บทความวิชาการ

Field cycling NMR relaxometry การศึกษายพลศาสตร์ของพอลิเมอร์เหลว

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บทคัดย่อ

Field cycling NMR relaxometry เป็นเทคนิคที่เหมาะสำหรับการศึกษาพลศาสตร์ของพอลิเมอร์เหลว โดยสามารถศึกษาพัฒนาการของพลศาสตร์ของพอลิเมอร์เหลว เริ่มต้นจากพอลิเมอร์ที่แสดงสภาพแบบแก้ว พัฒนาจนเกิดพลศาสตร์แบบ Rouse และจนมีพฤติกรรมแบบ Reptation ตามลำดับ โดยพัฒนาการนี้เป็นผลจากการเพิ่มความยาวของโมเลกุลของพอลิเมอร์ บทความนี้จะกล่าวถึงการวิเคราะห์ผลการทดลองในรูปของ NMR susceptibility แทนที่จะวิเคราะห์ในรูปแบบทั่วไป ซึ่งก็คือการวิเคราะห์การกระจายของ T_1 relaxation time ที่เป็นฟังก์ชั่นของความถี่ การวิเคราะห์ในรูปของ NMR susceptibility นี้ มีการนำไปใช้ในครั้งแรกเพื่อการศึกษาพลศาสตร์ของพอลิเมอร์เหลว Polybutadien (PB) โดยทั่วไปแล้วพลศาสตร์ของพอลิเมอร์เหลวจะประกอบด้วยพลศาสตร์ของพอลิเมอร์ที่แสดงสภาพแบบแก้ว ซึ่งเป็นพลศาสตร์ที่พบเห็นได้สำหรับสารโมเลกุลเล็กทั่วๆ ไป กับพลศาสตร์ของพอลิเมอร์ มีการนำสเปกตรัมที่เป็นผลรวมของพลศาสตร์ทั้งสองมาจำแนกออกเป็นสองส่วน นั่นคือ แยกส่วนของพลศาสตร์ของสารที่แสดงสภาพแบบแก้วกับส่วนของพลศาสตร์ของพอลิเมอร์ออกจากกัน ส่วนหลังนั้นแสดงผลที่สอดคล้องกับทฤษฎีของ Rouse ซึ่งแปรผันตรงกับน้ำหนักโมเลกุล M_w อย่างชัดเจน เมื่อเปรียบเทียบผลการทดลองกับทฤษฎีของ Rouse พบว่าสามารถหาค่าของน้ำหนักโมเลกุลที่แสดงสภาพของ Rouse หรือ M_R กับน้ำหนักโมเลกุลที่แสดงสภาพของ entanglement หรือ M_e ได้ นอกเหนือจากนั้น ผลการทดลองที่ได้จากเทคนิคนี้สามารถหาค่าของการจัดเรียงเป็นระเบียบ S ได้ โดยในการวิเคราะห์ผลการทดลองในรูปแบบที่กล่าวไปแล้วนั้น ให้ค่าของ S ที่ค่อนข้างสูง โดยค่านี้จะแปรผันตรงกับน้ำหนักโมเลกุลของพอลิเมอร์นั้นๆ ซึ่งเห็นได้ชัดสำหรับช่วงที่มวลโมเลกุลอยู่ในช่วงที่แสดงพลศาสตร์แบบ Rouse นั่นคือโมเลกุลมีขนาดที่ยาวขึ้นแต่ไม่มากนัก เมื่อมวลโมเลกุลเพิ่มขึ้นจนถึงระดับหนึ่ง นั่นคือ M_e ค่าของ S ยังคงแปรผันตรงกับมวลโมเลกุลอยู่แต่น้อยมากๆ และท้ายที่สุดแล้วให้ S ที่เป็นค่าคงที่ ผลการทดลองจาก Field cycling NMR relaxometry และการวิเคราะห์พลศาสตร์ของพอลิเมอร์เหลวในรูปของ NMR susceptibility สอดคล้องกับผลการทดลองที่ได้จากเทคนิคอื่น

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ARTICLE

Field Cycling NMR Relaxometry Study on Polymer Melts

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Abstract

Field cycling NMR relaxometry is a suitable technique to investigate the crossover from glassy dynamics through Rouse to reptation behaviour on polymer melts. Interpretation in term of the NMR susceptibility instead of the T_1 relaxation dispersion as a function of frequency, as usual, is reviewed. It has been applied for the first time to study the polymer dynamics on the polybutadiene (PB) melts. Usually, the dynamics of polymer melts consist of both the polymer specific dynamics and the glassy dynamics. Separating the contribution from the glassy dynamics presented on the total NMR relaxation spectra, the polymer contribution can be isolated. The latter shows typical Rouse relaxation features that grow with molecular weight M_w and saturate at high M_w. Comparing to Rouse theory, the Rouse unit M_R and the entanglement weight M_e are able to obtained. The dynamic order parameter S can also be obtained from the polymer relaxation spectra. A significantly high value of S for PB melts, S ~ 0.34, comes mainly from the Rouse spectra. A slightly M_w dependence of PB melts are observed and only a small dynamic order parameter, S ~ 0.02, are obtained when the M_w is higher than the entanglement weight M_e. These results correspond to those obtained by other techniques.

