

Relaxation processes in hyperbranched polyesters: influence of terminal groups

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Three hyperbranched polyesters with the same backbone structure but with different terminal groups: hydroxyl, benzoate or acetate groups, were studied by dielectric spectroscopy, differential scanning calorimetry and dynamic mechanical analysis. The benzoate- and acetate-terminated polymers exhibited only one subglass process (β), originating from reorientation of the ester groups, distinct from the glass transition (α). The hydroxyl-terminated sample exhibited a low-temperature subglass process (γ), due to motions of the hydroxyl groups, in addition to the β and α processes. The relaxation strengths of the hyperbranched polymers were found to be considerably lower than for those of linear analogues. The activation energies of the β process in the polymers studied increased in the order of hydroxyl, acetate and benzoate, indicating that the benzoate-terminated polymer is the most constrained. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Macromolecular architecture has received considerable and increasing interest during recent years. One of the more recently 'discovered' groups of substances with a unique type of molecular architecture is the group of dendritic macromolecules^{1,2}, comprising dendrimers^{3,4} and hyperbranched polymers⁵.

Dendrimers are molecules with a three-dimensional, globular shape, built of AB_x -functional monomers attached to a B_y -functional core ($y \geq 1$) (Figure 1a). Each repeating unit layer is referred to as a generation. In a polymer based on an AB_2 monomer, the outermost generation contains as many repeating units as the rest of the molecule. As a consequence, the molar mass and the number of end-groups are doubled with each successive generation. Dendrimers are ideal in the sense that all repeating units in the inner layers are fully reacted, i.e. the degree of branching is equal to unity. The degree of branching (DB) is defined according to Hawker *et al.*⁶ as follows:

$$DB = \frac{\sum_{\text{term}} + \sum_{\text{dendritic}}}{\sum_{\text{term}} + \sum_{\text{dendritic}} + \sum_{\text{linear}}} \quad (1)$$

where 'term', 'dendritic' and 'linear' refer to terminal groups, dendritic groups and linear groups. A hyperbranched macromolecule resembles a dendrimer except

that some AB_x monomers are linearly incorporated, leaving B groups unreacted in interior layers (Figure 1b).

The strategy for synthesizing dendrimers often includes several protection and/or deprotection steps, which means that the synthesis is both complex and time-consuming. It is currently difficult to produce dendrimers on a large-scale basis at an acceptable cost for use in material-consuming applications⁷. Hyperbranched polymers may be a suitable alternative because the synthesis is less complex and less time-consuming and the properties of hyperbranched polymers are believed to be similar to those of dendrimers⁸.

Dendritic macromolecules exhibit properties different from those of their linear counterparts¹, e.g. the melt viscosity for a hyperbranched molecule is considerably lower than that of a corresponding linear polymer of the same molar mass⁹. The relationship between hydrodynamic volume and molar mass is, for hyperbranched polymers, very different from that for linear polymers, due to the difference in architecture¹.

The thermal behaviour of hyperbranched polymers is less well understood. Kim and Webster⁵ suggested that the glass transition of hyperbranched polymers is due to translational motions and not to long-chain motions as it is for linear polymers. The glass transition temperature for dendrimers has been reported to increase with molar mass up to a certain limit, above which it remains practically constant¹⁰. The glass transition temperature increases with increasing polarity of the end-groups¹¹. Stutz¹² stated in a recent paper that the glass transition temperature of dendrimers is dependent on molar mass,

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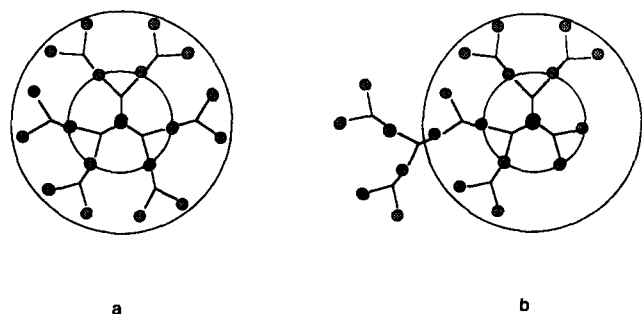


Figure 1 Schematic representation of a dendrimer (a) and a hyperbranched polymer (b) based on AB_2 monomers and a B_3 core

on the rigidity of the backbone, and on the nature of the terminal groups.

Most hyperbranched polymers reported in the literature have been synthesized from AB_x monomers alone without a core molecule of B_y functionality. The core molecule provides a tool for controlling the molar mass and polydispersity of the final polymer. These hyperbranched polymers are often referred to, for example, as a four-generation polymer when the stoichiometric ratio between the core and the repeating unit corresponds theoretically to a dendrimer of the fourth generation. The polymers used in this study are based on 2,2-bis(methylol)propionic acid (*bis*-MPA, AB_2 monomer) and trimethylolpropane (TMP, B_3 -functional core).

