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# Relaxation processes in hyperbranched polyesters

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## SUMMARY

Dielectric permittivity and loss have been measured over the frequency range $10^{-2}$ Hz - 10 kHz between 100 K and 350 K for samples of 50/50 mixtures of each of two hyperbranched polyesters, one five-generation hydroxy functional (5G-OH) and one three-generation alkyl-terminated polymer (3G), with dielectrically inactive linear polyethylene. The thermal transitions of the hyperbranched polymers were studied with differential scanning calorimetry. Three relaxation transitions were found in 5G-OH: $\alpha$, the glass-rubber transition and two subglass processes denoted $\beta$ and $\gamma$ showing Arrhenius temperature dependence both with an activation energy of 96±2 kJ $\mathrm{mol}^{-1}$. The low temperature process could be assigned to motions of the terminal hydroxyl groups whereas $\beta$ is due to reorientation of the ester groups. Sample 3G showed only a glass transition and one subglass process being assigned to reorientation of the ester groups. The high activation energy (202 kJ $\mathrm{mol}^{-1}$) of this process indicates that the ester groups are highly constrained in this polymer.

## INTRODUCTION

A field that has received attention during recent years is that of non-linear polymers, e.g. dendrimers, starburst or hyperbranched macromolecules (1-8) and star polymers (9-15). These branched polymers have a lower melt viscosity at the same molar mass and a different molar mass dependence of the glass transition temperature than their linear analogues.

Star polymers exhibit their highest density at the core of the molecule whereas the density profile for the dendrimers is believed to depend on the monomeric structure. A model presented by de Gennes et al (16) which assumes that all chain ends are located at the surface of the dendrimer sphere predicts a density maximum at the periphery of the molecule. The kinetic model of Lescanec et al (17), based on the assumption that all branches of the same generation grow simultaneously, shows that the terminal groups of the branches are randomly distributed over the molecular volume and that the density is at a maximum in the centre of the molecule.

This paper presents data from dielectric relaxation measurements and differential scanning calorimetry of two hyperbranched polyesters. No dielectric relaxation measurements have hitherto been reported for these polymers. The structures of the polyesters were chosen so that a structural assignment of the relaxation processes could be made. It was expected that the data would provide information about the segmental mobility of the hyperbranched polyester through comparison of dielectric data obtained for the different hyperbranched polymers and further comparison with literature data on poly(methyl acrylate) and poly(methyl methacrylate).

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## EXPERIMENTAL

2-Ethyl-2-(hydroxymethyl)-1,3-propanediol (trimethylolpropane, TMP) and 2,2-dimethylol propanoic acid (bis-MPA) were kindly supplied by Perstorp Polyols AB, Sweden. Methanesulfonic acid (MSA), sulphuric acid and propionic acid were supplied by Aldrich and used as received. Both a five-generation (referred to as 5G-OH) polymer with terminal hydroxyl groups and a three-generation (3G) polymer with terminal aliphatic groups were prepared. A simplified reaction path for a fully branched dendrimer is outlined in Figure 1.

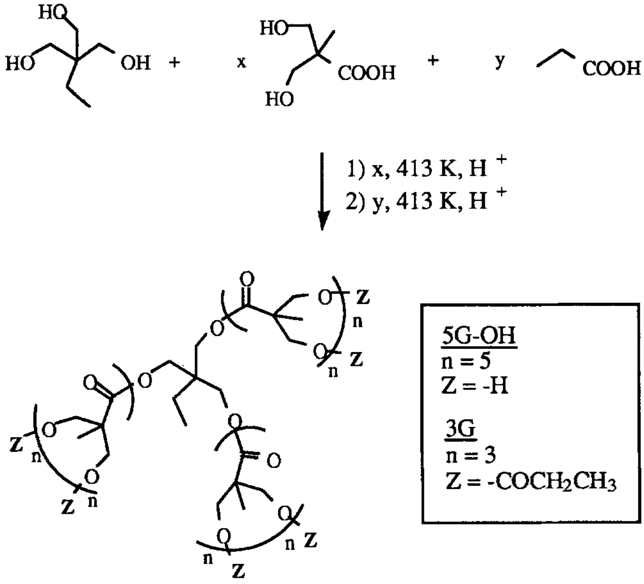

Figure 1. A schematic reaction path for a fully branched dendrimer (5G-OH: x=93, y=0, 3G: x=21, y=24)

