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Mössbauer and dielectric spectroscopy of the dynamic glass transition of a block copolymer

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Abstract. The enlargement of the time window achieved by combining ⁵⁷Fe Mössbauer investigations (10^{-7} to 10^{-9} s) with conventional dielectric spectroscopy (10^0 to 10^{-7} s) on poly(vinylferrocene-*b*-propylene sulphide) allows one to characterize three different relaxation processes. The main process of the glass transition is measured by dielectric spectroscopy and can be well described by the common Vogel–Fulcher–Tammann law, which is typical for cooperative processes. A secondary process is shown by dielectric spectroscopy to be Arrhenius activated, indicating a local process which leads to a broadening of the Mössbauer resonance line. The corresponding times can be determined via line-shape analysis. A third process, the so-called cage process, is responsible for an anomalous decrease of the Debye–Waller factor. Its characteristic times are assumed to be in the picosecond region.

1. Introduction

For polymers, the transition from the liquid to the amorphous state still presents many unsolved problems for theorists and experimentalists [1, 2]. The glass transition is a dynamical process, being connected to relaxation processes taking place on different timescales. Their characteristic relaxation times may range from days or years to times in the picosecond region. For this reason, experimental methods with a large time window are desirable.

Dielectric spectroscopy [3] deals with the influence of an alternating electric field on matter which induces a polarization of the permanent dipoles of the sample. The complex dielectric function $\epsilon(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$ is measured as a function of the frequency of the alternating field. A relaxation process, characterized by the relaxation time τ in the time domain, corresponds to a reduction of $\epsilon'(\omega)$ and to a peak of $\epsilon''(\omega)$. The inverse of the characteristic time $1/\tau$ is proportional to the maximum frequency of the loss peak.

Scattering methods can be divided into coherent and incoherent methods, probing the pair correlation and the self-correlation function, respectively [4]. Quasielastic incoherent neutron scattering experiments [5] as well as Mössbauer spectroscopy [6–9] are able to monitor the Fourier transform of the density autocorrelation function which contains information about the single-particle dynamics. ⁵⁷Fe Mössbauer spectroscopy directly

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monitors the movement of a single Fe nucleus and covers a time range of approximately 10^{-9} to 10^{-7} s. We have used ferrocene as a side group of the backbone of the polymer chain. Feyerherm *et al* [10] have shown that the motion of the ferrocene unit reflects the movement of the whole chain itself. Mössbauer investigations of polymers near their glass transition have been published by Hillberg *et al* [11].

In this article we report on the combination of Mössbauer and dielectric spectroscopy, which enlarges the time window from 10^0 to 10^{-9} s. Furthermore, it is possible to prove the existence of a dynamical process that occurs in less than 10^{-9} s. Using both methods allows us to determine different dynamic processes in connection with the glass transition.

2. Experimental procedure

The dielectric spectroscopy was performed with a commercial Novocontrol DK-Spectrometer [12] covering a frequency range from 10^{-2} Hz to 2×10^6 Hz. The spectra were recorded between 173 and 293 K.

The ^{57}Fe Mössbauer absorption spectra were recorded between 4.2 K and 310 K using a conventional spectrometer with a sinusoidal velocity sweep. The source was 870 GBq ^{57}Co in Rh kept at room temperature (diameter 8 mm, thickness $6 \mu\text{m}$, source recoil-free fraction $f_S = 0.69$ and linewidth $\Gamma = 0.113 \text{ mm s}^{-1}$). A continuous-flow liquid helium cryostat was employed. The temperature control was better than ± 0.5 K. Typical absorber thicknesses were about 10 mg Fe cm^{-2} , of natural abundance.

The samples were of poly(vinylferrocene-*b*-propylene sulphide) (PROPS 10 and PROPS 2; see figure 1). The block copolymers are not cross-linked and are synthesized by anionic polymerization initialized by butyl lithium. The samples are characterized by gel permeation chromatography, GPC, ^1H NMR, ^{13}C NMR, and by differential scanning calorimetry, DSC (20 K min^{-1}). The number-averaged molecular weights are $\overline{M}_n = 10\,000 \text{ g mol}^{-1}$ (PROPS 10) and $\overline{M}_n = 2000 \text{ g mol}^{-1}$ (PROPS 2). The glass transition temperatures are $T_g = 246 \text{ K}$ and $T_g = 238 \text{ K}$, respectively, which are comparable with $T_g = 226 \text{ K}$ for the poly(propylene sulphide) homopolymer.