Keywords: NMR relaxometry, Polymer Dynamics, Polymer Melts, Polybutadience

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Introduction

One of the key goals in polymer science is to understand the polymer dynamics that leads to establish the structure-properties relationships, which are important in order to improve and design new materials for new applications. The dynamics of polymer melts consist of both the polymer specific dynamics and the glassy dynamics. According to the molecular weight M_w, there are two important cases of the polymer specific dynamics. The first case is in the unentangled chains ($M_w < M_e$), where M_e is the entanglement molecular weight when the entanglements start. The second case is in the entangled chains ($M_w > M_e$), where the chain movements are restricted by topological constraints of the surrounding chains (M.Doi, S.F. Edwards: 1986), (T.C.B. McLeish: 2002), The glassy dynamics are the contribution of the local and the segmental dynamics within the polymer chains, defined by the structural relaxation time or the α-relaxation time τ_α and the segmental correlation time τ_s, respectively (T. Blochowicz, A.Brodin, E.A. Rössler: 2005).

So far, several techniques have been used to investigate the polymer dynamics on the entanglement scale. Rheology and rheo-optical measurements (J. A. Kornfield, G. G. Fuller, D. S. Pearson: 2005), (E. F. Brown, W. R. Burghardt: 1996), are used to analyze the macroscopic level. Neutron spin-echo (NSE) (J. S. Higgins, J. E. Roots: 1985), (D. Richter, et al.: 1989), (P. Schleger, et al.: 1998), and nuclear magnetic resonance (NMR) (R. Kimmich, M. Köpf, P. Callaghan: 1991), (P. G. Klein, et al.: 1998), (M. E. Komlosh, P. T. Callaghan: 1998), (C. H. Adams, et al.: 2000), are able to probe directly the molecular motion. Dielectric spectroscopy (DS) provides chain orientation dynamics and small angle neutron scattering (SANS) (R. Muller, J. J. Pesce, C. Picot: 1993), (T. C. B. McLeish, et al.: 1999), of selectively deuterated material in quenched-flow experiments has started to reveal the nature of the anisotropic structure on the lengthscale of the chain under step-strain deformations. Dynamic light scattering as well as SANS on concentrated solutions has begun to test the consequences of theory for relaxation of the composition of fluctuations (D. Vlassopoulos, et al.: 1997). These techniques are sharpened by the synthesis of monodisperse molecules of controlled architecture and deuteron-labelling via anionic methods. These days, by the power of computer simulations, it is possible to conduct molecular dynamics simulations of polymers that contain 50 chains each of 10,000 repeating units for which the entanglement is relevant (M. Pütz, K. Kremer, G. S. Grest: 2000). A few more techniques such as dielectric spectroscopy (DS) and light scattering (LS) (T. Blochowicz, A. Brodin, and E. A. Rössler: 2005), are used to probe the dynamics for much shorter time scales, within the time scale of 10^{-9} to 10^{-12} seconds, which are identify as the dynamics for the liquid state. Field cycling NMR relaxometry is one of the new techniques that favor the approach of liquid-like systems in a natural way. The main advantage of this technique over other NMR methods is the information obtained over several orders of magnitude in the frequency scale (R. Kimmich: 1980), (F. Noack: 1986), (E. Anoardo, G. Galli, and G. Ferrante: 2001), (R. Kimmich, E. Anoardo: 2004), (S. Kariyo, et al.: 2006), (S. Kariyo, et al.: 2008), (S. Kariyo, et al.: 2008), (A. Herrmann, V. N. Novikov, and E. A. Rössler: 2009), (A. Herrmann: 2009), (D. Kruk, A. Herrmann, and E. A. Rössler: 2012). A comparison of different NMR techniques as well as DS presented within the window of time scale is shown in Fig. 1 (R. Kimmich, E. Anoardo: 2004), (A. Herrmann, et al.: 2009).

Field Cycling relaxometry has been used to study the dynamics of polymer melts focusing on the Rouse and the reptation dynamics (R. Kimmich: 1980), (F. Noack: 1986), (E. Anoardo, G. Galli, and G. Ferrante: 2001), (R. Kimmich, E. Anoardo: 2004). Recently, it has been used to study the dynamics starting from a simple liquid to polymer melts by following the information from a few monomers to long chain polymers, such as polybutadiene melt (PB) (S. Kariyo, et al.: 2006), (S. Kariyo, et al.: 2008), (S. Kariyo, et al.: 2008), (A. Herrmann, V. N. Novikov, and E. A. Rössler: 2009), (A. Herrmann: 2009), (D. Kruk, A. Herrmann, and E. A. Rössler: 2012). The field cycling relaxometry and its application on the dynamics of the linear polymer melts is discussed in this review.

