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The effect of degree of branching on the rheological and thermal properties of hyperbranched aliphatic polyethers

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Abstract

A series of hyperbranched aliphatic polyethers with different degree of branching (DB) and molecular weights have been studied with respect to their rheological and thermal properties. The DB was shown to affect the ability of the polymers to crystallize and thereby also the rheological properties of the polymers. A low DB resulted in semi-crystalline polymers with melting points between 100 and 130°C. The polymers with a higher DB were essentially amorphous and behaved as non-entangled Newtonian liquids in the molten state. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Hyperbranched; Dendritic; Rheology

1. Introduction

Macromolecular architecture has been recognized as an important tool to obtain polymers with tailored properties. Due to this, the interplay between molecular architecture and macroscopic properties has rendered increasing interest in recent years. One example is the introduction of large amounts of branching units into polymers, dramatically changing the physical properties such as the viscosity and solubility [1]. One group of highly branched polymers is dendritic (tree-like) polymers, comprising hyperbranched polymers and dendrimers, based on AB_x-monomers [2]. The monomers introduce a potential branching point in each repeating unit, that is why a highly branched polymer is obtained. Dendrimers are well-defined, fully branched, monodisperse polymers, while hyperbranched polymers are polydisperse and contain linear segments. Dendrimers are produced via successive protection/deprotection procedures and often difficult, and expensive, to accomplish. Hyperbranched polymers, on the other hand, are more readily produced and can be obtained on a larger scale at a reasonable cost, making them more interesting for commercial applications. Even though hyperbranched polymers are polydisperse and not fully branched, they still exhibit very different properties compared to their linear counterparts. For example, hyperbranched polymers have been shown to have a lower viscosity in solution and in the molten state than their linear counterparts due to their highly branched structure [1]. Hyperbranched polymers have also been described in several applications, ranging from processing additives for thermoplastics to thermoset system components [3–8]. The toughness in acrylate thermoset resins [5] was improved by addition of methacrylate-functional hyperbranched polyesters. The addition of small amounts of alkylated hyperbranched polymer reduced the melt viscosity and prevented the formation of sharkskin in extrusion of LLDPE [3]. Similarly, the melt viscosity of polyamide-6 was reduced by addition of hyperbranched poly(ester-amide)s [7]. The addition of dendrimers to aqueous solutions of poly(ethylene oxide)s has been shown to affect the optical as well as the rheological properties of the solution [9].

Hyperbranched polymers are often described not only by their molar mass but also by their degree of branching (DB). The DB is a measurement on the content of branches in the molecular structure and is considered to be a main structural feature affecting the properties. Consequently, the DB for a perfect dendrimer equals 1, while a linear polymer has a DB of 0. Two different equations have been suggested for the average DB of hyperbranched polymers. The first, introduced by Fréchet et al. [10], compares the sum of the dendritic (D) and the terminal (T) repeating units to the sum of all repeating units in the structure (Eq. (1)), where L represents the fraction of linear units:

$$\mathrm{DB}(\%) = \left(\frac{D+T}{D+T+L}\right) \times 100 \tag{1}$$

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A more recent definition by Frey et al. [11], Eq. (2), does not include the terminal repeating units and is therefore claimed to be more accurate at low molar mass than (Eq. (1)).

$$\mathrm{DB}'(\%) = \left(\frac{2D}{2D + L}\right) \times 100 \tag{2}$$

Most often, the fractions of D, L and T-repeating units are determined by NMR spectroscopy. In the same context, an equation for the calculation of the molar mass from the relative fraction of each repeating unit has also been suggested. (Eq. (3)) [12].

$$\mathrm{DP}_n = \frac{D + L + T}{T - D} \tag{3}$$

Hyperbranched polymers and dendrimers in a few studies have been compared to their linear counterparts with respect to different properties. Differences in solubility [13], hydrodynamic volume, rheological and thermal [14] properties have been reported. The influence of different end-groups on the thermal properties has also been studied [15]. However, not much is reported on how the DB affects the macroscopic properties.

The present work describes the thermal and rheological properties of a series of hyperbranched aliphatic polyethers based on 3-ethyl-3-(hydroxymethyl) oxetane (TMPO) [16,17]. The polyethers were synthesized by cationically initiated bulk polymerization under different reaction conditions. Materials with different molar mass and DB were obtained. The precipitated polymers were analyzed with respect to molar mass, DB, thermal and rheological properties. Vandenberg et al. have synthesized and characterized linear poly(3-ethyl-3-(hydroxymethyl)) oxetane, which was found to be a highly crystalline polymer with crystalline melting points of 163 [18] and 175°C [19] depending on the method used for characterization. Yan et al. reported the synthesis and characterization of a similar polymer, poly(3-methyl-3-hydroxymethyl)) oxetane, where, the DB was reported to influence the crystallinity [20].