For both samples the ratio of the monomers, vinylferrocene:propylene sulphide, is 1:13. Details of the synthesis of the sample [13, 14] and results of further Mössbauer investigations concerning the influence of the length of the polymer chain and the swelling of the polymer with solvent will be published elsewhere.

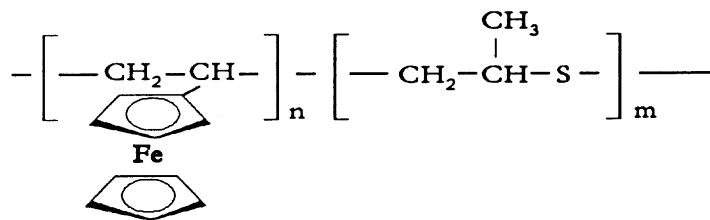


Figure 1. The structure of poly(vinylferrocene-*b*-propylene sulphide).

3. Results from dielectric spectroscopy

In most cases, dielectric spectra show multiple-relaxation behaviour loss peaks overlapping to some extent. Since, for relaxation processes, ϵ' and ϵ'' are connected by the Kramers–

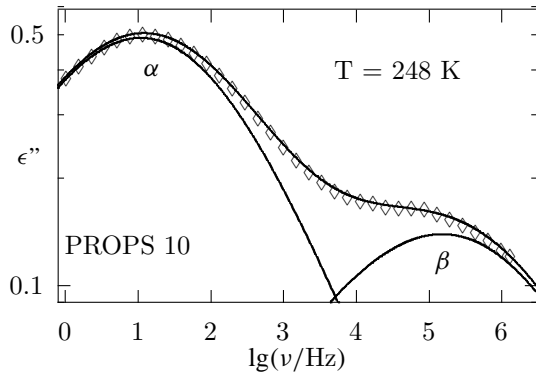


Figure 2. The loss part of the dielectric function, $\epsilon''(\nu)$, $2\pi\nu = \omega$, decomposed into α - and β -processes.

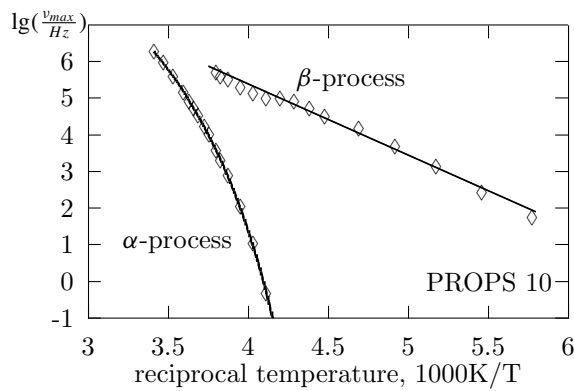


Figure 3. The temperature dependence of the frequency ν_{max} , where ϵ'' exhibits the maxima of the loss peaks.

Kronig relation, we focus on an interpretation of ϵ'' only. A typical dielectric spectrum with two loss peaks is shown in figure 2. For a quantitative analysis, least-squares fits are performed assuming that ϵ'' for the two peaks is additive. In the frequency domain several functions exist to describe broad symmetric or asymmetric loss peaks. We used the Havriliak–Negami (HN) [15] empirical relaxation function which is successfully applied to single peaks:

$$\epsilon(\omega) - \epsilon_\infty = \frac{\Delta\epsilon}{(1 + (i\omega\tau_{HN})^{\beta_{HN}})^{\gamma_{HN}}} \tag{1}$$

ϵ_∞ denotes the permittivity at high frequencies and $\Delta\epsilon$ characterizes the relaxation strength, being linked to the area of the loss peak. The parameters β_{HN} and γ_{HN} , $0 \leq \beta_{HN}, \beta_{HN}\gamma_{HN} \leq 1$, describe the shape of the loss peak, i.e. width and symmetry. τ_{HN} is a characteristic relaxation time related to the maximum of the loss peak [16]. In figure 3 we show the temperature dependence of the frequency ν_{max} for which ϵ'' exhibits loss peak maxima. For an overview of the dielectric properties of amorphous polymers and a detailed description of the evaluation procedure, we refer the reader to Schönhal's *et al* [17].