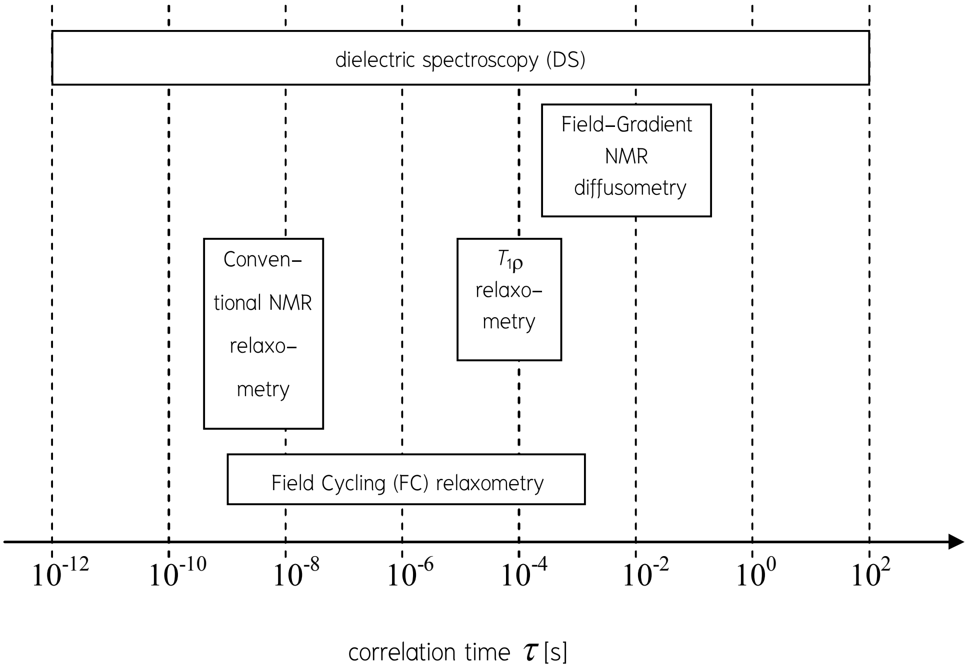


Figure 1: Schematic representation of the time scale covered by different NMR techniques compared with the dielectric spectroscopy (DS) (R. Kimmich, E. Anoardo: 2004), (A. Herrmann, et al.: 2009).

Analysis

Field Cycling Relaxometry

Field cycling relaxometry is one of the NMR techniques providing the information about the molecular motions at a wide range of time scales (Fig. 1). The term 'relaxometry' here mainly refers to the NMR spin–lattice relaxation time or the T_1 relaxation time. The NMR relaxometry is actually probing the fluctuation of dipolar coupling (DS) (R. Kimmich, E. Anoardo: 2004) (R. Kimmich: 1997), (R. Kimmich: 1004). The correlation function $F_2^m(\tau)$, described the dipolar interactions, relates to the second rank spherical harmonics

$$F_2^m(\tau) = \left\langle Y_{2,m}(\vartheta_0,\phi_0)Y_{2,-m}(\vartheta_\tau,\phi_\tau)\right\rangle / \left\langle \left|Y_{2,m}(\vartheta_0,\phi_0)\right|^2 \right\rangle \quad , \qquad (1)$$

where the indices *0* and τ refer to the initial and the final times, respectively. The isotropic system at the macroscopic scale gives an *m*–independence expression for the orientational correlation function $F_2^m(\tau)$ and expresses through the second rank Legendre polynomial equation $P_2(\cos\vartheta) = (1/2)(3\cos^2\vartheta - 1)$ (R. Kimmich, E. Anoardo: 2004). Thus, the correlation function in Eq. 1 becomes

$$F_2(\tau) = \left\langle P_2(\cos\vartheta_0)P_2(\cos\vartheta_\tau)\right\rangle / \left\langle \left|P_2(\cos\vartheta_0)\right|^2 \right\rangle = \left\langle P_2\cos(\vartheta_\tau - \vartheta_0)\right\rangle . \quad (2)$$

The spectral density function $J(\omega)$ is given as the Fourier transform of the correlation functions,

$$J(\omega) = \mathrm{Re}\int_0^\infty F_2(\tau)e^{-i\omega\tau}\,d\tau . \quad (3)$$

In the ^{1}H NMR, the so–called Bloembergen–Purcell–Pound theory (BPP theory) gives the relationship of the T_1 relaxation time and the spectral density function $J(\omega)$ for the monomer orientational dynamics,

$$\frac{1}{T_1} = C\left[J(\omega) + 4J(2\omega)\right] \quad , \quad (4)$$

where $\omega = \gamma B_0$ is the Larmor frequency depending on the gyromagnetic ratio γ and the magnetic field B_0, and *C* is the NMR coupling constant. The T_1 relaxation time in Eq. 4 is actually a contribution from both intra– and intermolecular interactions,

$$1/T_1 = 1/T_1^{\mathrm{intra}} + 1/T_1^{\mathrm{inter}} \quad . \quad (5)$$

However, the main contribution to the interaction is from the nearest proton pairs which belong to the same molecular chains. Therefore, the intermolecular term can be neglected because it is relatively very small.

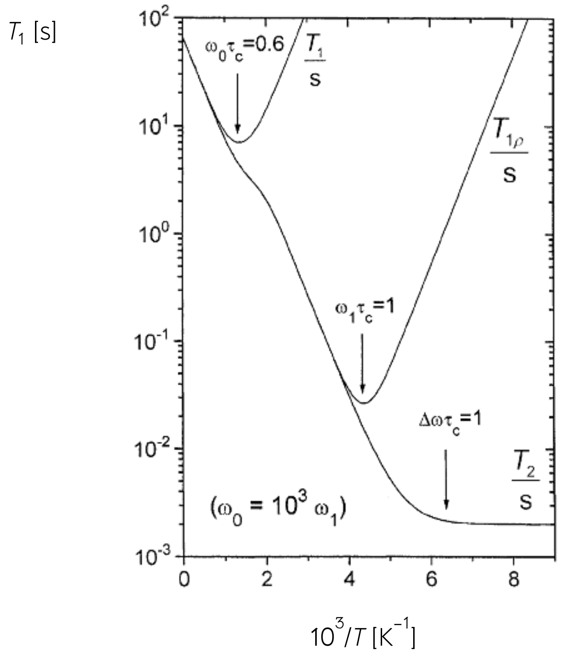


Figure 2: Temperature dependences of T_1, $T_{1\rho}$, and T_2 relaxation times (R. Kimmich, E. Anoardo: 2004).

