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Polymer 48 (2007) 2079–2086

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Physical crosslinking effects in α,ω-dihydroxy terminated polybutadienes

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Received 7 August 2006; received in revised form 19 December 2006; accepted 7 February 2007
Available online 14 February 2007

Abstract

Structure and molecular dynamics of α,ω-dihydroxy terminated polybutadienes of varying number averaged molecular weight (1320–10 500 g/mol) have been investigated by Fourier-transformed infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, dielectric relaxation spectroscopy (DRS), differential scanning calorimetry (DSC) and wide-angle X-ray scattering (WAXS). DSC and DRS revealed an increase in the glass transition temperature upon decrease of the molecular weight, accompanied by an increasing dynamic fragility m (or steepness index) of the dielectric α-process. This correlation between T_g and m for different molecular weights indicates the presence of a physical network, where H-bonded end-group clusters act as temporary crosslinks. From the dielectric relaxation strength $\Delta\varepsilon_\alpha(M_n)$, the fraction of associated hydroxy groups (f_{bond}) was estimated showing a peak value for the two but shortest polymers, a behaviour that strongly resembles the molecular weight dependence of the fragility. By considering the quantity $f_{bond}(M_n)$ in a modified Fox-Flory approach, the measured $T_g(M_n)$ behaviour could be reproduced in a satisfying way. FTIR results support this general picture and show a considerable dependence of the extent of hydrogen bonding and formation of hydroxy groups associates on the molecular weight. Further, WAXS and DSC results disprove the idea of formation of pseudo-crystalline hydrophobic microdomains in these compounds as suggested by other authors.

Keywords: Hydrogen bonding; Glass transition; Dielectric relaxation

1. Introduction

Hydroxylic compounds are well known for their strong association behaviour due to the formation of hydrogen bonds in the liquid (concentrated solution, polymer melts) and solid states [1]. Hydrogen bonds are dynamic, continually breaking and reforming under the influence of thermal motion. Consequently, in H-bonded systems, at any time a distribution of species consisting of monomers, dimers, trimers and higher multimers of hydroxy groups is present [2]. Hydroxy groups are also present in many industrially important polymers, e.g., polyvinylalcohol, polyvinylphenol or telechelic polymers [3]. Association of terminal hydroxy groups of telechelic polymers [4], which are used in preparation of segmented and crosslinked polyurethanes [5,6], polyamides, polyesters or polyepoxides [7] can play an important role in the process of the synthesis and have an impact on the resulting (microphase separated) structure of these products [8]. In hydroxy terminated telechelic polymers associating end groups can form domains, which are bridged by backbone polymer chains forming a matrix [9,10]. The materials of this kind behave as reversible polymer networks because of the finite lifetime of the end-group clusters. Hydrogen bonding has been used in the preparation of self-assembled supramolecular systems [11,12] and supramolecular polymer networks [13,14]. Hydrogen bonding and association of end groups in telechelic polymers have also a significant influence on the molecular

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doi:10.1016/j.polymer.2007.02.024

mobility of polymer chains as it is reflected in their viscoelastic, dielectric or thermal properties [15]. The molecular mobility and structure of telechelic polymers have also been investigated by means of nuclear magnetic resonance (NMR), e.g., temperature dependence of the chemical shift, spin–lattice and spin–spin relaxation times of ^{1}H NMR spectra [16]. Apart from (non-crystalline) associates of hydroxy groups, the presence of another kind of associates in telechelic polybutadienes, namely pseudo-crystalline clusters consisting of segments of polybutadiene chains as revealed by dynamic light scattering, was reported by Podešva et al. (see Ref. [4]). Such pseudo-crystalline clusters could directly be proven by X-ray diffraction techniques or differential scanning calorimetry.

This paper aims to study the relation between hydrogen bonding driven nanophase separation and the molecular dynamics in α,ω-dihydroxy terminated telechelic polybutadiene chains of variable molecular weight. For this purpose, various structural characterization techniques (FTIR, NMR, and WAXS) in combination with dynamic methods (DSC and DRS) are employed.

2. Experimental section

2.1. Materials

All α,ω-dihydroxy terminated polybutadienes used in this study were prepared in the Research Institute for synthetic rubber, Kralupy n.Vlt., Czech Republic by living anionic polymerization in polar media. Characterization of the polymers was provided by the manufacturer and is given in Table 1. Prior to our measurements, all polymers were dried in vacuum at 70 °C for one week and stored above P_2O_5.

2.2. Methods

2.2.1. DSC

Differential scanning calorimetry was performed using a Pyris 1 DSC from Perkin–Elmer. The purge gas (helium) was let through the DSC cell with a flow rate of 20 mL/min. The temperature of the equipment was calibrated with water and mercury. The heat of melting of mercury was used for calibrating the heat flow. The samples with a typical mass of 20 mg were subjected to a cooling scan from ambient temperature to −100 °C, followed by a heating scan from that temperature to 100 °C, both scans at a rate of 10 °C/min. Here, a somewhat higher mass was used because, besides the glass transition, the presence of weaker thermal transitions was expected. Glass transition temperatures were determined from half Δc_p values in the second heating run.