Two dynamic processes have been detected (figure 3). The main process or α -process is directly connected to macroscopic properties such as the viscosity. It is a cooperative

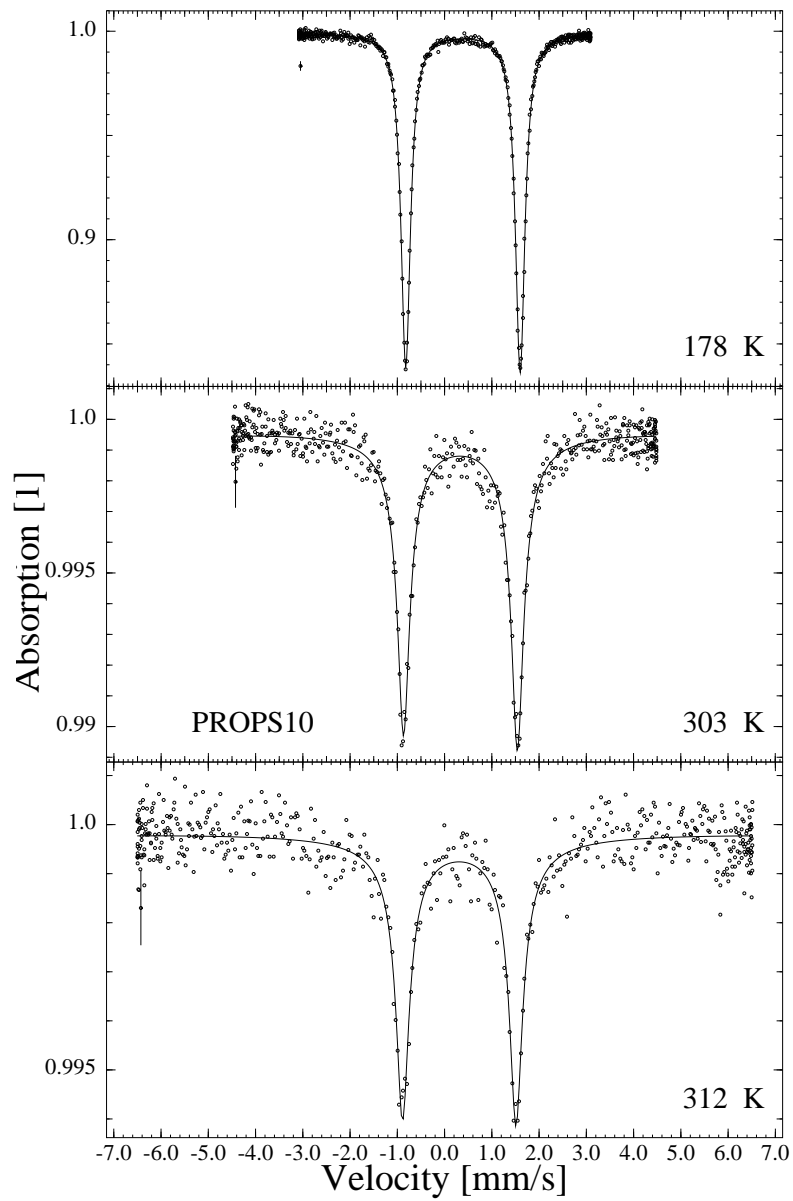


Figure 4. The temperature dependence of the ^{57}Fe Mössbauer spectra for PROPS 10. The solid lines are least-squares fits to the spectra as described in the text.