5G-OH: 0.1 g TMP, 0.9 g bis-MPA and 20 mg MSA were added to a three-necked flask equipped with an argon-inlet, a drying tube and a magnetic bar. The flask was placed in an oil bath previously heated to 413 K. After 1 h, 1.2 g bis-MPA was added. After a further 3 h, 2.4 g bis-MPA and 20 mg MSA were added and finally 4.8 g bis-MPA was added after a further 3 hours. The mixture was allowed to react overnight for completion. Characterization: NMR: Degree of branching ≈ 85 %. The theoretical molar mass is 10 933 g $mol^{-1}$.

3G: 1 g TMP, 9 g bis-MPA and 18 mg sulphuric acid were added to the flask, equipped as above. After 1 h reaction time, vacuum was applied to the flask for 2 h. After the pressure had been raised to 1 atm, 12 g bis-MPA and 24 mg sulphuric acid were added. After 1 h at 413 K, vacuum was applied for the subsequent 2 hours. After the reaction mixture had been cooled to 403 K, 13.3 g propionic acid was added and the reaction was left overnight for completion. The product was dissolved in toluene and shaken with an alkaline solution and dried with $MgSO_4$ to constant mass. Characterization: NMR: degree of branching ≈ 84 %. The theoretical molar mass is 3 919 g $mol^{-1}$.

The degree of branching, as defined by Fréchet et al (18), was determined with $^{13}C$-NMR using a Bruker 400 MHz NMR spectrometer.

The dielectric studies were made on 200 μm samples of 50/50 mixtures of each of the two hyperbranched polyesters (3G and 5G-OH) with linear polyethylene using a IMASS TDS time domain spectrometer equipped with a Hewlett Packard Series 300 computer. The time domain spectrometer is based on a design by Mopsik (19). At time t=0, a step voltage of 10 V or 100 V was applied between the indium tin oxide layers. This caused a charge Q(t) to flow through the sample and the complex capacitance as a function of frequency was obtained by a numerical Laplace transform, based on a cubic spline, of the time domain capacitance data. The latter covered a time period of 1 min and frequency domain data were obtained from $10^{-2}$ Hz to 10 kHz. All measurements were carried out after first cooling the sample to 100 K and then while heating it making measurements at progressively higher temperatures. Thermal equilibrium was established prior to the actual measurements. The glass transition temperature was obtained by heating 10±0.5 mg samples in a Perkin-Elmer DSC-7 at 10 K $\text{min}^{-1}$.

## RESULTS AND DISCUSSION

The presence of two dielectric loss processes in sample 5G-OH, referred to as β and γ, is shown in Figure 2. DSC showed a second order phase transformation at 303 K indicating the presence of a glass transition (α). The high temperature subglass process (β) is very narrow whereas the low temperature process (γ) is broader. The upturn appearing at the higher temperatures was due to the Maxwell-Wagner-Sillars polarisation.

Figure 3 shows the presence of two dielectric loss processes for sample 3G. DSC showed a glass transition at 247 K, which indicates that the high temperature dielectric process (α) could be identified as the glass transition. This is further supported by the non-linear "WLF" character of the α process for the 3G sample (Fig. 4).

Figure 4 shows that both β and γ for 5G-OH displayed an Arrhenius temperature dependence with the same activitation energy: 98 kJ $\text{mol}^{-1}$ for β and 94 kJ $\text{mol}^{-1}$ for γ. The low temperature (β) process of polymer 3G exhibited a very high activation energy, 202 kJ $\text{mol}^{-1}$. The high temperature process (α) followed the WLF equation typical of a glass transition.