Table 1
Molecular weight characterization and microstructure of α,ω-dihydroxy terminated polybutadienes studied, number average molecular weight, M_n, polydispersity, M_w/M_n and microstructure of PB chains (%)

Sample	M_n, [g mol^{-1}]	M_w/M_n	1,2	1,4-*cis*	1,4-*trans*
PBD1	1320	1.18	63	17	20
PBD2	2160	1.15	65	16	19
PBD3	2650	1.08	63	16	21
PBD4	4690	1.08	61	16	23
PBD5	10 500	1.05	57	18	25

2.2.2. WAXS

Wide-angle X-ray scattering experiments were carried out at room temperature on a HZG4A diffractometer (Freiberger Präzisionsmechanik, Germany) using Ni filtered Cu Kα radiation.

2.2.3. FTIR spectroscopy

Infrared spectra were carried out using a NICOLET IMPACT 400 Fourier transform infrared spectrometer in dry air environment. An ambient temperature deuterated triglycine sulphate detector was used for the wavelength range from 400 to 4000 cm^{-1}. A Happ–Genzel apodization function was used in all regions and spectral resolution was 2 cm^{-1}. Approximately 200 scans were averaged to achieve a good signal-to-noise ratio. The spectra were corrected for the H_2O and CO_2 content in the optical path. An aliquot of the sample was placed between two Si windows, the spectral features of which were accounted for by an absorption subtraction technique.

2.2.4. NMR spectrometry

NMR experiments were carried out on bulk samples (i.e. without using a solvent). NMR tube of diameter 5 mm was filled with (viscous) sample and a thin capillary containing small amount of the solution of sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) in D_2O as the standard was inserted and used to obtain the lock signal. High resolution ^{1}H NMR spectra were recorded with a Bruker Avance 500 spectrometer operating at 500.1 MHz in temperature range 280–350 K.

2.2.5. Dielectric relaxation spectroscopy

Samples for DRS measurements were prepared by assembling quartz fibres (50 ± 5 μm in diameter), together with the highly viscous liquid polymer material, between circular brass electrodes (effective diameter 20 mm) at room temperature. Subsequent insertion of this "sandwich" between the rigid electrode systems of the dielectric sample cell ensured both a well-defined area and sample thickness during the whole experiment.

Dielectric measurements were performed using a high precision dielectric analyzer (ALPHA analyzer, Novocontrol Technologies) in combination with a Novocontrol Quatro temperature system providing control of the sample temperature with high stability (<0.05 K). Temperature dependent experiments were realised by consecutive isothermal frequency sweeps (10^{-1}–10^7 Hz) in the temperature range from +100 °C to −140 °C in steps of 5 K, which resulted in an effective (mean) cooling rate of about 0.5 K/min. For an accurate determination of the relaxation time $\tau(T)$ and other relaxation parameters we fitted the dielectric loss spectra $\varepsilon''(\omega)$ to the empirical Havriliak–Negami (HN) relaxation function (Eq. (1)) [17]:

$$\varepsilon'' = -\mathrm{Im}\left\{\frac{\Delta\varepsilon}{\left(1+(\mathrm{i}\omega\tau)^{a}\right)^{b}}\right\} + \frac{\sigma}{\varepsilon_v\omega} \qquad (1)$$

where $\Delta\varepsilon$ corresponds to the relaxation strength, while the two 'shape parameters' a and b represent the logarithmic slope of the low frequency loss tail (a) and the high frequency loss tail ($-ab$). The second term in Eq. (1) accounts for ohmic conduction. A comprehensive description of analysis methods for dielectric data can be found in Refs. [18,19].

3. Results and discussion

3.1. Verification of the microstructure

The microstructure of all α,ω-dihydroxy terminated polybutadienes determined by ^{1}H NMR (Table 1) was found to be almost independent on the molecular weight. The spectra are shown in Fig. 1 and can be assigned to the protons of: 1,2 (−CH=) (a), 1,4 (−CH=) (b), 1,2 (CH$_2$) (c), 1,2 (−CH−) (e), 1,4 (−CH$_2$−) (f) and 1,2 (−CH$_2$−) (g). However, unlike the bands presented in Ref. [4], two more bands (d$_1$ and d$_2$) have been found for all polybutadienes at room temperature. The position of the former band is constant for all PB's (ca 4.2 ppm), however, the position of the latter band shifts remarkably with increasing molecular weight to lower parts per million. For the lowest molecular weight both bands overlap, for PBD4 and 5 the band d$_2$ merges with bands e and f. Since the integrated intensity of the band d$_1$ is inversely proportional to the molecular weight of PB, it can be attributed to the protons linked to terminal carbons of the polymer backbone chains. As regards the band d$_2$, we think it originates from the protons of terminal hydroxy groups part of which is H-bonded. This observation is confirmed by the measurements of ^{1}H NMR spectra for PB of the lowest molecular weight carried out at different temperatures (see Fig. 2). The position of band d$_1$ is independent of temperature, however, the band d$_2$ moves remarkably to lower parts per million due to a strong temperature dependence of hydrogen bonding. This effect has been already observed in low molecular weight alcohols, such as, methanol or ethylene glycol and exploited for temperature calibration in NMR [20].