process: movement of the backbone of a polymer chain is only possible if a rearrangement of neighbour molecules takes place. The α -process can be fitted to the Vogel–Fulcher–Tammann (VFT) law [18–21] which describes cooperative processes:

$$\nu \propto \exp\left(-\frac{\text{constant}}{T - T_0}\right). \quad (2)$$

A Vogel temperature, $T_0 = 201 \pm 2$ K, is obtained. It is often found for polymers that T_0 is 30 K to 70 K lower than the glass transition temperature T_g [18]. The β -process is Arrhenius activated:

$$\nu = \nu_0 \exp\left(-\frac{E}{k_B T}\right) \quad (3)$$

with a temperature-independent activation energy $E = 37 \pm 2$ kJ mol⁻¹, typical for a local process. It is usually attributed to the rotation of side groups or to flip movements of parts of the polymer chain. The experimental data show that the β -process is still active in the glassy state when the main process is frozen.

4. Results from Mössbauer spectroscopy

Mössbauer spectroscopy measures the absorption cross section as a function of energy, which is linked to the density autocorrelation function $\psi(t)$ as a function of time by means of Fourier transformation. The cross section is given by [4]

$$\sigma(E) = \frac{\sigma_0(\Gamma_0/2)}{2\hbar} \int dt e^{-i\omega t - (\Gamma_0/2\hbar)|t|} \psi(t). \quad (4)$$

σ_0 is the cross section for nuclear resonance absorption, Γ_0 the natural half-width of the resonance line and $\hbar\omega$ the energy transfer. The density correlation function $\psi(t)$ describes the strength of correlation between random density fluctuations after the time interval t . It characterizes the motional behaviour of the particles under study. Choosing the Debye relaxation function for $\psi(t) = \exp(-t/\tau)$, equation (4) can be evaluated analytically, resulting in a Lorentzian line shape, broadened by $\Delta\Gamma = 2\hbar/\tau$. Thus, the lifetime $\tau_n = 1.41 \times 10^{-7}$ s = $2\hbar/\Gamma_0$ of the excited nucleus determines a time window for ⁵⁷Fe Mössbauer spectroscopy from about 10^{-7} s to 10^{-9} s. The intensity of the resonance line is given by the Debye–Waller factor f containing information about motion that occurs in less than 10^{-9} s.

In figure 4 we show representative spectra for the sample PROPS 10. Due to a quadrupole splitting which is caused by the Fe(II) species of the ferrocene unit, two resonance lines are observed. The splitting of 2.4 mm s⁻¹ is typical for ferrocene compounds.

The sample exhibits a linear temperature dependence of $\ln f$, as is expected for harmonic vibrations up to 240 K. After correcting the $\ln f$ data by subtracting the small intramolecular contributions f_{inter} of the ferrocene unit [10], one can calculate the Debye temperature Θ_D in this temperature range [22]:

$$-\ln f_{vib} = \frac{6E_r}{k_B \Theta_D^2} T. \quad (5)$$

$E_r = \hbar^2 k^2 / 2m$ denotes the recoil energy and m is the mass of the vibrating ferrocene unit. f_{vib} is the corrected Debye–Waller factor and $\ln f_{vib} = \ln f - \ln f_{inter}$. The results are depicted in figure 5. The resulting Debye temperature is $\Theta_D = 73 \pm 3$ K.

At $T_{cage} = 240 \pm 10$ K the onset of a dramatic decrease of the Debye–Waller factor is observed. This decrease can be attributed to random motions like uncorrelated jumps that occur in less than 10^{-9} s which are restricted to cages formed by surrounding particles. The radius R of this cage can be calculated via [23]

$$\frac{\sin^2(kR)}{(kR)^2} = f_{cage}. \quad (6)$$

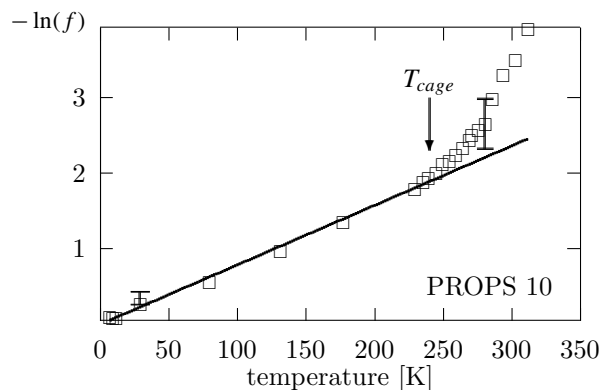


Figure 5. The temperature dependence of $-\ln f$; intramolecular contributions are subtracted. Below $T_{cage} = 240$ K the data can be well described by $-\ln f \propto T$ (the solid line).