Dielectric spectroscopy provides information about the segmental mobility within a polymer. To our knowledge, only one paper has been published on the dielectric relaxation behaviour of hyperbranched polymers. Malmström *et al.*¹³ found three relaxation processes in a 'five-generation' hyperbranched polyester with terminal hydroxyl groups: the glass-rubber transition, α , and two subglass processes, β and γ . The low-temperature process, γ , was assigned to motions of the terminal hydroxyl groups and the β process to a reorientation of the ester groups. A three-generation hyperbranched polyester with terminal $-\text{CO}-\text{CH}_2\text{CH}_3$ groups exhibited, in addition to the glass transition (α), only one subglass process (β), presumably because it had no hydroxyl groups as terminal groups.

The aim of this study was to investigate further how the thermal transitions are affected by different terminal groups. This paper presents data obtained by dielectric spectroscopy, differential scanning calorimetry (d.s.c.) and dynamic mechanical analysis (d.m.a.) for three hyperbranched polyesters with different terminal groups: hydroxyl, acetate and benzoate. The polyesters all originated from the same base polyester, having a ratio of core molecule to repeating units (1:93) corresponding to a 'five-generation' dendrimer. Three relaxation phenomena were found in the sample with terminal hydroxyl groups whereas only two processes were recorded in the acetate- and benzoate-terminated polymers. The activation energies obtained from the subglass relaxation process associated with reorientation of the ester groups indicated that the benzoate-terminated sample is the most constrained.

EXPERIMENTAL

Materials

2-Ethyl-2-(hydroxymethyl)-1,3-propanediol (trimethylolpropane, TMP) and 2,2-dimethylolpropionic acid (*bis*-MPA)

were kindly supplied by Perstorp Polyols AB, Sweden. Sulfuric acid, acetyl chloride, benzoyl chloride, dimethylaminopyridine (DMAP) and triethylamine (TEA) were supplied by Aldrich and were used as received. All solvents were distilled prior to use.

Instrumentation

A Bruker AC-400 FT-NMR spectrometer was used for n.m.r. characterization. Size exclusion chromatography (s.e.c.) was performed in tetrahydrofuran (THF) on a Waters s.e.c. system equipped with a solvent delivery system (Waters 510), an automated injector (WISP 710B) and a Waters 410 differential refractometer. μ -Styragel columns were used (500, 10^5 , 10^4 , 10^3 and 100 Å). Linear polystyrene standards with low polydispersity indices were used for calibration. All molar masses are reported in polystyrene equivalents. Dielectric spectroscopy was performed using an IMASS TDS time domain spectrometer equipped with a Hewlett Packard Series 300 computer. The time domain spectrometer is based on a design by Mopsik¹⁴. Calorimetric studies were performed on a Perkin-Elmer DSC-7 equipped with a Perkin-Elmer 7700 computer. The instrument was calibrated according to the standard procedure, using indium as a reference. Dynamic mechanical analysis was carried out on a Rheometrics RDAII.

