Structure and Molar Mass Characterization of Commercial Aliphatic Hyperbranched Polyesters

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Introduction

Hyperbranched polymers (HB) are, like dendrimers, part of the family of multibranched or dendritic polymers. Since they can be produced on a large-scale at a reasonable cost by one-pot or pseudo-one-pot reactions they have attracted great scientific attention in recent years. However, due to imperfect branching and a higher possibility of side reactions taking place they are polydisperse with respect to molar mass, molecular structure, and composition. The exact effect of their imperfectly branched structure and polydisperse character on their properties is not yet entirely clear.

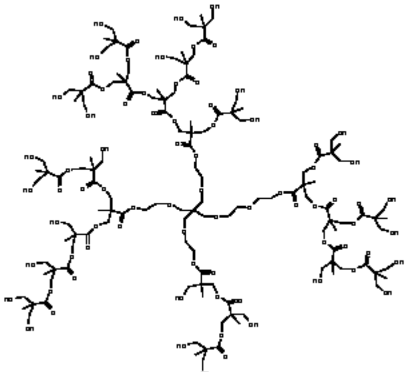


Figure 1. Schematic structure of aliphatic hyperbranched polyester based on 2,2-bis(methylol)propionic

In this contribution the effects of annealing the commercial aliphatic HB polyesters onto an H-bond network microstructure and, consequently, on the thermal and rheological properties of samples will be discussed. The changes in the H-bond network microstructure induced by the annealing process were studied by FTIR and X-ray diffraction measurements. To elucidate how the irregular structure, i.e. the presence of linear repeat units in the HB structure, influences the properties of HB polyesters, the composition, degree of branching, the presence of side products (ether and cyclic structures, structures without core molecules), and absolute molar masses of samples were determined.

Experimental

Materials. Commercially available aliphatic HB polyesters of the second, third, and fourth pseudo-generation, Boltorn H20, H30 and H40, synthesized from 2,2-bis(methylol)propionic acid as AB_2 repeating unit, and ethoxylated pentaerythritol as tetrafunctional B_4 core molecule (Perstorp Specialty Chemicals AB, Sweden, **Figure 1**). Our sample denotation is H20 and H40.

Thermal Characterization was carried out using differential scanning calorimeter (DSC) Perkin-Elmer Pyris 1. In annealing experiments, the sample was heated to 150 °C (heating rate 10 °C min^{-1}) in order to remove the effect of sample thermal pre-history. It was then rapidly cooled down (quenched: cooling rate 200 °C min^{-1}) to the predetermined temperature (50, 60, 70, 80, 90, and 100 °C, respectively). At each temperature the sample was annealed for different annealing times (from 1 hour to 4 days). After annealing, the sample was quenched to −10 °C for two minutes to stabilize it, and subsequently reheated to 160 °C at 10 °C min^{-1}. All analyses were performed under a nitrogen atmosphere.

Rheological Characterization. For rheological tests the sample was pre-heated for 15 min at 150 °C in order to break down the H-bond structure. After that the sample was cooled down to the pre-determined annealing temperature. A controlled stress rheometer Haake RS150 was used for all rheological measurements. Time sweep tests under non-destructive conditions of oscillatory shear were performed at a constant frequency of 1 Hz. In order to perform the measurements under conditions of linear viscoelastic response (LVR) throughout the whole 3 hour experimental time, tests were carried out at a constant strain amplitude of 3 % at 90 - 70 °C, and at 1 % of strain amplitude at 60 °C.

X-ray Diffraction (XRD). XRD experiments were performed using a Philips 17-10 diffractometer with Cu K_α radiation ($\lambda = 1.54$ Å). The scattering intensities were detected using a scintillation counter with an angular range 2° - 35° (in 2θ), an angular step of 0.04°, and a measurement time of 1 s per step.

SEC-MALS. The molar mass averages (MMA) and molar mass distributions (MMD) of samples were determined by size exclusion chromatography coupled to a multi-angle light scattering detector (SEC-MALS) after thermal pretreatment and subsequent dissolution of samples in solvent *N,N*-dimethylacetamide (DMAc) with added LiBr to a concentration of 0.7 %.