Thus, the Debye–Waller factor f can be further decomposed: $f = f_{inter} f_{vib} f_{cage}$. Whereas f_{vib} results from harmonic vibrations, f_{cage} is caused by the fast, uncorrelated jumping or ‘rattling’ in the interior of the cage, the so-called ‘cage process’. The calculated radii R are shown in figure 6. Values up to $R = 0.4$ Å are detected. For higher values, the intensity of the resonance line is below the spectroscopical limit. The ‘jump’ distances R can be fitted to the square-root law

$$R^2 = R_c^2 \left(1 - \frac{\text{constant}}{2} \sqrt{T_c - T} \right)^2 \quad (7)$$

with $T_c = 310 \pm 10$ K, which is in the $\alpha\beta$ -splitting region (figure 7). This temperature dependence is predicted by the mode-coupling theory (MCT) [24].

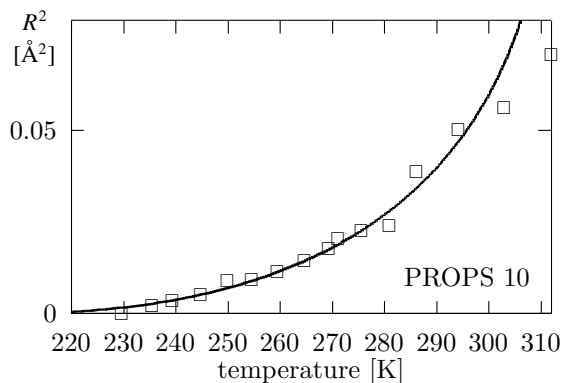


Figure 6. The temperature dependence of the rattling jump distances R^2 , calculated via equation (6). Contributions due to harmonic vibrations are subtracted. The fit according to the square-root-law equation given by (7) is indicated by the solid line.

Whereas the temperature dependence of the Debye–Waller factor monitors processes that occur in less than 10^{-9} s, the width and shape of the resonance line allow one to determine relaxation times for slower processes. At temperatures below 265 K, the width of the resonance lines does not vary. In this temperature range, the relaxation times of α - and β -processes, measured by dielectric spectroscopy, are longer than 10^{-7} s (figure 3;

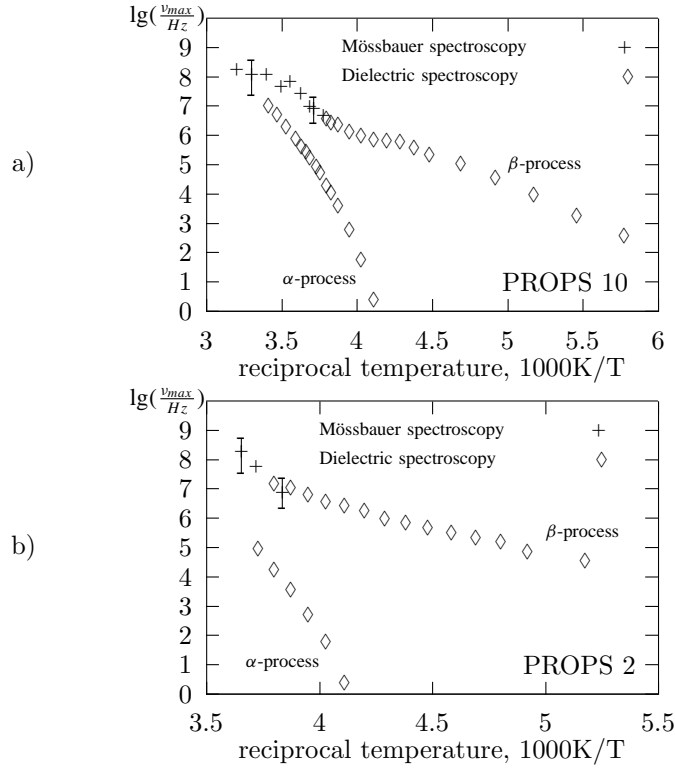


Figure 7. The temperature dependence of the frequency ν_{max} for both Mössbauer and dielectric data. The two samples show a coincidence of the relaxation times for the β -process.