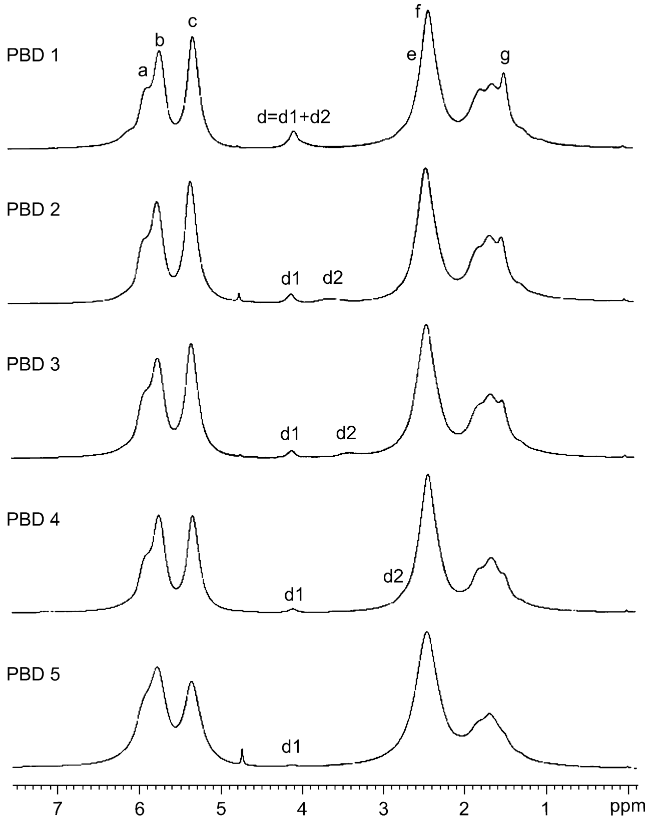

Fig. 1. ^{1}H NMR spectra at 293 K of α,ω-dihydroxy terminated polybutadienes of different molecular weight.

3.2. Manifestation of hydrogen bonding in vibrational spectra

The ν(OH) band of stretching vibration of hydroxy group is very useful for the investigation of its association behaviour due to its sensitivity to the presence of the hydrogen bonding. Hydrogen bonding weakens the O−H bond and shifts the ν(OH) absorption band towards lower wavenumbers. The effect depends on the size of hydroxy multimer and, consequently, a composite band consisting of the bands from free (monomeric), dimeric, trimeric, etc. hydroxy groups is observed. Infrared spectra obtained for α,ω-dihydroxy terminated PB's in the region from 3800 to 3100 cm^{-1} are shown in Fig. 3. It is known that all aliphatic monohydric alcohols

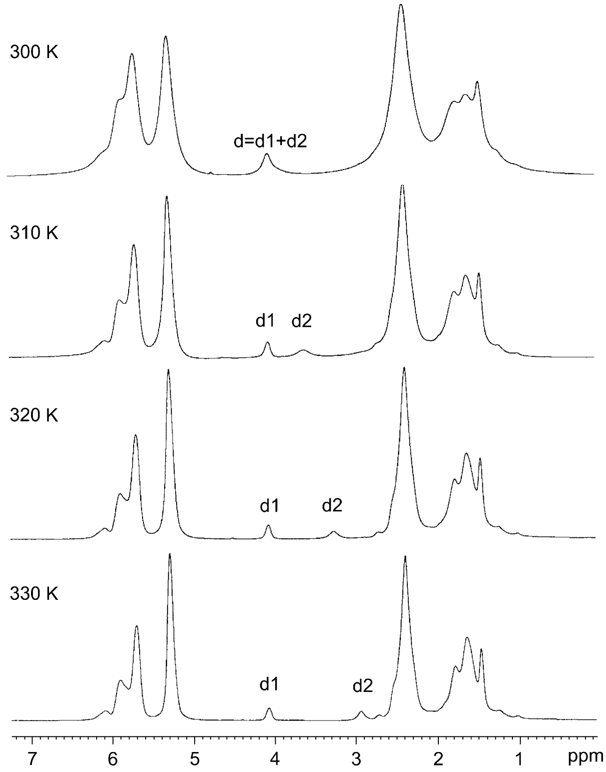

Fig. 2. ^{1}H NMR spectrum of PBD1 at different temperatures.

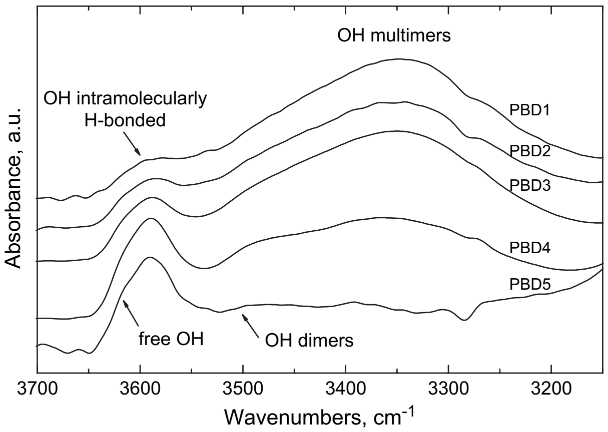

Fig. 3. FTIR spectra of α,ω-dihydroxy terminated polybutadienes of different molecular weight.