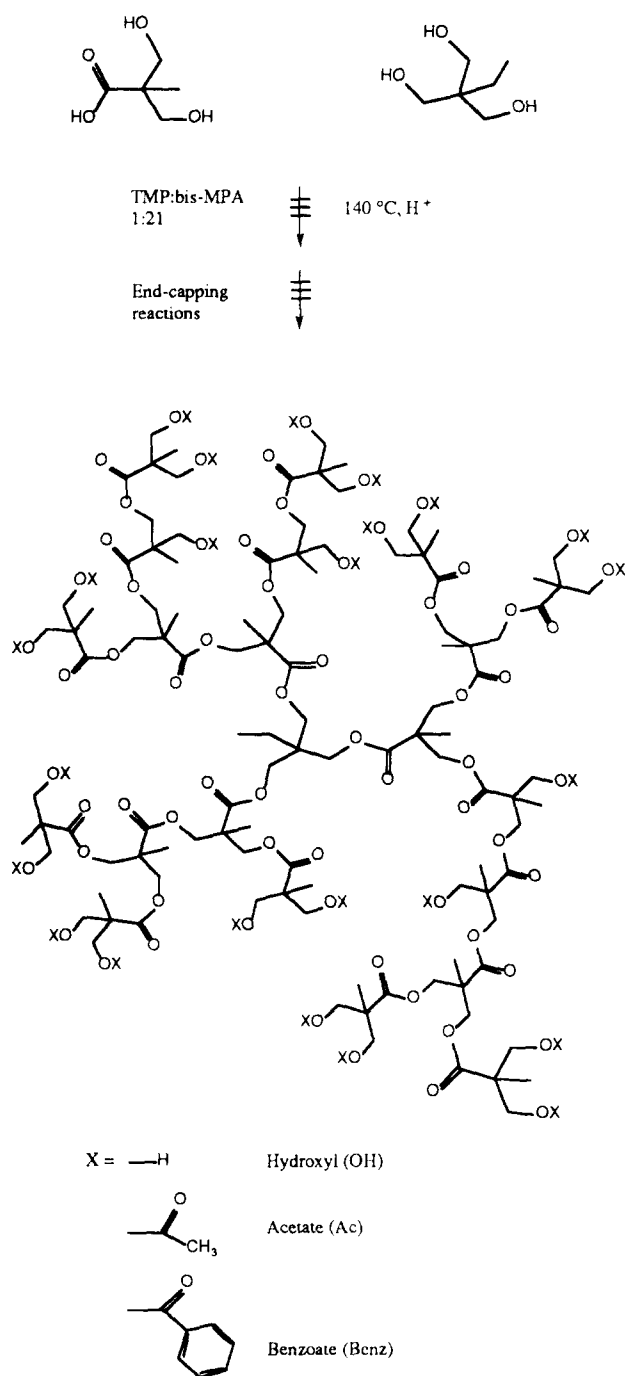
Synthesis

The synthesis of a hyperbranched polymer with core:*bis*-MPA ratio 1:21 is schematically outlined in *Scheme 1*.

5G-OH (3): 1.5 g *bis*-MPA (**1**, 0.011 mole), 0.50 g TMP (**2**, 0.0037 mole) and 1.5 mg sulfuric acid were added to a three-necked flask equipped with an argon inlet, a drying tube and an overhead stirrer. The flask was placed in an oil bath previously heated to 413 K. The flask was left, under stirring, with an argon flow for 30 min. Vacuum was then applied to the flask for 30 min. Subsequently, 45 g *bis*-MPA and 45 mg sulfuric acid were added in 39 small portions during the subsequent 6 h with alternating argon flow and vacuum. The flask was left for 1 h under vacuum for the reaction to reach completion after the final addition of *bis*-MPA. **Characterization:** n.m.r.: degree of branching = 82%¹⁵, s.e.c.: $\bar{M}_n = 1400 \text{ g mol}^{-1}$, $\bar{M}_w = 2700 \text{ g mol}^{-1}$. The theoretical molar mass is $10\,900 \text{ g mol}^{-1}$.

5G-Ac (4): 3.0 g 5G-OH, 0.32 g DMAP (2.6 mmole) 4.0 g TEA (3.95 mmole) and 50 ml acetone were mixed in a two-necked flask equipped with a magnetic bar. The flask was cooled on an ice-bath, and 2.3 g acetyl chloride (22.7 mmole) diluted in 10 ml acetone was added dropwise. The hydrochloric salt of TEA started to precipitate immediately. After 2 h, the precipitate was filtered off and the acetone was evaporated. The crude product was dissolved in CH_2Cl_2 and extracted once with 2 M HCl, twice with NH_4Cl (10%) and twice with Na_2CO_3 (10%). The organic phase was dried with MgSO_4 and the solvent was evaporated. **Characterization:** i.r.: no hydroxyl groups left (3600 cm^{-1}); s.e.c.: $\bar{M}_n = 2300 \text{ g mol}^{-1}$, $\bar{M}_w = 4500 \text{ g mol}^{-1}$. The theoretical molar mass is $15\,000 \text{ g mol}^{-1}$.

5G-Benz (5): 30 g 5G-OH, 0.32 g DMAP (2.6 mmole),



Scheme 1 An outline of the synthesis of a hyperbranched polyester with TMP:bis-MPA ratio 1:21. The polymers used in this study have a TMP:bis-MPA ratio of 1:93

4.0 g TEA (39.5 mmole) and 50 ml methylene chloride were mixed in a two-necked flask equipped with a magnetic bar. The flask was cooled on an ice-bath, and 4.1 g benzoyl chloride (29.2 mmole) diluted in 20 ml methylene chloride was added dropwise. After reaction overnight, the work-up was performed in accordance with the procedure described for 5G-Ac. *Characterization*: i.r.: no hydroxyl groups left (3600 cm^{-1}); s.e.c.: $\bar{M}_n = 2700\text{ g mol}^{-1}$, $\bar{M}_w = 5200\text{ g mol}^{-1}$. The theoretical molar mass is $18\,500\text{ g mol}^{-1}$.

Techniques

Degree of branching. The degree of branching was assessed using ^{13}C -n.m.r. spectroscopy (INVGATE,

$T_1 = 10\text{ s}$) in accordance with a procedure described earlier¹⁵. The samples were dissolved in acetone- d_6 and the solvent signal was used as a reference.