The relaxation strength ($\varepsilon_r - \varepsilon_u$; where $\varepsilon_r$ is the relaxed and $\varepsilon_u$ is the unrelaxed dielectric permittivity) were obtained from Argand plots fitting the Havriliak-Negami equation (20) to the dielectric ($\varepsilon^*$) data:

$$\varepsilon^* = \varepsilon_u + \frac{\varepsilon_r - \varepsilon_u}{\left(1+(i\omega\tau)^{\bar{\alpha}}\right)^{\bar{\beta}}} \qquad \text{...(1)}$$

where ω is the angular frequency, $\bar{\beta}$ is the asymmetric broadening factor and $\bar{\alpha}$ is the symmetric broadening factor.

The broadening was dominantly symmetric ($\bar{\beta}$ was equal to 1), although the β process of polymer 3G showed some asymmetric broadening. Data for the broadening factors obtained by fitting Eq. (1) are presented in Table 1. The increase in symmetric broadening factor with increasing temperature is a well-known feature and can be explained by a narrowing of the relaxation time spectrum due to the Arrhenius temperature dependence of the relaxation processes (21). The β process of polymer 5G-OH exhibited $\bar{\alpha}$ values between 0.8 and 1 whereas the γ process always exhibited lower $\bar{\alpha}$ values, at a given temperature.

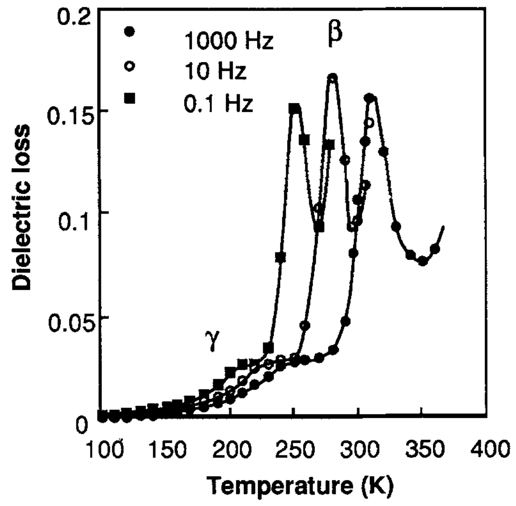

Figure 2. Dielectric loss for sample 5G-OH at the frequencies shown in the graph as a function of temperature.

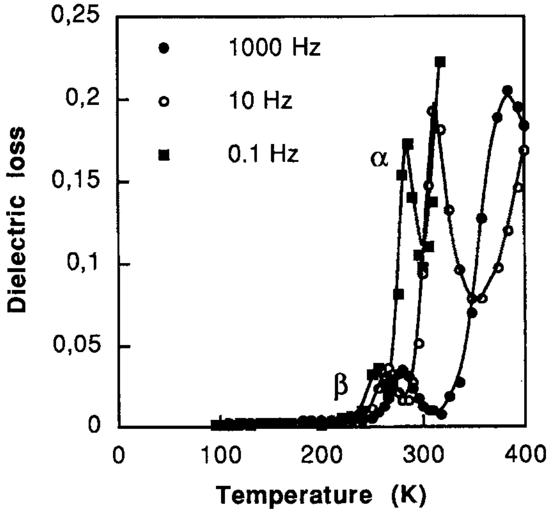

Figure 3. Dielectric loss for sample 3G at the frequencies shown in the graph as a function of temperature.

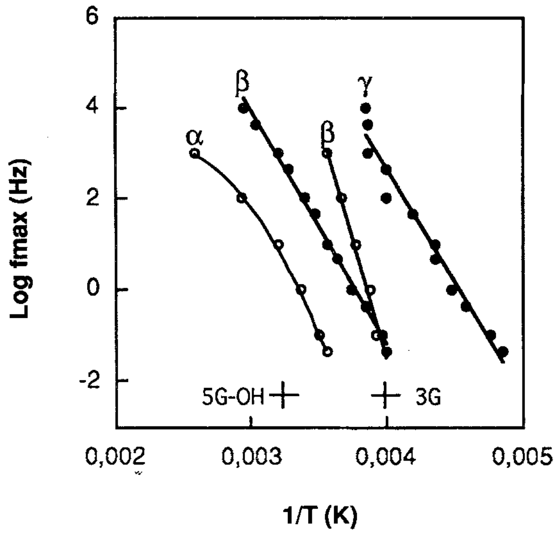

Figure 4. Temperature dependence of relaxation processes as obtained from plots of isochronal dielectric loss vs. temperature: ● 5G-OH; ○ 3G. The glass transition temperatures obtained by DSC are indicated by crosses in the graph.