[21], except methanol, exhibit a free O–H stretching band in the region 3640–3600 cm^{-1}. The shoulder located for all PB's at about 3620 cm^{-1} can be assigned to this *non-bonded* free hydroxy group. In accordance with the results of Podešva et al. [4], the absorption maximum at ca. 3600 cm^{-1} can be attributed to intramolecular hydrogen bonding interaction between terminal OH and C=C bond on the adjacent (last) monomer unit of the polymer backbone. A clear shoulder at ca. 3500 cm^{-1} present in the spectra of PBD3–5 originates from H-bonded dimers, for PB's of lower molecular weights is overlapped by a broad band located around 3350 cm^{-1} from a large variety of H-bonded *hydroxy multimers*. Comparing the spectra in Fig. 3 it can be seen that with increase in molecular weight of polybutadiene the relative intensity of the bands corresponding to the free and *intramolecularly* H-bonded hydroxy groups grows at the expense of the fraction of *intermolecularly* bonded species.

3.3. *Effect of molecular weight on the cooperative (glass transition) dynamics*

Fig. 4 shows DSC traces measured on the α,ω-dihydroxy terminated PB's during second heating scan. Apart from the glass transition indicated by a step in the heat flow curves, no hints for another phase transition like melting or crystallisation are found. The effect of a H-bonded network in the system is clearly manifested by the dependence of the glass transition temperature on the molecular weight (Fig. 5).

The actual trend, a glass transition temperature that decreases with increasing molecular weight of the linear polymer, is in contradiction with the common effect of end groups on T_g [22] as described by the Fox-Flory equation for linear chain polymers [23]

$$T_g = T_{g,\infty} - \frac{K}{M_n}, \tag{2}$$

which is based on the idea that chain ends posses an *enhanced mobility* and thus speed-up the overall dynamics according to their concentration. This scenario does not clearly apply for α,ω-dihydroxy terminated polybutadiene, where *associating* end groups cause a *decrease* in the end-group mobility and act as physical crosslinks that slow down the glass transition dynamics. Polybutadienes without interacting terminal groups obey the Fox-Flory equation [24].

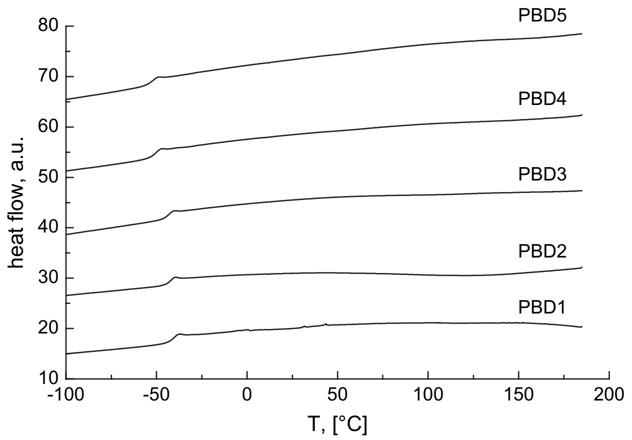

Fig. 4. DSC traces of α,ω-dihydroxy terminated polybutadienes of different molecular weight.

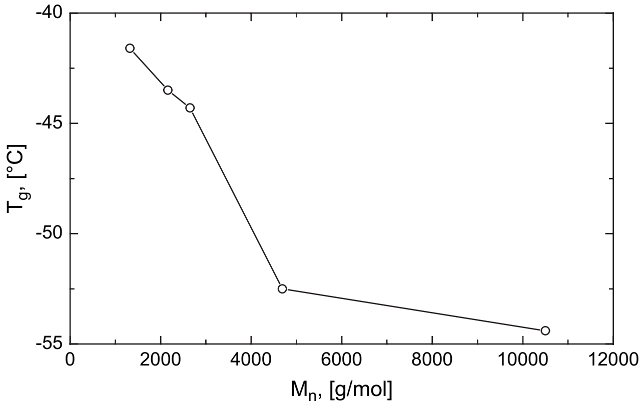

Fig. 5. Calorimetric glass transition temperatures of α,ω-dihydroxy terminated polybutadienes as function of the molecular weight.

In order to prove the idea of a modified cooperative dynamics governed by (physical) crosslinks, we have applied broadband dielectric spectroscopy (BDS), which allowed us to study the dielectric manifestation of the dynamic glass transition (α-process) in great detail in a wide frequency range. A representative result is given in Fig. 6, which reveals the systematic shift with molecular weight of the dielectric loss peaks $\varepsilon''(f)$, measured at −30 °C, towards higher frequencies. Further analysis of the dielectric loss spectra at different temperatures yielded the actual temperature dependence of the peak relaxation times τ for each polymer sample, which are plotted in the activation diagram shown in Fig. 7. The common feature of the α-process is that the temperature dependence of the relaxation time, $\tau(T)$, obeys the VFT-law (fit lines in Fig. 7).