Dielectric spectroscopy. The neat polymers did not form films. To obtain films suitable for dielectric spectroscopy the polymers were mixed 1:1 by weight with dielectrically inactive linear polyethylene. The measurements were performed on $200\text{ }\mu\text{m}$ thick film samples. The samples were purged with dry nitrogen for 24 h to ensure complete removal of water. At time $t = 0$, a step voltage of 10 V or 100 V was applied between the electrodes. This caused a charge $Q(t)$ to appear on the capacitor plates, and the complex capacitance was obtained as a function of frequency 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. Dielectric data were taken under isothermal conditions between periods during which the specimens were heated. The lowest temperature for the measurements was 100 K and data were taken every fifth kelvin, except for the loss peak regions at which data were taken every second kelvin. Thermal equilibrium was established prior to the actual measurements.

Differential scanning calorimetry. Samples were analysed using a heating/cooling rate of 10 K min^{-1} between 250 K and 420 K. Glass transition temperatures were determined on the second heating as the inflexion point of the heat-flow curves.

Dynamic mechanical analysis. Dynamic mechanical analysis was carried out using auto-tension and auto-strain in shear. The sample geometry was parallel plates with a diameter of 7.9 mm. The measurements were made at 1 Hz between 240 K and 330 K. The glass-rubber transition temperature was measured as the temperature of the $\tan\delta$ peak maximum.

RESULTS AND DISCUSSION

At sufficiently low temperatures, all amorphous polymers are glassy and stiff. When they are warmed, the polymers soften in a characteristic glass-rubber transition region. The glass transition has been defined as the temperature at which long-range coordinated molecular motion starts¹⁶. Amorphous polymers always exhibit a glass transition (α) and one or more subglass processes (denoted β , γ , δ etc., where β occurs at the highest temperature). The temperature dependence of the glass transition is best described by the following equation, which is equivalent to the WLF equation:

$$f_{\max} = f_0 \cdot e^{-\frac{A}{(T-T_0)}} \quad (2)$$

where A is a constant, T and T_0 are temperatures, f_{\max} is the frequency associated with the loss maximum and f_0 is a constant. Subglass processes follow the Arrhenius equation:

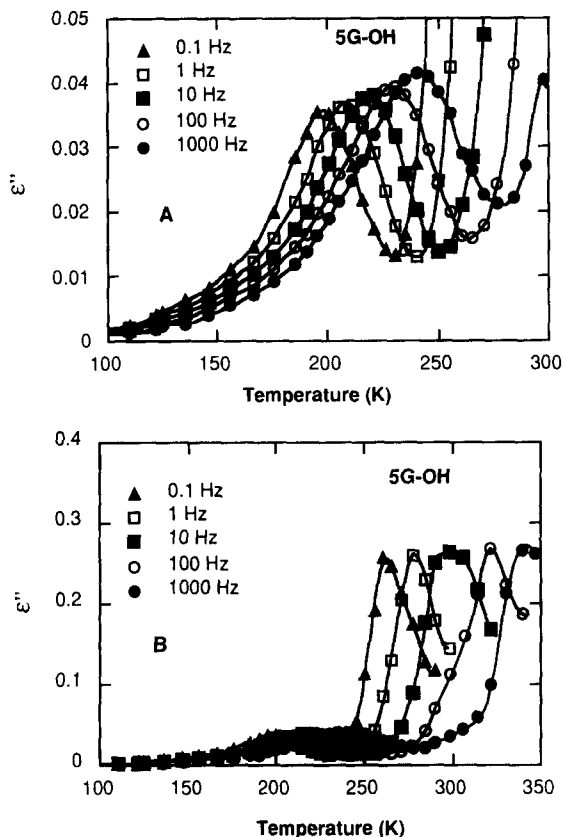
$$f_{\max} = f_0 \cdot e^{-\frac{\Delta E}{RT}} \quad (3)$$

where ΔE is the activation energy and R is the gas constant.

Different measuring techniques yield different transition temperatures due to differences in measuring frequency. The nature of the transition can be revealed in an Arrhenius plot, e.g. a plot of $\log f_{\max}$ as a function of $1/T$. The glass transition appears curved in the

Table 1 Characteristics of glass transition and the subglass processes

	5G-OH	5G-Ac	5G-Benz
T_{α} (1 Hz; K)	—	279	327
T_{β} (100 Hz; K)	320	282	327
ΔE_{β} (kJ mol ⁻¹)	86	180	260
T_{γ} (1 Hz; K)	209	—	—
ΔE_{γ} (kJ mol ⁻¹)	87	—	—
$\Delta\epsilon$ (100 Hz)	1.2	0.3	0.6

**Figure 2** Dielectric loss (ϵ'') for 5G-OH at the frequencies shown in the graph as a function of temperature

Arrhenius plot, whereas the subglass processes appear as straight lines (see Figures 3 and 6).