NMR Spectrometry. The ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a Varian VXR 300 NMR spectrometer using DMSO-d_6 as a solvent and tetramethylsilane (TMS) as an internal reference. ^{13}C NMR spectra of samples were obtained using 10 % solutions and an inverse gated decoupling mode with a suppressed NOE effect. ^{1}H NMR spectra were recorded for sample solutions with a concentration of 0.5 % both at room temperature and at 75 °C.

FTIR Spectrometry. Infrared spectra were recorded on a Perkin-Elmer PE 2000 spectrometer equipped with a liquid nitrogen cooled MCT detector. The films were heated up to 150 °C, subsequently cooled to 50 °C or 90 °C, and tempered for 24 h. The variations in spectra were monitored by difference spectroscopy.

Results and discussion

Thermal and Rheological Characterization.

The thermal and rheological properties of Boltorn HB polyesters were studied in dependence of the annealing temperature and annealing time. The results revealed that annealing of Boltorn HB polyesters above their glass transition temperatures significantly affects their thermal and rheological properties. The kinetics of H-bond formation was tracked by measuring the H-bond cleavage enthalpy of annealed samples (**Figure 2**). The process of H-bond formation is similar to the process of crystallization and its kinetics can be adequately described by the crystallization kinetics. The cleavage enthalpy is a linear function of the logarithm of annealing time. The samples' glass transition temperatures are almost unaffected by the annealing process, whereas the heat capacities at the glass transition decrease with increasing cleavage enthalpy.

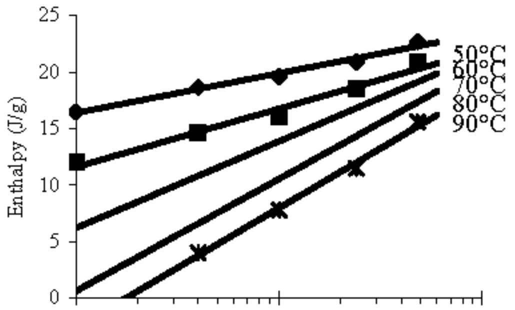


Figure 2. H-bond cleavage enthalpy, Δ*H*, of H20 as a function of annealing time for different annealing temperatures.

At the beginning of the annealing process, the melt of HB polyesters exhibit, depending on the temperature and pseudo-generation, only viscous or predominantly viscous behavior. With increasing annealing time the elastic contribution to the viscoelastic response increases for all samples at all annealing temperatures. (**Figure 3**).

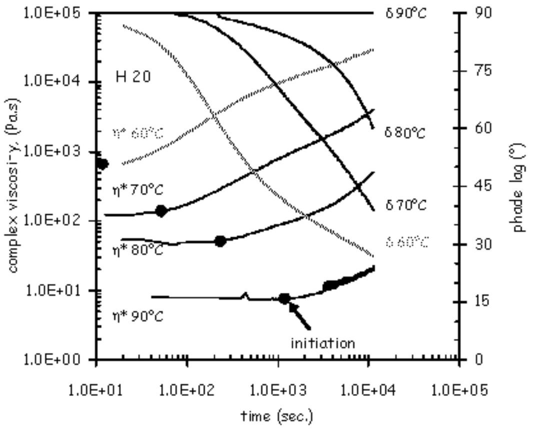


Figure 3. The influence of annealing time on complex viscosity and phase lag under non-destructive conditions of oscillatory tests at frequency of 6.28 rad/s under the conditions of LVR for investigated H20 at 60, 70, 80, and 90 °C.

XRD and FTIR Characterization.

XRD and FTIR results reveal that during annealing the amorphous HB polyesters develop a more ordered and thermally stable H-bond network structure (**Figure 4**). By comparing the XRD and FTIR results of HB polyesters and the dendrimer analogue of H40, we propose that during annealing of amorphous HB polyesters, their structure becomes more ordered as a consequence of formation of multiple intermolecular H-bonds between long linear sequences in the HB structure. Structure ordering is more pronounced for the lower pseudo-generation HB polyester, which has a low molar mass, more open structure and lower degree of branching. The ordering is a consequence of the interpenetration of branches through the intermolecular H-bond interactions between linear sequences, which is in the case of low pseudo-generation HB polyesters additionally facilitated by lower core functionality. Namely, the number of unreacted hydroxyl groups of the core increases with decreasing pseudo-generation (**Figure 5**). The elastic contribution to the viscoelastic response of HB polyesters increases with annealing time at all annealing temperatures due to formation of thermally stable H-bond network microstructure.