2. Experimental

2.1. Materials

TMPO was supplied by Perstorp AB, Sweden, and used as received. Benzyltetramethylenesulfonium hexafluoroantimonate ($\mathrm{BTSSbF_6}$), *p*-methylbenzyltetramethylenesulfonium hexafluoroantimonate (*p*-$\mathrm{CH_3BTSSbF_6}$) and *p*-methoxybenzyltetramethylenesulfonium hexafluoroantimonate (*p*-$\mathrm{CH_3OBTSSbF6}$) were prepared according to the literature procedures [21]. All other chemicals were purchased from Merck or Aldrich and used as received.

2.2. Apparatus

The rheological measurements were performed on a Rheometrics RDAII equipped with parallel plates with a diameter of 7.9 mm using auto-tension and auto-strain.

The ^{1}H NMR spectra of the hyperbranched poly(3-ethyl-3-hydroxymethyl) oxetanes were performed on a Bruker 400 MHz spectrometer. All ^{13}C NMR experiments were performed on a Varian 600 MHz spectrometer at 40°C. The DB was calculated from the relative intensity of the $-\mathrm{CH_2CH_3}$ peaks in proton decoupled, quantitative ^{13}C NMR spectra. DMSO-d_6 was used as solvent in all NMR experiments. $T1$ was set to 12 s in the quantitative analysis. Size exclusion chromatography (SEC) was performed with a Waters 6000A pump, a PL-EMD 960 light scattering evaporate detector, two PL gel 10 μm mixed-B columns (300 × 7.5 mm) from Polymer Labs and one Ultrahydrogel linear column (300 × 7.8 mm) from Waters. All measurements were performed at 70°C. DMF was used as solvent at a flow rate of 1 ml min^{-1}. Linear polyethylene oxides were used as standards. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) experiments were performed on a Hewlett Packard G2025a MALDI-TOF system using dihydroxy benzoic acid as matrix and ethanol as solvent. Differential scanning calorimetry (DSC) was performed on a Mettler DSC 820 calibrated using standard procedures.

2.3. Materials

A series of hydroxyfunctional hyperbranched polyethers based on TMPO were prepared according to a procedure described elsewhere [22] (Fig. 1). The obtained polymers have varying molar mass and DB (Table 1).

2.4. Thermal characterization

Thermal characterization of the samples was accomplished by DSC. All samples were ramped twice between 0 and 220°C using a heating/cooling rate of 10°C min^{-1} unless otherwise indicated in the text. The crystallization temperature, T_m and the glass transition temperature, T_g, were obtained from the second cooling scans.

The annealing behavior of polymer **10** was further investigated. The sample was heated to 200°C and then rapidly

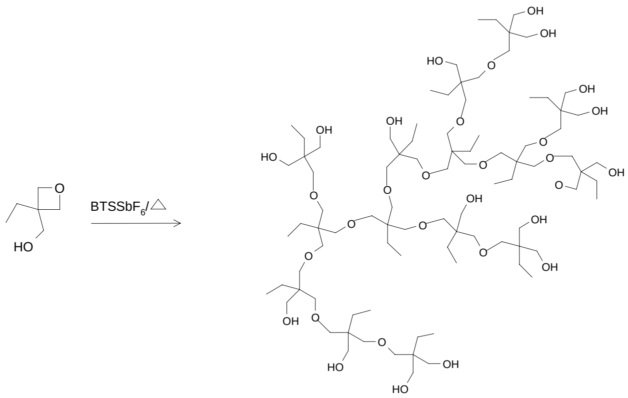

Fig. 1. Idealized reaction scheme for the oxetane polymerization.