The spectral density function $J(\omega)$ is related to the correlation time τ_c as follows:

$$J(\omega) = \frac{2\tau_c}{1+\omega^2\tau_c^2} \tag{6}$$

The correlation time τ_c itself depends on the temperature as shown in Fig. 2. It shows that the T_1 relaxation time passes through a minimum at $\omega\tau_c \approx 1$ ($\omega_1\tau_c = 1$ for the case of $T_{1\rho}$). The region of $\omega\tau_c << 1$, where these T_1 (spin-lattice relaxation time in the laboratory frame), $T_{1\rho}$ (spin-lattice relaxation time in the rotating frame), and T_2 (spin-spin or transverse relaxation time) are equal, gives the spectral density function $J(\omega) = 2\tau_c$. It is known as the extreme narrowing limit (R. Kimmich, E. Anoardo: 2004).

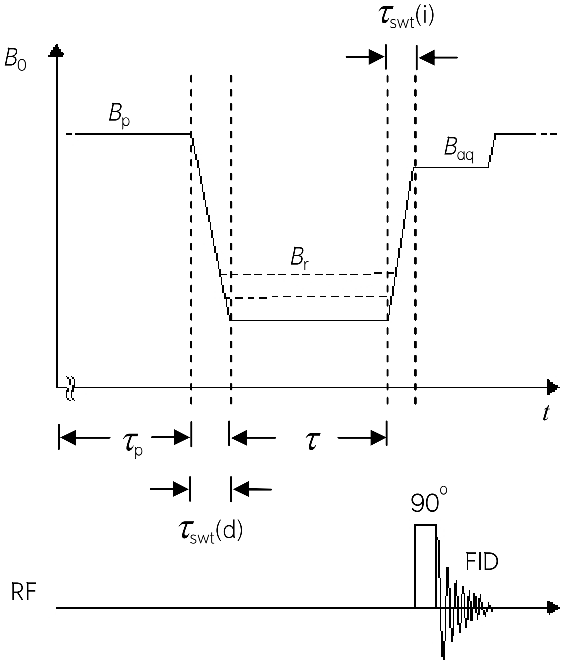


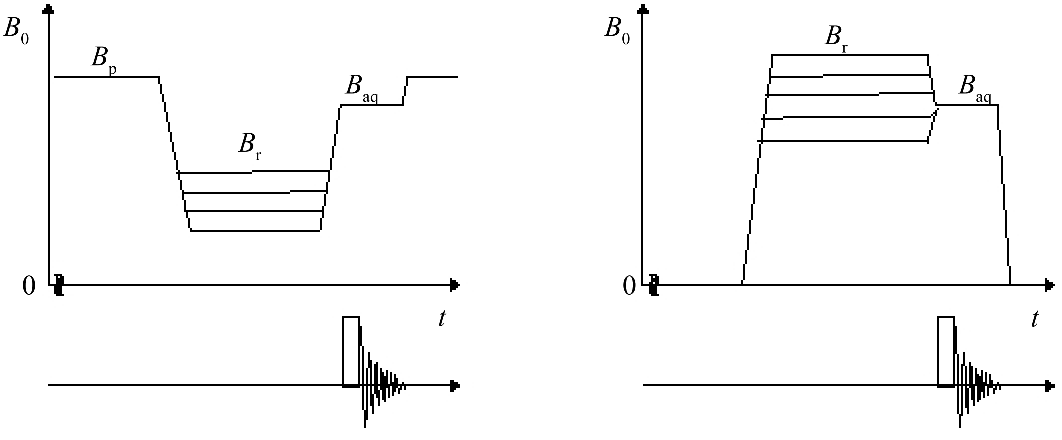
Figure 3: Schematic representation of a typical cycle of the main magnetic field B_0 employed with field cycling relaxometry, where $\tau_{\mathrm{swt}}(\mathrm{d})$ and $\tau_{\mathrm{swt}}(\mathrm{i})$ represent the switching times to decrease and increase the magnetic fields, respectively.

A typical experiment of the field cycling relaxometry is illustrated in Fig. 3. At first, the sample is polarized at the polarization field B_p as high as technically possible in order to avoid the signal-to-noise problem until its magnetization achieves saturation, *i.e.* the polarization time τ_p should be longer than five times the T_1 relaxation time at that polarization field B_p. The magnetic field is then switched to a value of the relaxation field B_r where the relaxation process takes place. At the end, the magnetic field is switched to a value of the acquisition field B_{aq} which is again as high as possible. The signal is acquired after applying an radio frequency pulse (rf pulse) with a frequency equal to $\omega = \gamma B_{\mathrm{aq}}$. The T_1 relaxation time at the relaxation field B_r is measured by varying the time interval τ. For obtaining the T_1 relaxation dispersion profile, new relaxation fields