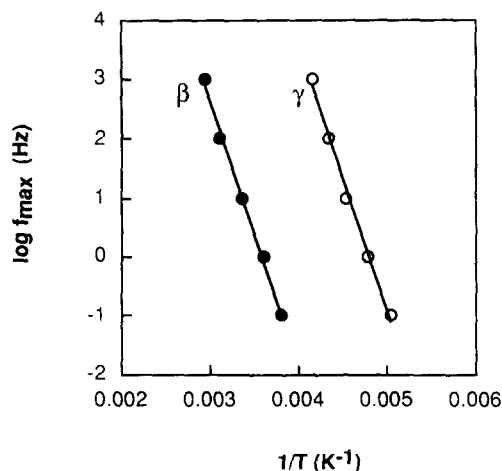
Dielectric spectroscopy

All results obtained by dielectric spectroscopy are summarized in Table 1.

5G-OH

The relaxation behaviour of a fifth-generation polymer with terminal hydroxyl groups was reported by Malmström *et al.*¹³. A similar polymer, here denoted 5G-OH, was used in this study. The relaxation behaviour of 5G-OH (Figure 2) agreed with the results reported earlier¹³.

A low temperature process, denoted γ , appeared at about 209 K (1 Hz) and a very distinct high temperature process (β) was found at 278 K (1 Hz) (Figure 2). It was concluded in the previous paper¹³ that the high temperature process, β , could be assigned to a reorientation of the ester groups. This was based on the finding that the glass transition temperature obtained by d.s.c. was 50 K higher than the temperature associated with the maximum of the β loss peak at the corresponding frequency¹³. Furthermore, the dielectric β process obeyed an

**Figure 3** Temperature dependence of dielectric relaxation processes in 5G-OH; f_{\max} were obtained from isochronal ϵ'' -temperature data

Arrhenius temperature dependence, typical of a subglass transition process (Figure 3). The low-temperature γ process was assigned to motions of the terminal hydroxyl groups. Meaningful dielectric data in the temperature range where the α process should appear were not obtained for this polymer because of Maxwell–Wagner–Sillars polarization.

A close examination of the dielectric loss peaks at 10 to 1000 Hz (Figure 2) revealed the presence of a weak loss process appearing only as a shoulder at 300–310 K at 1000 Hz, at 300 K at 100 Hz and at 290 K at 10 Hz. No structural assignment of this weak relaxation process has been made at this stage.

Figure 3 shows the Arrhenius plots for the dielectric relaxation processes obtained for 5G-OH. The β and γ relaxation processes obey the Arrhenius equation [equation (3)]. The activation energies were 86 kJ mol⁻¹ for β and 87 kJ mol⁻¹ for γ , which are close to the values of 98 and 94 kJ mol⁻¹ previously reported¹³. The magnitude of the Arrhenius dependence indicates that the recorded dielectric processes (β and γ) are subglass processes.

5G-Ac and 5G-Benz

Two dielectric relaxation processes were found in 5G-Ac (Figure 4). The dielectric permittivity remained constant at temperatures between 100 and 240 K; i.e. no dielectric relaxation process occurred in this temperature range. At 240 K, an increase in dielectric permittivity was observed. The peak was resolved into two peaks at higher frequencies. A low-temperature process, denoted β , appeared only as a weak shoulder on the low-temperature side of the peak associated with the larger α process peak in the isochronal dielectric loss-temperature curves (Figure 4a). The α peak shifted more strongly in temperature with increasing frequency than the β process, and the two processes overlapped almost completely at 0.1 Hz.

The 5G-Benz polymer exhibited no dielectric relaxation processes below 250 K. As in 5G-Ac, two relaxation processes were revealed in the dielectric loss-temperature plot (Figure 5). A weaker low temperature process, β , appeared as a shoulder on the low-temperature side of the larger and stronger high-temperature process, α . The frequency-induced shifts of the relaxation peaks were