$$\tau = \tau_\infty \exp\left(\frac{E_V}{R(T - T_V)}\right) \tag{3}$$

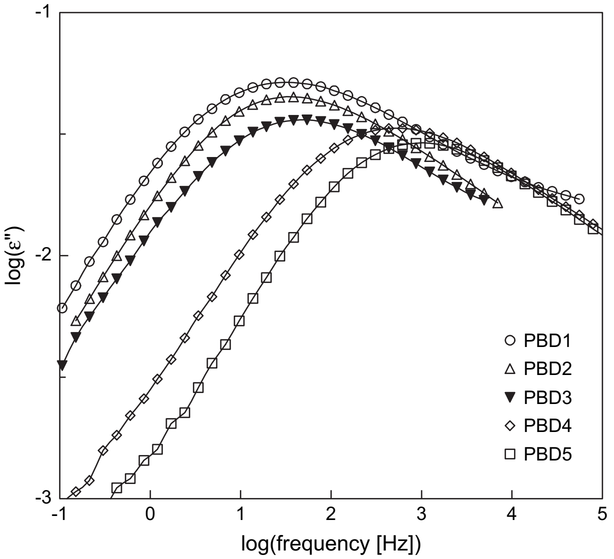

Fig. 6. Dielectric loss spectrum $\varepsilon''(f)$ at $T = -30\,^{\circ}\mathrm{C}$ for five α,ω-dihydroxy terminated PB's of different molecular weight.

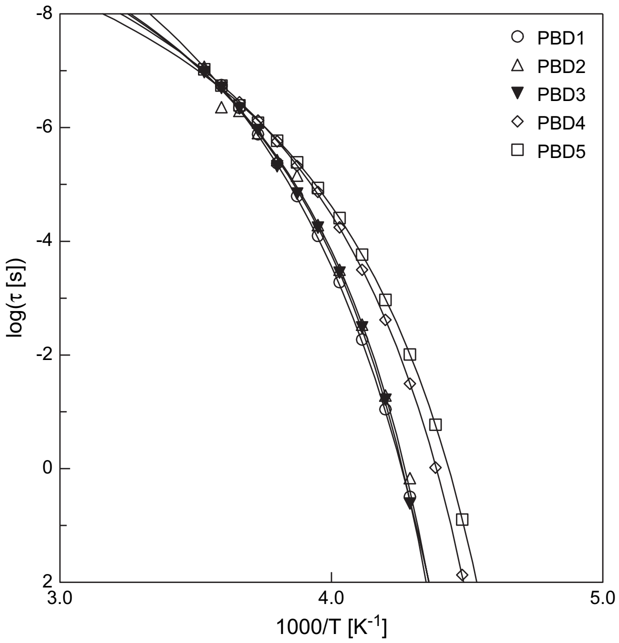

Fig. 7. Activation plot of the relaxation time τ_α for all α,ω-dihydroxy terminated PB's.

where E_V and T_V are the "Vogel activation energy" and the Vogel temperature [25–27]. The other parameters, R and τ_∞, have the usual meaning. Fitting of Eq. (3) to the relaxation time data $\tau(T)$ yields the VFT parameters from which we can extrapolate an operationally defined "dielectric" glass transition temperature using the simple convention $T_g = T(\tau = 100\ \mathrm{s})$. These T_g-values are displayed in Fig. 8 and, together with the VFT parameters, are listed in Table 2.

From Figs. 7 and 8a two observations can be made:

1) The "dielectric" T_g decreases with increasing molecular weight and follows thus roughly the same trend as found for the calorimetric glass transition temperature (cf. Fig. 5),

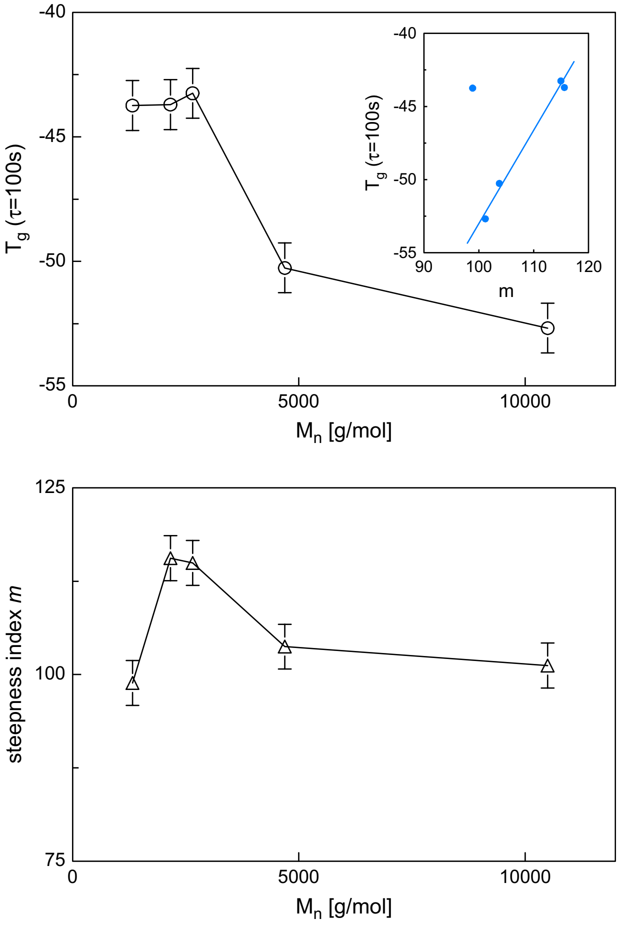

Fig. 8. Top: Dependence of the glass transition temperature as a function of the molecular weight for five α,ω-dihydroxy terminated polybutadienes as determined from dielectric relaxation data. Bottom: Effect of molecular weight on the dynamic fragility (steepness index) for all compounds. Inset figure (top): Correlation between glass transition temperature and dynamic fragility.