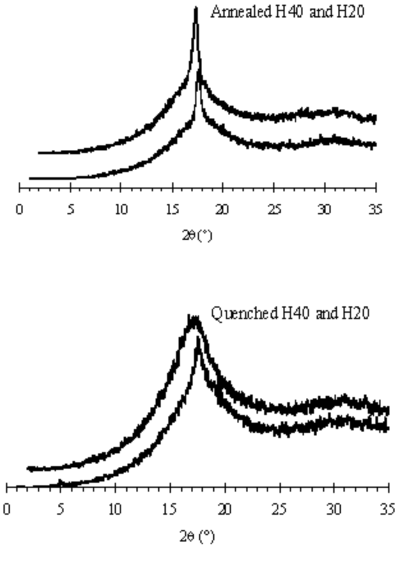
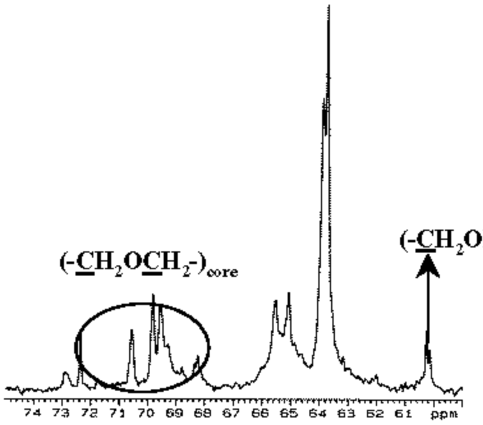


Figure 4. X-ray diffractograms of quenched (Q) and annealed (A: 50 °C, 14 days) H20 and H40 HB polyesters.



$$\boxed{\overline{\mathrm{DP}}_{\mathrm{n}} = \left(\frac{T+L+D}{T-D}\right)x_{\mathrm{B4}}\boxed{f}+\left(\frac{T+L+D}{T-D}\right)x_{\mathrm{B2}}}$$

f

Figure 5. Methylene region of ^{13}C NMR spectra of H30 HB polyester.

The degree of branching, molar mass, and core functionality have been found to be the main structural features of aliphatic HB polyesters influencing the formation of the H-bond network, its type and strength, and, consequently, the thermal and rheological properties of HB poly(bis-MPA) polyesters.

Due to the H-bonding network microstructure, HB polyesters were not soluble in solvent LiBr/DMAc on a molecular level. Therefore, the sample solutions for SEC-MALS measurements were prepared by thermal pretreatment of samples prior to dissolution. Molar mass averages (MMA) of thermally pretreated HB polyesters were independent on solution concentration indicating dissolution on a molecular level. The comparison of experimentally determined absolute number MMA determined by SEC-MALS to those calculated from samples' NMR spectra indicated the absence of the cyclic structures formed by intramolecular esterification reaction. The calculations from NMR spectra revealed also that the main side reaction in the synthesis of aliphatic HB polyesters is a self-condensation of bis(methylol)propionic acid leading to the HB structures without the core molecules, which content increases with pseudo generation. Besides, NMR spectra indicated that the average number of unreacted core hydroxyl groups increases with decreasing pseudo-generation and that intramolecular etherification as a side reaction took place during the synthesis of HB polyesters to a minor extent.

Conclusions

We investigated the effects of annealing on the rearrangement of H-bonding structure and its influence on the thermal and rheological properties of different pseudo-generation aliphatic hyperbranched (HB) polyesters based on 2,2-bis(methylol)propionic acid. During annealing of amorphous HB polyesters, the structure becomes more ordered as a consequence of multiple H-bonds formation between linear sequences. Structure ordering is more pronounced for the lower pseudo-generation HB polyester with low molar mass, low degree of branching and incompletely reacted core hydroxyl groups which greatly increases the possibility for multiple H-bond interactions.

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