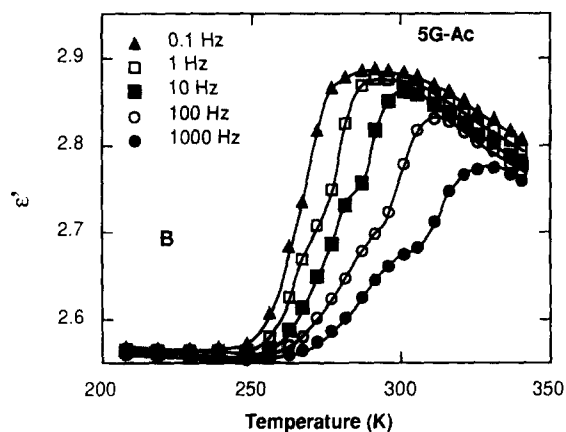
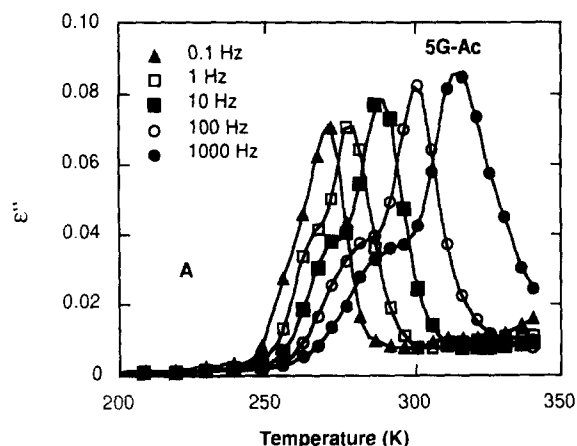


Figure 4 (A) Dielectric loss (ϵ'') for 5G-Ac at the frequencies shown in the graph as a function of temperature. (B) Real part of the dielectric permittivity (ϵ') for 5G-Ac at the frequencies shown in the graph as a function of temperature

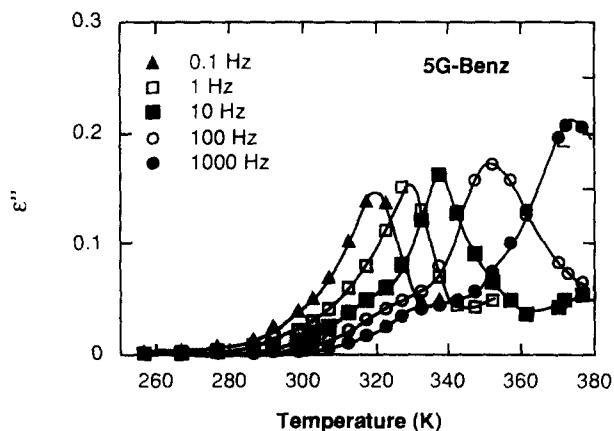


Figure 5 Dielectric loss (ϵ'') for 5G-Benz at the frequencies shown in the graph as a function of temperature

similar to those found in 5G-Ac: the α peak shifted more strongly in temperature with increasing frequency than the low-temperature β process. The peaks associated with the two processes overlapped almost completely at 0.1 Hz.

Figure 6 indicates that the temperature dependence of the α processes of 5G-Ac and 5G-Benz is best described by equation (2), which makes it possible to conclude that these processes originate from the glass-rubber transition.

The β -processes, according to Figure 6, follow the

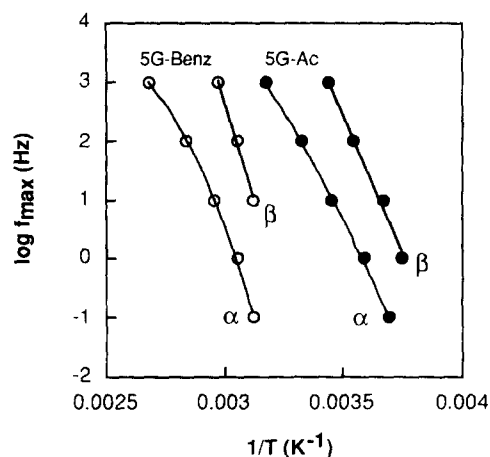


Figure 6 Temperature dependence of relaxation processes in 5G-Ac and 5G-Benz; f_{\max} were obtained from isochronal ϵ'' -temperature data

Arrhenius law [equation (3)], as expected for subclass processes. Their activation energies are comparatively high: 180 kJ mol^{-1} for 5G-Ac and 260 kJ mol^{-1} for 5G-Benz. However, because the low-temperature processes (β) interfered with the more intense high-temperature processes (α), f_{\max} values for the β processes are associated with a greater uncertainty than the corresponding data for the α process.

The results are in accordance with the earlier reported results for a 3G-propionate¹³ where the activation energy for the β -process was found to be 202 kJ mol^{-1} . The higher activation energies for 5G-Ac and 5G-Benz may indicate that the ester groups are more constrained in these polymers than in 5G-OH. The activation energy is highest for the benzoate-terminated sample; i.e. the ester groups are most constrained in this polymer, which seems reasonable considering the segmental inflexibility of the terminal groups.