Table 2
Values of the parameters obtained for α,ω-dihydroxy terminated polybutadienes

Sample	E_V [kJ/mol]	$\log \tau_\infty$/[s]	T_V [K]	T_g [°C]	m
PBD1	9.84	−12.88	194.9	−43.7	98.9
PBD2	6.82	−11.40	202.9	−43.7	115.6
PBD3	7.00	−11.52	202.9	−43.2	115.0
PBD4	7.23	−11.26	194.4	−50.3	103.7
PBD5	6.97	−10.93	192.3	−52.7	101.2

2) In contrast to the *slow* dynamics, expressed by the trend in $T_g(M_n)$, no significant M_n-effects on the relaxation time τ_α are found for high frequencies/temperatures, as seen by the virtual merging of all $\tau(T)$ curves at $\tau \sim 10^{-6}$ s.

These two observations are consistent with a systematic change in the *shape* of the VFT-dependence that can be quantified by the *steepness index* or *fragility index m* [28] according to Eq. (4)

$$m = \left. \frac{d \log \langle \tau \rangle}{d(T_g/T)} \right|_{T=T_g}. \tag{4}$$

From the VFT parameters we can obtain the steepness index in a convenient way using the expression (5)

$$m = \frac{E_V}{2.303R}\frac{T_g}{\left(T_g - T_V\right)^2}. \tag{5}$$

Inspecting the *m*-values given in Table 2 and Fig. 8b reveal a systematic decrease in the fragility index for the α-process with increasing molecular weight from 2160 to 10 500 g/mol. Furthermore, the glass transition temperature and the steepness index show a linear correlation for all PB-samples (cf. inset Fig. 8), except the one with the lowest M_n.

Behaviour such as, an increase in T_g accompanied by an increase in the ‘‘fragility index’’ is a known feature of covalently bonded networks that show both an increase in T_g and *m* with increasing crosslink (or branching point) density [29–34]. While a solely increase in T_g upon crosslinking can also be rationalised by local stiffening of the polymer structure by introducing less flexible crosslinking agents, the correlated increase in T_g and *m* might be interpreted in terms of an increased *degree of intermolecular cooperativity* of the dynamic glass transition [33]. In this picture, enhanced intermolecular cooperativity provoked by the presence of strong intermolecular interactions (covalent bonds, H-bonds etc.) facilitates the progressive slow down of the glass transition dynamics and thus drives the polymer system into the glassy state at a higher temperature.

The fact that the glass transition dynamics of our system, α,ω-dihydroxy terminated polybutadienes, resembles the dynamics of a covalently crosslinked polymer network, supports the idea of a physical network, where (phase separated) associates of hydroxy groups play the role of physical crosslinks. Obviously, such a network behaves like a ‘‘real’’ polymer network at an intermediate ‘‘molecular weight between crosslinks’’, given by the M_n of the linear PB’s, however, the network character gets lost for very short (PBD1) and very long PB’s. While for the longest polybutadiene, phase separation and thus effective hydrogen bonding is missing (cf. Fig. 1), i.e., PBD5 effectively reveals the structure and dynamics of a linear polybutadiene, the shortest PBD-‘‘network’’ deviates substantially from the general trend in $m(M_n)$ and $T_g(M_n)$. A possible explanation for this exceptional behaviour might be sought in conformational restrictions of the end groups in case of very short chains to join OH-rich clusters.

Another manifestation for the ‘‘non-ideal’’ network-behaviour of the PBD-series is the M_n-dependence of the relaxation strength $\Delta\varepsilon$ of the α-process given in Fig. 9. Since both the types and concentration of the molecular dipoles contributing to the α-relaxation in α,ω-dihydroxy terminated polybutadienes are known, we are able to model the $\Delta\varepsilon(M_n)$ dependence by the simple relation (Eq. (6)) assuming that density and dipole–dipole correlation effects can be neglected:

$$\Delta\varepsilon = x_{OH}\Delta\varepsilon_{OH} + x_{BD}\Delta\varepsilon_{BD}. \tag{6}$$

Here, x_{OH} and x_{BD} denote the volume fraction of the respective hydroxy and butadiene dipole according to Eq. (7)