B_r are set and the corresponding T_1 relaxation times are measured (R. Kimmich, E. Anoardo: 2004), (R. Kimmich: 1980). The magnetization along the z-axis M_z relates to the magnetic fields and the T_1 relaxation time as follows

$$M_z(\tau) = M_0(B_\mathrm{r}) + \left[M_0(B_\mathrm{p}) - M_0(B_\mathrm{r})\right] e^{-\tau/T_1(B_\mathrm{r})} . \tag{7}$$

The field cycling experiment can be performed by changing the relaxation field B_r either mechanically or electronically. The first case refers to as 'a sample shuttle technique' where mechanical or pneumatic systems move the sample between positions of different magnetic fields (D. P. Weitekamp, et al.: 1983), (D. J. Kerwood, P. H. Bolton: 1987), (D. Wu, C. S. Johnson: 1995), (S. Wagner, et al.: 1999), (A. G. Redfield: 2003). The time lost during shuttling the sample is in the order of hundreds of milliseconds. Therefore, the shuttling technique is not suitable for measuring short T_1 relaxation times especially for investigating the polymer dynamics. The second case often refers to as 'Fast Field Cycling Relaxometry (FFC)'. The relaxation field B_r is switched electronically between the desired values. Special electric networks combined with sophisticated air cored magnets allowed to switch the magnetic fields between zero and 1 Tesla within the switching time τ_{swt} of a few milliseconds. This technique permits the measurement of T_1 relaxation times down to the local-field regime and that overlaps with the time scale accessible by the field-gradient NMR (FG-NMR) diffusometry (Fig. 1).



a) b)

Figure 4: Two basic types of field sequences with the 90° rf pulse used in the field cycling measurement, a) basic pre-polarized sequence (PP) and b) basic non-polarized sequence (NP).

The switching time τ_{swt}, the time used to switch between different magnetic fields (Fig. 3), is one of the most important parameters for the field cycling relaxometry. It becomes more critical when measure a very short T_1 relaxation time which often occurs at low frequency. Usually, the switching time τ_{swt} has to be much smaller than the T_1 relaxation time. However, if the course of the magnetic field during the switching intervals is reproducible after the field cycle, this condition becomes less restrictive (F. Noack: 1986). The T_1 relaxation time from Eq. 7 measured after the time $\tau + \tau_{\mathrm{sw}t}$ is given by

$$M_z(\tau + \tau_{\mathrm{swt}}) = M_0(B_\mathrm{r}) + k\left[M_0(B_\mathrm{p}) - M_0(B_\mathrm{r})\right] e^{-\tau / T_1(B_\mathrm{r})} \quad , \qquad (8)$$

where k is a constant for reproducible field transition (R. Kimmich, E. Anoardo: 2004), (R. Kimmich: 1980), (E. Anoardo, G. Galli, and G. Ferrante: 2001).

The general field sequence as shown in Fig. 3 is suitable for the measurement when the difference of polarization field B_p and relaxation field B_r is sufficiently large. For the case of high relaxation field B_r, the difference between polarization field B_p and relaxation field B_r in Eq. 8 can be too small for causing a sufficient deviation from the equilibrium and for accurate evaluation of the T_1 relaxation time. In this case, it is more favorable to start the cycle in the absence of any polarization field B_p. Therefore, field cycling relaxometry contains basically the pre-polarized (PP) field sequence for the measurement at low fields and the non-polarized (NP) field sequence for the measurement at high fields as shown in Fig. 4 (R. Kimmich, E. Anoardo: 2004), (R. Kimmich: 1980), (E. Anoardo, G. Galli, and G. Ferrante: 2001).

Field cycling NMR Relaxometry Study on Polymer Melts

Recently, a commercial FFC relaxometer is available which provides the measurement of the field dependence of T_1 relaxation times within a wide range of temperature. It is suitable to study the polymer dynamics. Kimmich and his co-workers have investigated the Rouse and reptation dynamics for various polymers (R. Kimmich: 1980), (F. Noack: 1986), (E. Anoardo, G. Galli, and G. Ferrante: 2001), (R. Kimmich, E. Anoardo: 2004). The investigations on the restricted molecular dynamics of polymers were published for the case of natural rubbers (NR) and butadiene rubbers (BR) (S. Kariyo, S. Stapf: 2004), (S. Kariyo, S. Stapf: 2004), (S. Kariyo, S. Stapf: 2005), (S. Kariyo, S. Stapf: 2005), (S. Stapf, S. Kariyo: 2005). These works presented the information in term of T_1 relaxation dispersion and compared them with the theoretical works developed by Kimmich and his co-workers. which provides for Rouse and reptation dynamics for polymer melts (R. Kimmich, N. Fatkullin: 2004).