Relaxation strength

The relaxation strength, $\Delta\epsilon$, is given by:

$$\Delta\epsilon = \epsilon_r - \epsilon_u \quad (4)$$

where ϵ_r is the relaxed dielectric permittivity and ϵ_u is the unrelaxed dielectric permittivity. Dielectric spectroscopy was carried out on samples consisting of equal amounts of dielectrically inactive polyethylene and hyperbranched polymer, which means that the relaxation strength of the pure hyperbranched polymer is twice that determined from the measurement. The relaxation strength is preferably obtained from isothermal complex plane data (Argand plots, ϵ'' plotted as a function ϵ'). However, an estimate of $\Delta\epsilon$ can be obtained from isochronal data recording the 'jump' in the real part of the dielectric permittivity associated with each relaxation process. The latter method was used in this study.

Figure 7 shows the isochronal (100 Hz) dielectric permittivity as a function of temperature for the three polymers studied. 5G-OH showed a large increment in dielectric permittivity from 2.5 (unrelaxed) to about 3.7 (relaxed), i.e. $\Delta\epsilon = 1.2$ (Table 2). The relaxation strength of the high-temperature (β) process was roughly twice that of the low-temperature (γ) process. The other two polymers showed a considerably smaller change in dielectric permittivity, from 2.55 to 2.85 ($\Delta\epsilon = 0.3$)

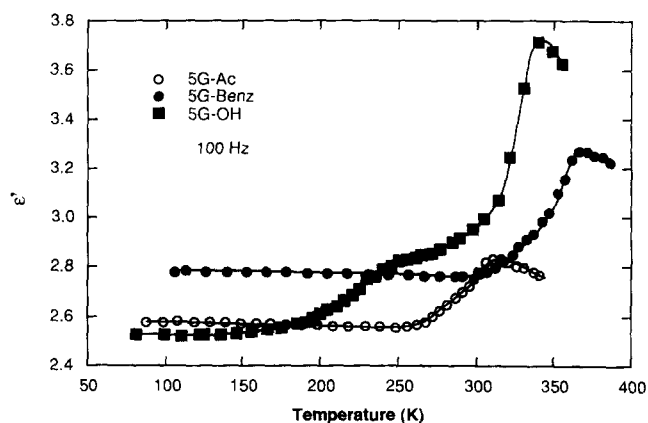


Figure 7 Real part of the dielectric permittivity (ϵ') (100 Hz) for the polymers indicated in the figure as a function of temperature

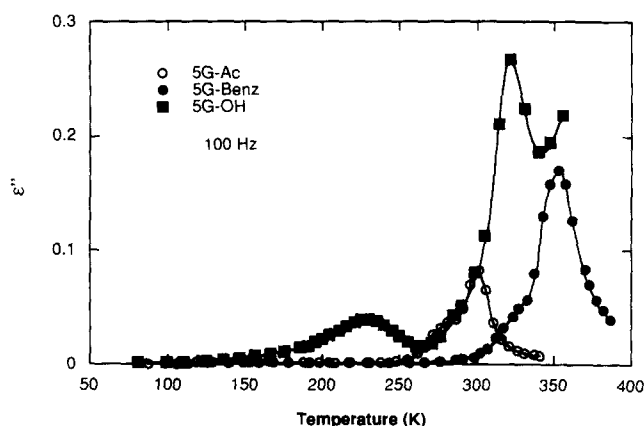


Figure 8 Dielectric loss (ϵ'') (100 Hz) for the polymers indicated in the figure as a function of temperature

for 5G-Ac and from 2.75 to 3.35 ($\Delta\epsilon = 0.6$) for 5G-Benz. The higher value of unrelaxed dielectric permittivity for 5G-Benz than for the other two polymers can be attributed to the terminal phenyl groups which are known to increase the unrelaxed dielectric permittivity^{17,18}.

Coburn and Boyd¹⁹ reported for poly(ethylene terephthalate) a relaxation strength of 2.5, including both the α and β processes. Ishida *et al.*²⁰ have studied poly(vinyl acetate) (PvAc) and poly(vinyl benzoate) (PvBz) and have reported that the relaxation strength for PvAc is approximately 5. They also report that the relaxation strength is smaller for PvBz than for PvAc. The difference in relaxation strength between these related polymers was attributed to the higher dipole concentration in PvAc. Purely amorphous poly(vinyl alcohol) was reported to have a relaxation strength between 9 and 13 (-60 to -20°C)^{21,22}.

The relaxation strength of the hyperbranched polymers is considerably lower than that of their linear analogues. This can be attributed to the less flexible structure in the hyperbranched polymers than in their linear polymer analogues. 5G-Benz exhibited a relaxation strength twice as large as that of 5G-Ac, which was unexpected and for which we have no good explanation.