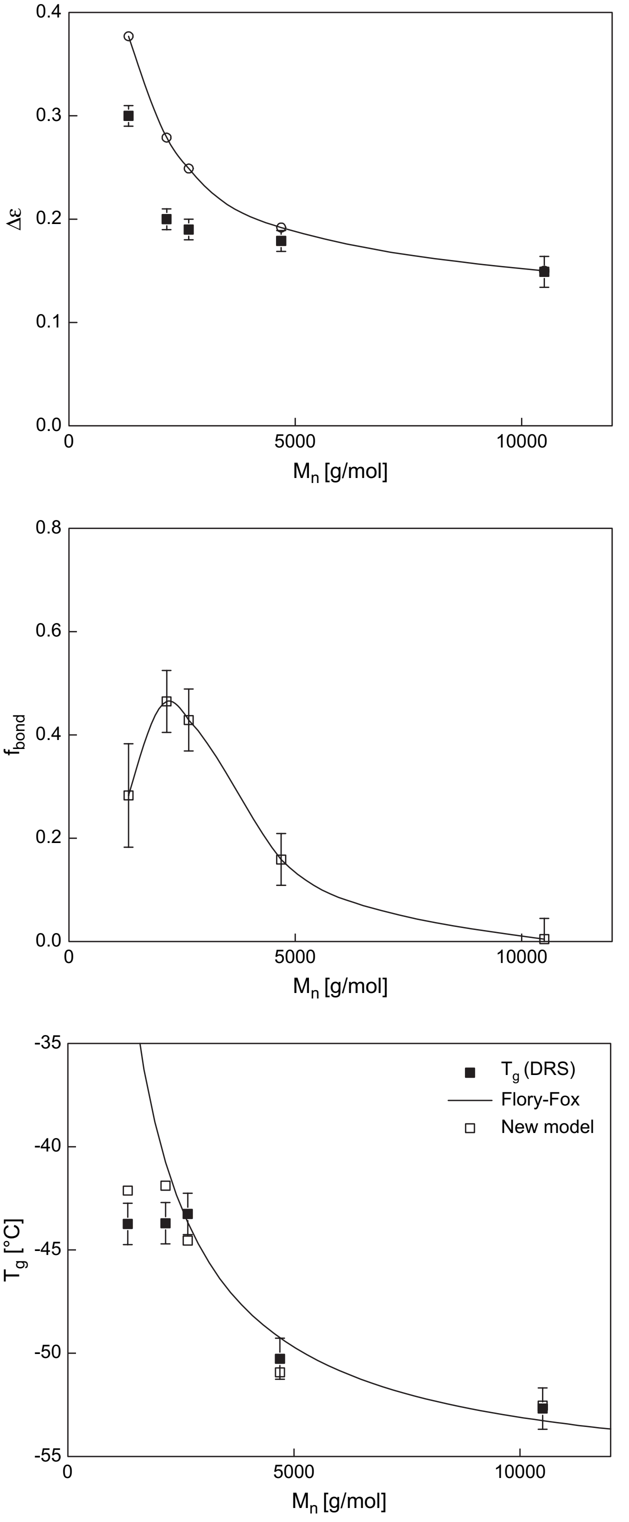

Fig. 9. (a) Dielectric relaxation strength of the α-process $\Delta\varepsilon_\alpha$ in α,ω-dihydroxy terminated polybutadienes as function of the molecular weight. The filled squares represent experimental data, the open circles refer to a fit according to Eq. (6). (b) Fraction of associated hydroxy groups as calculated using Eq. (8) and the data are given in Fig. 9a. (c) The glass transition temperature as a function of the molecular weight for five α,ω-dihydroxy terminated polybutadienes. Open squares: fit based on the new model (Eq. (9)), solid line: fit to Eq. (2). For comparison, the original T_g-data are shown as solid squares.

$$x_{\mathrm{OH}} = \frac{108}{108 + M_{\mathrm{PBD}} - M_{\mathrm{OH}}}, \quad x_{\mathrm{BD}} = \frac{M_{\mathrm{PBD}} - M_{\mathrm{OH}}}{108 + M_{\mathrm{PBD}} - M_{\mathrm{OH}}}, \qquad (7)$$

the two other parameters correspond to the ultimate relaxation strength of pure polybutadiene (infinite M_n) and an equivalent contribution due to the end-group dipole $\Delta\varepsilon_{\mathrm{OH}}$. We have fitted the data points $\Delta\varepsilon(M_n)$ to Eq. (6) assuming $\Delta\varepsilon \approx \Delta\varepsilon_{\mathrm{BD}} = 0.115$ for PBD5 as well the parameter $\Delta\varepsilon_{\mathrm{OH}} = 3.5$. The result is presented in Fig. 9a and shows a good agreement for high molecular weights while there is a clear discrepancy at lower M_n-values that could not be resolved by any meaningful set of parameters. The obvious reason for the shortcoming of Eq. (6) is the fact that we have not accounted for a fraction of associated (bonded) end groups f_{bond} ($0 \le f_{\mathrm{bond}} \le 1$), which does not contribute to the overall relaxation strength $\Delta\varepsilon_\alpha$. To arrive at a more realistic description of the measurable relaxation strength $\Delta\varepsilon_{\mathrm{exp}}$ we can extend Eq. (6) to the following expression:

$$\Delta\varepsilon_{\mathrm{exp}} = (1 - f_{\mathrm{bond}}) x_{\mathrm{OH}} \Delta\varepsilon_{\mathrm{OH}} + x_{\mathrm{BD}} \Delta\varepsilon_{\mathrm{BD}}, \qquad (8)$$