Table 1
Data on polyethers **1–10**

Sample no.	DB (Fréchet)[a]	DB (Frey)[b]	M_{Frey} (g mol^{-1})[c]	$M_{\mathrm{n,\,MALDI}}$ (g mol^{-1})[d]	$M_{n,\,\mathrm{SEC}}$ (g mol^{-1})[e]
1	0.43	0.41	3900	2017	2600
2	0.45	0.41	1600	2391	2100
3	0.44	0.40	1900	1987	2600
4	0.40	0.36	1900	2022	2200
5	0.43	0.41	2700	2191	2700
6	0.40	0.30	800	1835	1400
7	0.36	0.30	1300	3363	3500
8	0.21	0.11	1000	1506	1600
9	0.38	0.32	1300	2782	3000
10	0.30	0.24	1500	2407	2100

[a] DB determined from ^{13}C-NMR calculated by definition by Frechét et al. [10].

[b] DB′ according to definition by Frey et al. [11].

[c] Molar masses according to Eq. (3) calculated from ^{13}C-NMR.

[d] Molar masses determined with MALDI-TOF-MS.

[e] Molar masses determined by SEC.

cooled to 70°C where it was kept for 2 h. The sample was then quenched to 15°C and subsequently heated to 200°C at 10°C min^{-1} while registering the melt transition. The same procedure was repeated changing the annealing temperature to 90, 110, and 130°C, respectively. All analyses were performed under nitrogen atmosphere.

2.5. Rheological characterization

2.5.1. Rheological behavior as a function of temperature

Approximately 0.2 g of a polymer sample was melt at 170°C between two parallel plates with a diameter of 7.9 mm. The sample was then cooled to 0°C. The dynamic mechanical properties versus temperature were measured between 0 and 140°C with a frequency of 6.28 rad s^{-1} using auto-tension and auto-strain. All polymers were analyzed following the same procedure. Frequency sweeps were also performed at 100°C on polymers **1** and **8**.

3. Results and discussion

3.1. Determination of molar mass and calculation of degree of branching

The determination of molar mass of dendritic polymers is difficult due to the polydispersity and their highly branched nature. The samples in this study have been analyzed both by SEC and by MALDI-TOF, Table 1. The SEC instrument was calibrated according to linear poly(ethylene glycol)s which have a different correlation between hydrodynamic volume and elution time than the analyzed hyperbranched polymers. SEC values for hyperbranched polymers are often claimed to be too low since the dendritic polymers hydrodynamic volumes are smaller than the corresponding linear counterparts used for calibration [23]. MALDI-TOF analysis on polydisperse samples is difficult due to the possible discrimination of the higher molar mass fraction. This is an effect of both the more difficult ionization of the higher molar mass fraction and detector saturation.

In this study, quite good agreement between SEC and MALDI-TOF was obtained. This is believed to be due to the fact that, the analyzed samples have rather low molar mass so that the limitations discussed above are not so significant. The molecular weights calculated from Eq. (3) are also given in Table 1. In theory, this equation should give the exact value of M_{n}. However, the denominator is very sensitive to the quantification of the dendritic and terminal repeating units. A very small error in their quantification will cause large errors in the calculated molar mass and the quality of the spectrum needed for an accurate quantification is difficult to obtain in practice. The calculated value is not very accurate.

The calculations of DB have been performed according to both Fréchet et al. [10] and Frey et al. [11], Table 1. The values obtained according to Frey et al. [11] are lower than the ones obtained by the method of Fréchet et al. [10]. The former method has been suggested to be more accurate for lower molar mass and a larger difference between the values is also observed for the polymers having lowest molar mass.

3.2. Rheological properties

The rheological behavior of all samples were analyzed by carrying out a temperature sweep at 6.28 rad s^{-1}. Even though the analyzed samples covered a rather limited range of DBs, 0.11–0.41, their rheological behavior were found to be significantly different which can be seen in Fig. 3, where the complex dynamic viscosity (η^*) is plotted as a function of temperature. The sample with the highest DB, polymer **5**, exhibits a completely amorphous behavior with a rather broad glass transition. The viscosity drops above the glass transition without any traces of a rubbery plateau. This suggests that polymer **5** is essentially non-entangled with no rheological indication of a crystalline phase.

Samples having lower DB, e.g. polymer **9**, behaves more like a semi-crystalline polymer, with only a small drop in viscosity at the glass transition and the presence of a rubbery plateau before the viscosity drops rather rapidly at the crystalline melting temperature. The presence of a plateau in the viscosity curve is indicative of the presence of a crystalline phase or entanglements. The latter is, however, not very probable in this case since the molecular weights are well below the critical entanglement molecular weight.

Interestingly, there is a strong relationship between DB (determining the crystallization ability) and viscosity. Even though sample **5** has one of the highest molar masses found, it has the absolutely lowest melt viscosity at 100°C, ca. 100 Pa s. However, since no absolute values of molar mass can be determined, no far-reaching conclusions on how the molar mass and melt viscosity are related can be drawn at this stage.

