viscosity, η_0, which increases with increase of the number of pseudo generation. The existence of η_0 indicates that Boltorn® samples at these experimental conditions exhibit Newtonian behaviour, because of their globular shape and absence of the physical entanglements. Values of the glass transition temperature, T_g, determined from the maximum of loss modulus temperature dependence (Fig. 1b) and listed in Table 1 do not change significantly with increase of the molar mass.

Table 1. The theoretical molar mass, M_{theor}, theoretical number of –OH groups, n_{OH}, number average molar mass determined by VPO, M_{VPO}, values of degree of branching, *DB* [1], zero shear viscosity, η_0, glass transition temperature, T_g, and characteristic temperatures of thermal degradation for the Boltorn® samples

Sample	M_{theor}, $gmol^{-1}$	n_{OH} theor.	M_{VPO}, $gmol^{-1}$	*DB*	η_0, mPa · s	T_g, °C	T_{10}, °C	T_{50}, °C	T_{80}, °C
BH-20	1747	16	1340	0.30	63.1	21	274	339	379
BH-30	3604	32	3080	0.31	137.9	31	295	353	409
BH-40	7316	64	-	0.34	209.4	31	301	365	416

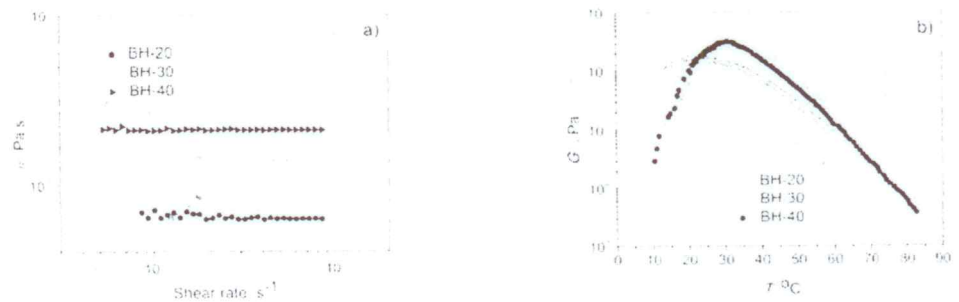

Fig.1. (a) Viscosity versus shear rate of the 40 wt.% solutions in NMP, at 30 °C and (b) temperature dependences of the loss modulus, *G''*, of Boltorn® samples.

From the TG curves presented in Fig. 2a and temperatures obtained for mass losses of 10, 50 and 80 wt. % (T_{10}, T_{50} and T_{80}, respectively) listed in Table 1

it can be observed that thermal stability of Boltorn® samples increases with increase of the generation number. Under the given experimental conditions a measurable mass loss starting between 220 and 275 °C is detected. Using the Ozawa-Flynn-Wall method the activation energy of thermal degradation, E_a, of these samples was determined and presented in Fig. 2b. The various tendencies of E_a for different generations of Boltorn® samples imply that the thermal degradation of these polymers is a complex process.

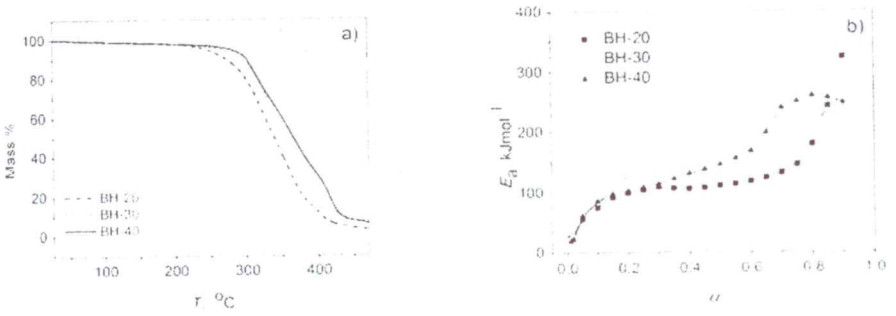

Fig.2. (a) TG curves of Boltorn® samples determined at heating rate of 10 °C/min and (b) change of the activation energy of thermal degradation, E_a, with degree of reaction, α.

Conclusions

The results presented in this work show that under the given experimental conditions solutions of Boltorn® samples show Newtonian behaviour. Values of the zero shear viscosity increase with increase of the molar mass. Values of the glass transition temperature of investigated samples show only slight increase with increase of the generation number. According to the results obtained by thermogravimetric analysis, it was observed that thermal stability of Boltorn® samples increases with increase of the molar mass and that thermal degradation of these polymers is a complex process.

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