Figure 8 shows the isochronal (100 Hz) dielectric loss as a function of temperature for the three polymers studied. The low-temperature process centring at 230 K is indeed unique for a hydroxyl-terminated polymer. The

Table 2 Glass transition temperatures (K) by different methods

Method	5G-OH	5G-Ac	5G-Benz
d.s.c.	306	273	290
d.m.a.	296	267	281
dielectric spectroscopy	—	264	315

unexpectedly large differences in total relaxation strength found among the different polymers are somewhat moderated by the consideration that the terminal groups constitute one-half (in terms of number) of the entire sample and that the molar masses of the three terminal groups are indeed very different. The concentration of dipoles per mass unit (and per volume unit) is thus different for the different polymers.

Comparison of glass transition temperatures assessed by different techniques

All the results regarding the glass transition temperatures are summarized in Table 2. The hyperbranched polyesters used in this study have been reported to be very sensitive to their thermal prehistory²³. The different measurements reported have been preceded by slightly different thermal treatments, so that deviations were expected in glass transitions assessed by different techniques. Samples for dielectric spectroscopy were prepared by melt-mixing at 423 K and were rapidly cooled to room temperature and left for some time before measurement. Samples for dynamic mechanical analysis (d.m.a.) were heated above 413 K before the measurements started. D.s.c. samples were all given the same thermal pre-treatment involving heating the samples to 413 K, and glass transitions were all recorded upon the second heating.

D.s.c. measurements showed second-order phase transitions, characteristic of glass transitions, in all three polymers. Dynamic mechanical analysis showed corresponding typical peaks in $\tan\delta$ (Table 2). The acetate-terminated sample, 5G-Ac, exhibited agreement between dielectric data and data obtained by d.s.c. and d.m.a. (Table 2). The difference in glass transition temperatures assessed by the three methods is less than 10 K. The calorimetric glass transition temperature is 6 K higher than the temperature for $\tan\delta_{\max}$ in the 1 Hz data from the d.m.a. The calorimetric glass transition temperature is generally considered to be a low-frequency measure corresponding to a frequency of about 10^{-2} Hz, which then would lead to an even greater difference between the mechanical and calorimetric glass transition temperatures.

The difference in glass transition between d.s.c. and d.m.a. data for 5G-OH was about 10 K, which is as expected since the measurements were performed at different frequencies. No comparison with the dielectric data could be made since no data for the α process were available because of the Maxwell–Wagner–Sillars polarization.

Large differences in the glass transition temperatures determined by different measuring techniques were obtained for the benzoate-terminated sample. The dielectrically determined glass transition was found to be markedly higher than its calorimetric analogue. The 5G-Benz polymer turned opaque after storage for some time at room temperature, which suggests that it crystallized. End-group crystallization of hyperbranched

polyesters terminated with long alkyl chains has been reported by Malmström *et al.*²⁴. The crystallinity was also observed by d.s.c. as a crystalline melting point at about 325 K. No crystallization could be seen during cooling, indicating that the crystallization is kinetically controlled. X-ray scattering revealed crystalline, Bragg reflections. The dynamic mechanical analysis was preceded by heating the sample to 413 K, which melts all possible crystallinity. The difference between d.m.a. and d.s.c. was similar to that in the case of 5G-Ac. The intensity of the dielectric α process was markedly suppressed and shifted towards higher temperatures due to the presence of crystals in this particular polymer, which were assessed by this technique.

CONCLUSIONS

Three differently end-capped hyperbranched polyesters were studied by dielectric spectroscopy, differential scanning calorimetry and dynamic mechanical analysis. The polyesters with terminal benzoate and acetate groups exhibited a subglass process (β) originating from reorientation of ester groups and a glass transition. The sample with terminal hydroxyl groups exhibited two subglass processes apart from the glass transition: one subglass process (β) similar to those found in the acetate- and benzoate-terminated samples, and an additional low-temperature subglass process (γ) due to motions of the hydroxyl groups. These hyperbranched polymers exhibited relaxation strengths markedly lower than those of their linear analogues. This was explained as being due to a lower segmental flexibility of the backbone in a hyperbranched polymer than in a linear polymer.

The glass transition temperatures obtained by different techniques agreed well for both the hydroxyl- and acetate-terminated polymers. The small differences can be attributed to differences in measuring frequencies. The results obtained for the benzoate-terminated polymer differed markedly. The glass transition temperatures obtained by dielectric spectroscopy were 20–30 K higher than those obtained by dynamic mechanical analysis and differential scanning calorimetry.

The benzoate-terminated sample was found to crystallize upon storage and it was suggested that the α -transition measured by dielectric spectroscopy was shifted towards higher temperatures due to the presence of a constraining crystallinity. The identical glass transition temperatures obtained by dynamic mechanical analysis and differential scanning calorimetry after heat

treatment causing melting of possible crystals substantiate this suggestion.

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