As the DB is decreased, it seems reasonable to believe that the polymers ability to crystallize increase. It is also experimentally observed that polymers having lower DB, exhibits a rheological behavior similar to what is expected for a semi-crystalline polymer.

Fig. 2 details the dynamic viscosity obtained as a function of temperature for the samples having DBs higher than 0.36, samples **1**–**5**. The melt viscosity drops above T_g without almost no trace of a rubbery plateau. This further corroborates our hypothesis that the samples having higher DB are essentially amorphous and non-entangled.

Combining the results from Figs. 2 and 3, it can be seen that the DB has an important influence on the rheological behavior of the hyperbranched polymers. The most highly branched polyethers are amorphous materials with essentially no chain entanglements. Due to the highly branched structure, these materials are unable to crystallize. The less branched materials, on the other hand, seem to have linear sequences in the chain long enough for partial crystallization to take place. These materials have a distinct rubbery plateau and a significantly higher viscosity at a given temperature than their more branched counterparts. Effects of differences in molar mass between the different samples may play a role for the results but according to Fig. 3, this effect should be of minor importance.

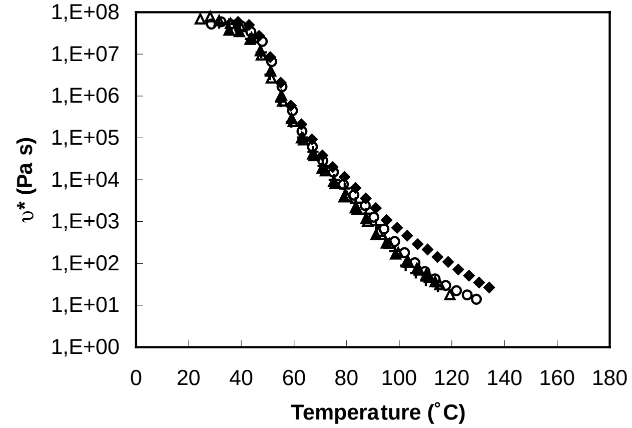

Fig. 2. Complex dynamic viscosity (η^*) versus temperature for polyethers **1** (○), **2** (△), **3** (◆), **4** (+), and **5** (▲).

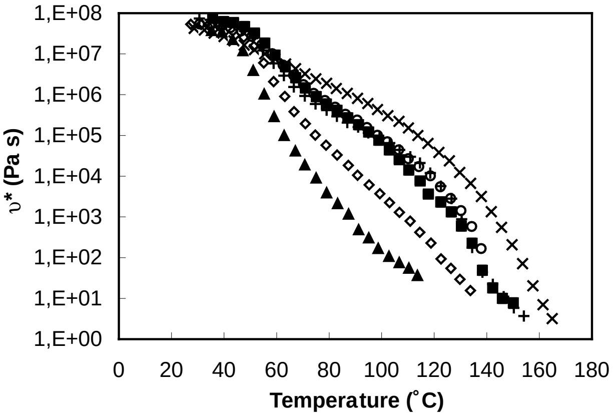

Fig. 3. Complex dynamic viscosity (η^*) versus temperature for polyethers **5** (▲), **6** (+), **7** (■), **9** (◇), and **10** (○).

In order to elucidate the influence of a crystalline phase, two samples, polymer **1** and **8**, were subjected to a frequency sweep at 100°C, above the glass transition, Fig. 4. Polymer **1**, which is almost fully amorphous, exhibit an increase in G' with shear rate, which is consistent with Newtonian flow behavior for a non-entangled polymer. G' is, on the other hand, almost constant for polymer **8** within the frequency range tested. This indicates that the crystals act as effective crosslinks, so that a network structure is obtained in the crystalline region even though the molecular weight is too low for entanglements.