Table 1. Results of fitting the Havriliak-Negami equation

| Sample/ process | Temperature (K) | $\bar{\alpha}$ | $\bar{\beta}$ | $\Delta\varepsilon^a$ |
|---|---|---|---|---|
| 3G/α | 260 | 0.90 | 1 | 0.9 |
| 3G/α | 280 | 0.82 | 1 | 0.9 |
| 3G/α | 300 | 0.86 | 1 | 0.94 |
| 3G/β | 260 | 0.44 | 0.6 | 0.42 |
| 3G/β | 280 | 0.50 | 0.6 | 0.34 |
| 3G/β | 300 | 0.56 | 0.6 | 0.20 |
| 5G-OH/β | 250 | 0.80 | 1 | 0.92 |
| 5G-OH/β | 290 | 0.83 | 1 | 0.86 |
| 55G-OH/β | 340 | 0.94 | 1 | 0.66 |
| 5G-OH/γ | 200 | 0.23 | 1 | 0.50 |
| 5G-OH/γ | 250 | 0.29 | 1 | 0.50 |
| 5G-OH/γ | 300 | 0.47 | 1 | 0.30 |

a) $\Delta\varepsilon = \varepsilon_r - \varepsilon_u$. The displayed values were obtained by doubling the experimental values since the studied samples were 50/50 mixtures of hyperbranched polyester and dielectrically inactive polyethylene.

Relaxation strength data were also obtained by fitting Eq. (1) to the dielectric data. The 5G-OH sample displayed a relaxation strength of the β process which was typically twice as high as that of the γ process (Table 1). The relaxation strength of the subglass process of 3G was significantly smaller than that of the sum of the relaxation strengths of the two subglass processes of 5G-OH, 0.2-0.4 compared with 1.0-1.4.

The nature of the relaxation processes cannot be revealed with absolute certainty. The five-generation polymer (5G-OH) showed three relaxation processes: a glass transition (α) and two subglass processes, β and γ. The similarity in activation energies of the β and γ processes does not prove that the processes are of the same origin. The β process is most probably due to reorientation of the ester group. Early dielectric work on poly(methyl methacrylate) showed the presence of a subglass process assigned to ester group motion of an activation energy of 90±10 kJ $mol^{-1}$ (22-26). Poly(methyl acrylate) showed a similar relaxation process of the activation energy of 60 kJ $mol^{-1}$ (22, 27) which also agrees with that of poly(ethylene sebacate), 50 kJ $mol^{-1}$ (28). The pronounced difference in activation energy for ester group reorientation in these related polymers demonstrates the strong effect from the surrounding structure. The low temperature process (γ) can be assigned to the hydroxyl groups. The relatively small relaxation strength of this process compared to that of the β process may be explained by the fact that the dipole moment (μ) of the hydroxyl groups is smaller than of the ester groups (effective μ in polymers (29): ester-linkage=0.70 D, ether-linkage=0.45 D, in low molar mass liquid the corresponding values are 1.7 D and 1.1 D, respectively). The narrowness of the β process in 5G-OH (high $\bar{\alpha}$ values) demonstrates that the "inner" structure is regular and that the available free volume is relatively homogeneously distributed. The three-generation polymer (3G) showed apart from the glass transition (α) only one relatively weak subglass process (β). This polymer has only an unpolar aliphatic terminal group which is not dielectrically active. The β process occurring in 3G must be due to reorientation of the ester groups and is thus analogous to the β process in 5G-OH. The location of the β's in the Arrhenius diagram is similar for both polymers, but the activation energy is twice as large in 3G as in 5G-OH and the relaxation strength of 3G is only half that of 5G-OH. Both these observations indicate that the ester groups are more constrained in 3G than in 5G-OH. The difference in glass transition temperature between the two polymers can be attributed to the relatively strong intermolecular interactions involving hydroxyl groups in the peripheral parts of the molecules of 5G-OH.

## ACKNOWLEDGEMENTS

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