The power law dependences of the T_1 relaxation time on the Larmor frequency were introduced (R. Kimmich, E. Anoardo: 2004), (R. Kimmich: 2004), as follows

$$T_1(\omega) \propto \omega^\gamma : \begin{cases} \gamma = 0.50 \pm 0.05 & \text{(region I; 'high - mode number limit')} \\ \gamma = 0.25 \pm 0.03 & \text{(region II; 'low - mode number limit')} \\ \gamma = 0.45 \pm 0.03 & \text{(region III; 'inter - segment interaction limit')} \end{cases} . \quad (9)$$

These power laws are not identical with those proposed by the Doi/Edwards limit of the mean square displacement of a chain segment within a tube constraint, $<r^2> \propto t^\gamma$. However, the Doi/Edwards limit can be verified if molecular chains are confined to artificial tubes prepared in a solid polymer matrix (M. Doi, S. F. Edwards: 1986), (R. Kimmich, et al.: 1999). So far, the power law in Eq. 9 has been applied to study the dynamics for the case where the correlation time $\tau > \tau_s$ (R. Kimmich: 1980), (F. Noack: 1986), (E. Anoardo, G. Galli, and G. Ferrante: 2001), (R. Kimmich, E. Anoardo: 2004), (S. Kariyo, S. Stapf: 2004), (S. Kariyo, S. Stapf: 2004), (S. Kariyo, S. Stapf: 2005), (S. Kariyo, S. Stapf: 2005), (S. Stapf, S. Kariyo: 2005). The result shown in Fig. 5 is an example of the investigation on the dynamics of NR compared to BR (S. Kariyo, S. Stapf: 2005). The master curves for both NR and BR shown here are after applying the frequency temperature superposition. The difference in the power law found for NR is not a consequence of deviating dynamics of intermolecular contribution to the relaxation, but rather reflects the spectrum of segmental dynamics, *i.e.* the shape of the probability distribution of segmental correlation time τ_s which expects to be different in polyisoprene or in NR compared to other polymers (S. Kariyo, S. Stapf: 2005). Accordingly, for better understanding, the investigations down to a simple liquid for those polymer melts are necessary.

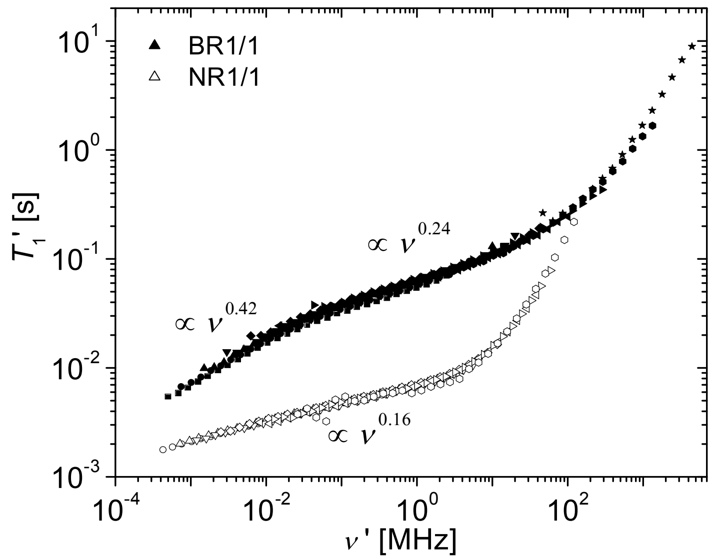


Figure 5: The master curves for the data measured individually for each sample at different temperatures obtained by applying the frequency temperature superposition (S. Kariyo, S. Stapf: 2005).

In order to study the dynamics of a simple liquid, the local relaxation or α–relaxation time τ_α and the segmental correlation time τ_s need to take into account. Usually, the data measured by the field cycling relaxometry are the T_1 relaxation dispersion as a function of frequency. The possibility to look at the result in term of susceptibility $\chi''(\omega)$ for T_1 relaxation time in Eg. 4 can be written as

$$\frac{\omega}{T_1(\omega)} = C\left[\chi''(\omega) + 2\chi''(2\omega)\right] \equiv 3C\,\tilde{\chi}''(\omega) \quad , \tag{10}$$

where the susceptibility $\chi''(\omega) = \omega J(\omega)$. The term $\tilde{\chi}''(\omega)$ is called the 'normalized NMR susceptibility' or simply called the 'susceptibility'. For a broad relaxation spectrum obtained for the polymer dynamics, the two susceptibilities in Eq. 10 hardly be distinguished. Therefore, it can be sum up as $3C\,\tilde{\chi}''(\omega)$. The factor 3 is for keeping the integral over the susceptibility $\tilde{\chi}''(\omega)$ normalized to $\pi/2$. This equation is suitable to analyze the data for the case of polymer dynamics so that the results from different experiments, such as from DS, can be compared (S. Kariyo, et al.: 2006), (S. Kariyo, et al.: 2008), (S. Kariyo, et al.: 2008), (A. Herrmann, V. N. Novikov, and E. A. Rössler: 2009), (A. Herrmann: 2009), (D. Kruk, A. Herrmann, and E. A. Rössler: 2012).

The studies on the dynamics of a simple liquid to polymer melts investigated by the field cycling relaxometry in term of the susceptibility $\widetilde{\chi}''(\omega)$ in Eq. 10 were started for polybutadiene melts (PB) with different molecular weights M_w as shown in Fig. 6 (S. Kariyo, et al.: 2006). The relaxation maxima which contain the information of the segmental correlation time τ_s were shifted to higher frequencies at higher temperatures (Fig. 6a). The same investigation was found for *o*–terphenyl (OTP), which used as a reference for the dynamic of a simple liquid. At high temperature, where $\omega\tau_\alpha \ll 1$, the susceptibility becomes $\widetilde{\chi}''(\omega) \propto \nu^1$, which is typical for the case of a simple liquid. However, the results for PB melts were slightly different due to the segmental dynamics within the polymer chains. The master curves for PB with different M_w and for OTP can be obtained by applying the frequency temperature superposition as shown in Fig. 6b (S. Kariyo, et al.: 2006). All master curves can be rescaled vertically so that the peaks are overlapped. The results for PB with low molecular weights, M_w = 355, 466 g/mol, and those for OTP are identical. It shows that the polymer specific dynamics might start at the molecular weights 466 < $2M_R$ < 777 g/mol (each chain contains at least two units), where M_R is the molecular weight for the Rouse dynamics. The master curves for PB melts with molecular weight M_w > 56500 g/mol are identical indicating that the entanglement is fully established (S. Kariyo, et al.: 2006). Since the master curves for PB with M_w = 355, 466 g/mol and for OTP are identical, these mean the relaxation spectra for polymer melts with very low molecular weights represent purely the spectrum for the segmental dynamic (Fig. 6b). The spectra of these two molecular weights are identifiable as the dynamics of a simple liquid.