3.3. Thermal analysis

All samples were also analyzed by DSC. The DSC measurements support the aforementioned conclusion that,

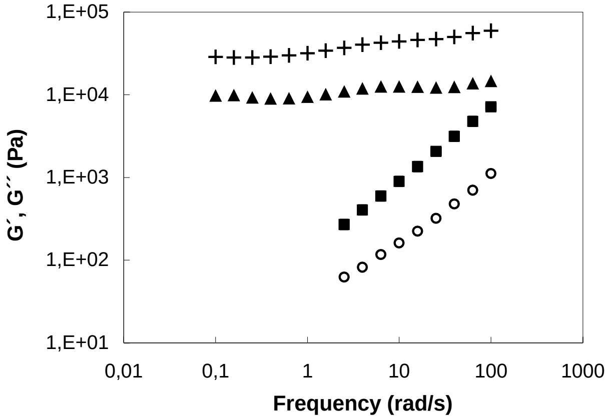

Fig. 4. G' and G'' versus frequency at 100°C for polyether **1** (G' (○), G'' (■)) and **8** (G' (▲), G'' (+)).

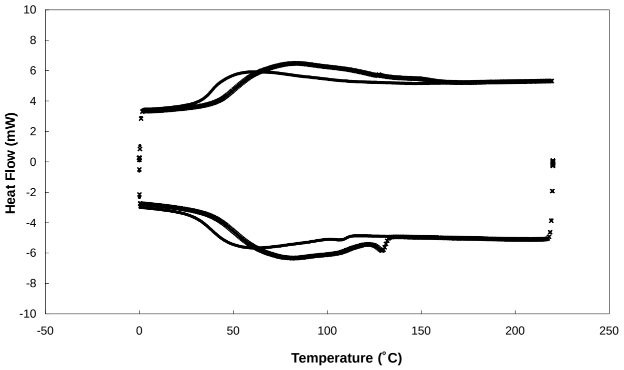

Fig. 5. DSC curves on polyethers **2** (·) and **10** (×). First cooling and second heating at a rate of 10°C min^{-1}.

crystallization exotherms can be observed for the samples having the lowest DB, Fig. 5.

The crystallization exotherms are almost non-existing for polymers **1–3** and not at all detectable for polymers **4** and **5**. However, the crystallization is more pronounced for polymers **6–10**, although the crystallinity is still limited. The melting temperatures are slightly increased for the samples with higher degree of crystallinity. In conclusion, it is observed that the crystallinity increases with decreasing DB, which is expected since the presence of branches in a polymer, render crystallization more difficult than in a linear polymer.

All crystallization peaks were very broad, making it very difficult to calculate the crystallization enthalpy and determine the peak value with any accuracy. Only very small peak enthalpies were recorded because the degree of crystallization in the samples was very low, only a few percent. All enthalpies were recorded on the cooling scan since the melting peak upon heating was even broader and more difficult to evaluate. The peaks are, however, too small to make any possible quantitative comparisons between the different polyethers.

The glass transition as recorded by DSC is also affected by the presence of a crystalline phase as seen in Fig. 5. Samples having a higher crystallinity exhibit a higher melting temperature and a higher glass transition temperature.

3.4. Annealing experiments

To further investigate the degree of crystallinity sample 10, having an intermediate DB and molar mass, was subjected to annealing experiments. The annealing was carried out at 70, 90, 110, and 130°C and with subsequent quenching to15°C before running a heating scan resulted in detectable melting exotherms with very different melting temperatures of the polymers. The annealing resulted in T_m's of 85, 106, 125, and 140°C, respectively. The melting enthalpies were approximately $10\ \mathrm{J\,g^{-1}}$ for the two lower annealing temperatures, indicating an increase in crystallinity after annealing. The melting peaks at the higher annealing temperatures were too low and broad, and therefore impossible to integrate. The shift in T_m due to changes in thermal history is consistent with rather small crystallites and low degree of crystallinity [24].

3.5. Solubility

The DB was also found to affect the solubility properties of the hyperbranched polyethers. This was clearly seen during the preparation of the samples for NMR-analysis. All polymers did eventually dissolve in DMSO-d_6 but the samples having high DB, polymers **1–5**, were much more readily dissolved than the samples having lower DB. Similar results have been reported for dendrimers (DB = 1) and their exact linear analogues (DB = 0) where the solubility was much higher for the dendrimer [25].

4. Conclusions

A series of hyperbranched polyethers based TMPO having DB's between 0.11 and 0.41 and molar masses from 1500 up to $3300\ \mathrm{g\,mol^{-1}}$ have been studied with respect to rheological and thermal properties. It was found that the DB affected the rheological as well as the thermal properties significantly. Hyperbranched polyethers with a high DB were found to be amorphous and essentially non-entangled polymers, having a T_g of 40°C. Polymers having a lower DB resulted in semi-crystalline materials with a melting transition between 100 and 130°C.

The DB indirectly influence the rheological properties by determining the ability for the polyether to crystallize.

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