265 K corresponds to $1000 \text{ K}/T = 3.77$). They correspond to energy transfers that are small compared to the natural linewidth Γ_0 . Therefore for this dynamic regime no relaxation times are obtained by Mössbauer spectroscopy.

Above the temperature $T_\beta^M = 265 \pm 5 \text{ K}$ we observe the onset of a broadening of the resonance lines. We attribute this to the Arrhenius-activated β -process which is also seen by means of dielectric spectroscopy. The broadening becomes observable when τ is comparable to or shorter than τ_n . Due to a continuum of inelastic energy transfers, the line shapes can no longer be described by Lorentzians. Instead, we find that they can be well reproduced (figure 4) by choosing the Kohlrausch–Williams–Watts (KWW) function for the density correlation function:

$$\psi(t) = \exp(-(t/\tau_{KWW})^{\beta_{KWW}}). \quad (8)$$

The relaxation rate $1/\tau_{KWW}$ is related to ν_{max} of the HN function [16]. The Kohlrausch parameter β_{KWW} , $0 < \beta_{KWW} \leq 1$, describes the width of the relaxation time distribution, which is wider for smaller β_{KWW} . We evaluate equation (4) numerically by means of a fast-Fourier-transform (FFT) algorithm. As we use thick absorbers, we additionally need large-thickness corrections. The method for calculating the transmission integral of the Mössbauer spectra [25] is also based on FFT. The parameter β_{KWW} obtained from the fit does not show a temperature dependence. In a first fit with f , ν and β_{KWW} variable, an average value of $\beta_{KWW} = 0.42$ is determined in the temperature range where $T > T_\beta^M = 265 \text{ K}$ for which a line broadening is observed.

Using this β_{KWW} -value, all of the spectra for the whole temperature range can be described. The negative decadic logarithm of the characteristic times $\tau_{max} = 1/\nu_{max}$ is depicted in figure 7 as crosses. Similar phenomena have been observed in incoherent inelastic neutron scattering experiments [5].

5. Discussion

By means of dielectric experiments (time window: 10^0 s to 10^{-7} s), it is possible to interpret the Mössbauer data on a broader basis. Figure 7 shows both Mössbauer and dielectric data for the samples PROPS 10 and PROPS 2.

For a more accurate discussion we have to consider the limits of the resolution of the two methods. Due to the small intensity of the Mössbauer resonance line at higher temperatures, the derived relaxation frequencies ν have an uncertainty as depicted in figure 7. Dielectric spectroscopy indicates rather small values [17] for the parameters β_{HN} and $\beta_{HN}\gamma_{HN}$ for both peaks, describing their broadness and symmetry: $0.4 \leq \beta_{HN} \leq 0.5$ and $0.5 \leq \beta_{HN}\gamma_{HN} \leq 0.6$.

Mössbauer spectroscopy probes the movement of the ^{57}Fe nucleus as a part of the monomer vinylferrocene, whereas dielectric spectroscopy gives a view of the movement of permanent dipoles of the angled C–S–C bonding of propylene sulphide. Nevertheless the relaxation times obtained by the two methods coincide very well (figure 7). These results support those of Feyerherm *et al* [10], who pointed out that the movement of the ^{57}Fe nucleus seems to reflect the movement of the whole chain.

In the relevant temperature range, the relaxation times τ_{max} of the α -process, obtained by dielectric spectroscopy, are far too long to be detectable by Mössbauer spectroscopy.