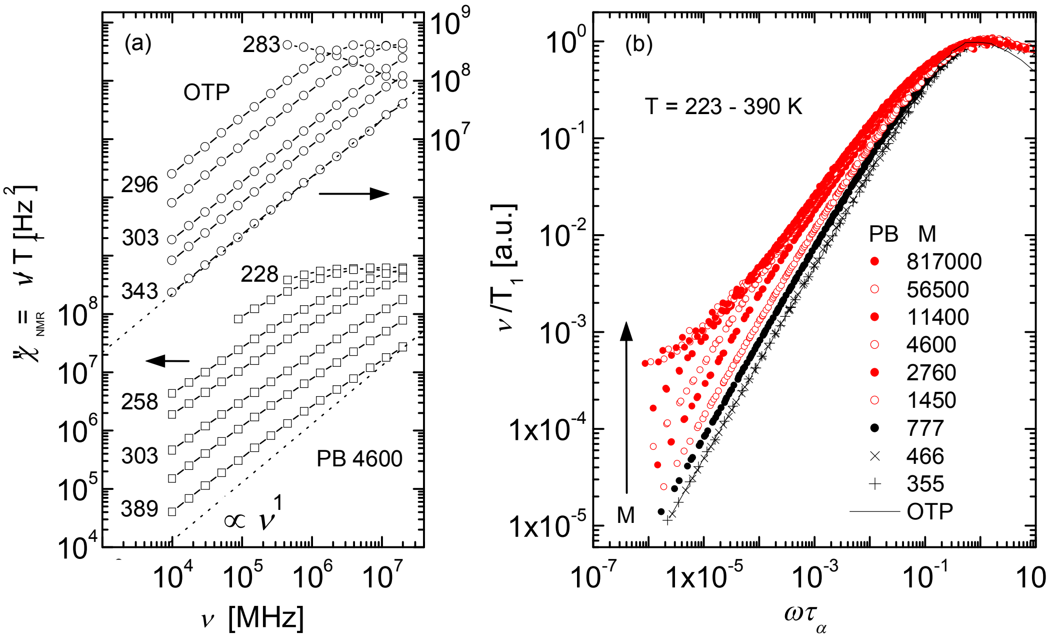


Figure 6: (a) NMR susceptibility $\chi''_{\mathrm{NMR}}(\nu)=\nu/T_1(\nu)$ at indicated temperatures for polybutadiene (PB) with molecular weight M_w of 4600 and for *o*-terphenyl (OTP). (b) The master curves for PB with different M_w, obtained by applying frequency temperature superposition (S. Kariyo, et al.: 2006).

Usually, the correlation function $F_2(\tau)$ reflects the segmental reorientation motion. For the case of a very low molecular weight M_w which can be considered as liquid, the correlation function $F_2(\tau)$ probes the glassy dynamics which lead to measure the α-relaxation time τ_α. For the case of polymer with high molecular weight M_w, the correlation function $F_2(\tau)$ contains both the slow polymer chain and the segmental dynamics. The latter is identified as glassy dynamics (τ_s = τ_α). Assuming the relaxation spectra of both liquid and polymer dynamics are statistically independent, their contributions in the correlation function become

$$F_2(\tau)=F_{\mathrm{glass}}(\tau)F_{\mathrm{polymer}}(\tau) \quad . \tag{11}$$

Depending on the molecular weight, the second term may contain both the Rouse and the reptation dynamics. The relative magnitude *f* for polymer dynamics was introduced as follows

$$F_2(\tau)=\lfloor(1-f)\phi_{\mathrm{glass}}(\tau)+f\rfloor F_{\mathrm{polymer}}(\tau) \quad , \tag{12}$$

where $\phi_{\mathrm{glass}}(\tau)$ is the normalized correlation function describing the glassy dynamics alone (S. Kariyo, et al.: 2006), (S. Kariyo, et al.: 2008).