which now solely considers the fraction of *free* end groups contributing to the actual dielectric response. From this relation, after rearranging, we can now evaluate f_{bond} from the data (cf. Fig. 9a) that are displayed in Fig. 9b. As expected, the degree of associated OH-groups reaches a maximum around the sample PBD2. It should be noted that, despite the remaining uncertainties in the parameters for Eq. (6) (and (8)), the result $f_{\mathrm{bond}}(M_n)$ appeared to be surprisingly robust as indicated by the error bars in Fig. 9b, which actually mark the range of possible solutions for $f_{\mathrm{bond}}(M_n)$ assuming realistic values of $\Delta\varepsilon_{\mathrm{OH}}$ and $\Delta\varepsilon_{\mathrm{BD}}$. In particular, the peak position was found to be completely insensitive for inaccuracies in $\Delta\varepsilon_{\mathrm{OH}}$ and $\Delta\varepsilon_{\mathrm{BD}}$ and strongly resembles the molecular weight dependence of the dynamic fragility.

The identification and quantification of a molecular weight dependent degree of physical crosslinking prompts us for a consistency check with the above discussed T_g-effects (cf. Fig. 8). For this purpose, the $T_g(M_n)$ data were re-plotted in Fig. 9c together with a curve representing the best fit of Eq. (2) in the meaning of the equivalent *Fox-Loshaek* equation ($K < 0$, $M_x = M_n$) through the three rightmost data points, which immediately demonstrates the limitations of this simple approach. However, by considering the quantity $f_{\mathrm{bond}}(M_n)$, we can easily extent Eq. (2) to a modified expression

$$T_g = T_{g,\infty} - (1 - f_{\mathrm{bond}})\frac{K_e}{M_n} + f_{\mathrm{bond}}\frac{K_x}{M_x}, \qquad (9)$$

which combines the effect of end-group driven T_g-reduction (2nd term) with a term accounting for the effect of T_g-increase due to end crosslinking (in our case $M_n = M_x$) in a linear manner, the parameter $f_{\mathrm{bond}}(M_n)$ acts as a weight factor between both terms. Using Eq. (9) with $T_{g,\infty} = -52.5\,^\circ\mathrm{C}$ and the $f_{\mathrm{bond}}(M_n)$-data according to Fig. 9b, we arrive at a fit curve, which is in reasonable agreement with the measured T_g-values, even for the exceptional sample PBD1.

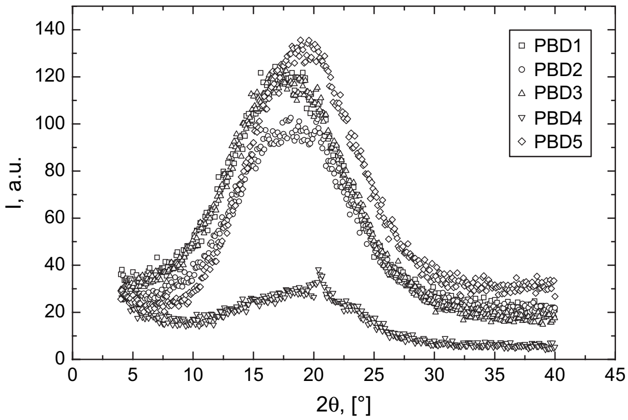

Fig. 10. Scattering intensity as function of the scattering angle for five α,ω-dihydroxy terminated polybutadienes of different molecular weight.

Finally, to rule out that crystalline clusters play any role in the physical network properties of α,ω-dihydroxy terminated PB's we have taken WAXS patterns on all samples at room temperature. The results are shown in Fig. 10 and reveal exclusively broad hallows being indicative for the absence of any long-range translational order.

4. Conclusions

The structure and molecular dynamics of α,ω-dihydroxy terminated polybutadienes of varying number averaged molecular weight by FTIR, NMR, dielectric relaxation spectroscopy, DSC and wide-angle X-ray scattering. DSC and DRS revealed an increase in the glass transition temperature upon decrease of the molecular weight, accompanied by an increasing dynamic fragility *m* of the dielectric α-process. This correlation between T_g and *m* for different molecular weights indicates the presence of a physical network, where H-bonded end-group clusters act as temporary crosslinks.

From the dielectric relaxation strength $\Delta\varepsilon_\alpha(M_n)$, the fraction of associated hydroxy groups (f_{bond}) was estimated showing a peak value for the two but shortest polymers, a behaviour that strongly resembles the molecular weight dependence of the fragility. By considering the quantity $f_{\mathrm{bond}}(M_n)$ in a modified Fox-Flory approach, the measured $T_g(M_n)$ behaviour could be reproduced in a satisfying way.

FTIR results support this general picture and show a considerable dependence of the extent of hydrogen bonding and formation of hydroxy groups associates on the molecular weight. Further, WAXS and DSC results disprove the idea of formation of pseudo-crystalline hydrophobic microdomains in these compounds as suggested by other authors.

Acknowledgements

The authors would like to thank Dr. J. Pytela (Research Institute for Synthetic Rubber, Kaučuk Kralupy n.Vlt., Czech Republic) for providing the sample materials used in this study. Financial support from the Ministry of Education of the Czech Republic (project MSM 0021620835) is gratefully acknowledged.

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