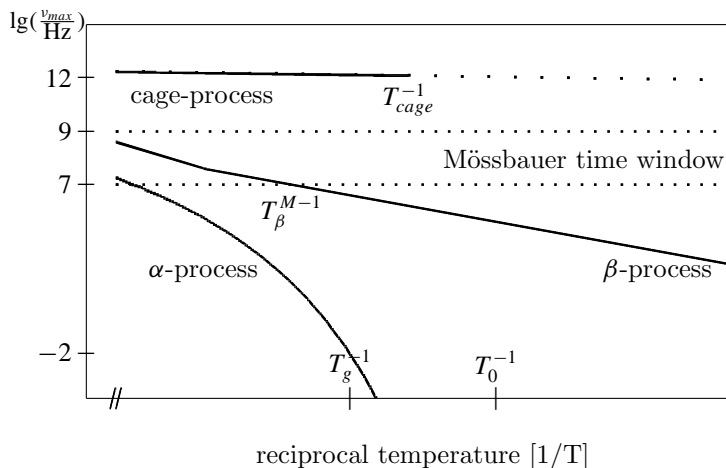


Figure 8. The proposed scenario for the block copolymers studied, including all three processes; cf. also reference [27].

Parak and Frauenfelder carried out Mössbauer investigations on proteins [6], assigning the broadening of the resonance line to cooperative motions—that is, the α -process. Hillberg *et al* [11] performed Mössbauer investigations on a sample similar to the one used in this work (PROPS 12) and also attributed the line broadening to the α -process. From the present data, however, the line broadenings for PROPS 2 and 10 are unambiguously related to a local, Arrhenius-activated process, the β -process.

The question of the cause of the dramatic decrease of the Debye–Waller factor remains open. As stated above, it is attributed to fast random motions, $\tau \ll 10^{-9}$ s. Qualitatively the same temperature dependence of the Debye–Waller factor has been observed by Bartsch *et al* [5, 26] performing quasielastic incoherent neutron scattering experiments on the Van der Waals glass orthoterphenyl: a linear temperature dependence of the logarithm of the Debye–Waller factor at low temperatures, followed by a decrease at higher temperatures. The authors describe the process responsible with a small-amplitude motion that proceeds in a time shorter than the time window of the neutron scattering experiment, e.g. a motion in the picosecond region. The increasing amplitude is interpreted as a widening of the cage for the rattling motion of small chain portions. Thus neutron scattering and Mössbauer spectroscopy indicate very similar processes. This does not lead to any contradiction, although a Van der Waals glass and a polymer should show quite different behaviour. The very fast processes seem to be an intrinsic property for amorphous materials. On such timescales, specific polymer properties such as entanglement or chain length are no longer relevant. The possibility that this fast process is the ‘normal’ β -process which becomes faster at higher temperatures can be discarded: the onset temperature $T_{cage} = 240$ K of this process, indicated by the decrease of the Debye–Waller factor, is lower than the onset temperature of the line broadening, which is attributed to the β -process.

6. Conclusion

This work combines Mössbauer investigations with dielectric spectroscopy on identical polymer samples. It demonstrates that Mössbauer spectroscopy alone is insufficient for a thorough interpretation of the motional dynamics. For our block copolymers, a typical scenario is shown in figure 8.

From our results, three processes can be distinguished.

(i) The cooperative α -process, which is connected to the glass transition temperature T_g (DSC) is observable by means of dielectric but not Mössbauer spectroscopy. It obeys the VFT law, yielding $T_0 = 201 \pm 2$ K.

(ii) The local, Arrhenius-activated β -process is detected by means of dielectric spectroscopy and by means of Mössbauer spectroscopy from the broadening of the resonance line. Its temperature-independent activation energy is 37 ± 2 kJ mol⁻¹.

(iii) An anomalous decrease of the Debye–Waller factor is attributed to the onset of the so-called cage process at $T_{cage} = 240 \pm 10$ K. It is assumed to be fast ($\tau \ll 10^{-9}$ s), small-amplitude motion, restricted to a cage (≤ 0.5 Å) formed by surrounding particles. Since no additional barrier can be imagined within the cage, this process is expected to be not or only weakly activated.

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