The relative magnitude *f* relates to the so-called local order parameter or the dynamic order parameter *S* (the order of the segments within the polymer chains) as $f = S^2$ [21, 42]. For the case of polymers with entanglements, the dynamic order parameter *S* means the order of the segments between the two entangled points. The relation of the correlation functions of both glassy and polymer dynamics in Eq. 12 is approximately

$$F_2(\tau)\approx(1-S^2)\phi_{\mathrm{glass}}(\tau)+S^2F_{\mathrm{polymer}}(\tau) \quad . \tag{13}$$

In term of the NMR susceptibility, the contributions of both the glassy and the polymer dynamics are

$$\tilde{\chi}''(\omega)=(1-S^2)\tilde{\chi}''_{\mathrm{glass}}(\omega)+S^2\tilde{\chi}''_{\mathrm{polymer}}(\omega) \quad . \tag{14}$$

According to Eq. 14, the relaxation spectrum measured by the field cycling relaxometry would represent purely the polymer dynamic when the second term dominates. However, it is not the case in reality. Therefore, the interpretation of the polymer dynamics alone without taking the first term into account is not sufficient (S. Kariyo, et al.: 2006), (S. Kariyo, et al.: 2008), (S. Kariyo, et al.: 2008), (A. Herrmann, V. N. Novikov, and E. A. Rössler: 2009), (A. Herrmann: 2009), (D. Kruk, A. Herrmann, and E. A. Rössler: 2012).

The relaxation spectra contributed to polymer dynamics for PB melts can be obtained by subtract the spectra in Fig. 6b with the relaxation spectrum for segmental dynamics measured from PB melts with M_w = 466 g/mol. After the subtraction, the master curves in Fig. 6a give the polymer spectra for PB melts as shown in Fig. 7a (S. Kariyo, et al.: 2006). The amplitude of the polymer spectra for PB melts with molecular weight $M_w \le 4600$ g/mol is increasing with increasing the molecular weight M_w. At $M_w > 4600$ g/mol, the polymer spectra are almost identical. The development of such intensities is identified as the development of the Rouse dynamics for PB melts starting from a simple liquid to a polymer chain. The NMR susceptibility in Eq. 10 calculated from the Rouse theory for several numbers of Rouse units *N* (Fig. 7b) can be used as a comparison with the results shown in Fig 7a (S. Kariyo, et al.: 2006), (S. Kariyo, et al.: 2008), (S. Kariyo, et al.: 2008).

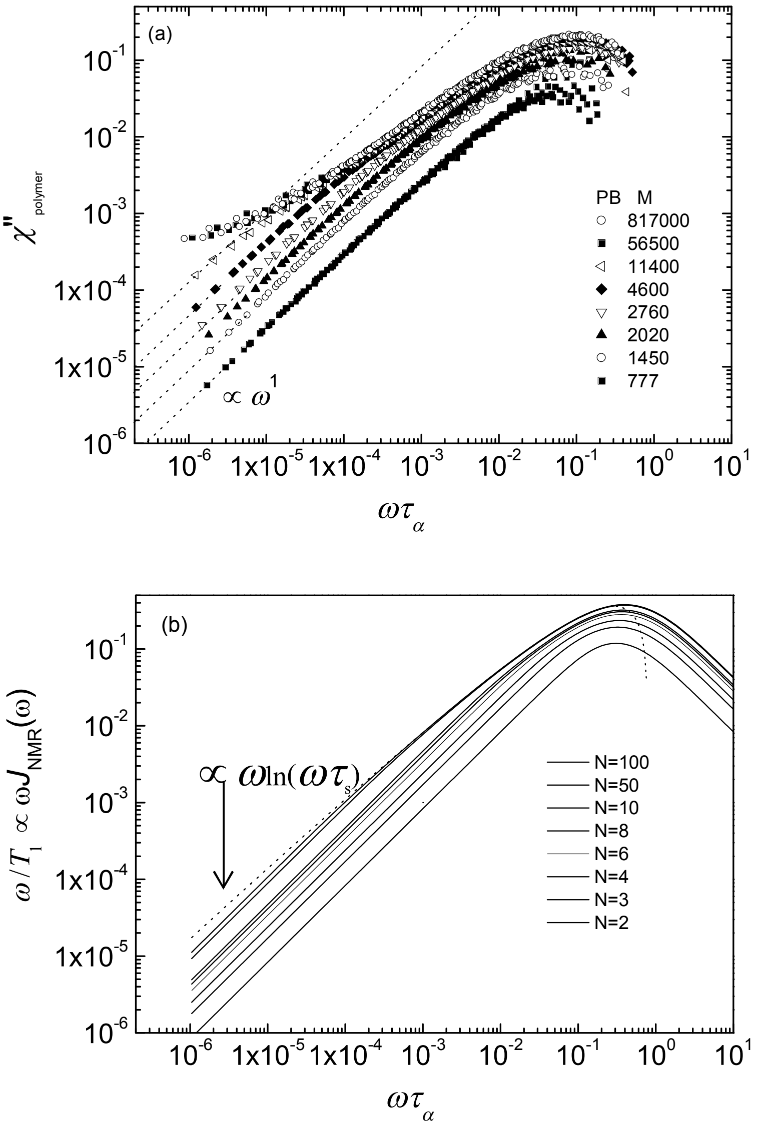


Figure 7: (a) Relaxation spectra attributed to polymer dynamics obtained from the data in Fig. 6b after the subtraction. (b) NMR susceptibility calculated from the Rouse theory for several numbers of Rouse units *N* (S. Kariyo, et al.: 2006).

The squared dynamic order parameter S^2 can be calculated from

$$S^2(M_w) = I_{pol}(M_w)/\left[I_{polymer}(M_w)+I_g\right] \quad , \tag{15}$$

where I_{pol} and I_g are the integral intensities over the polymer and the glass spectra, respectively. Figure 8 shows the dynamic order parameter *S* as a function of molecular weight M_w [23]. The dynamic order parameters *S* for PB melts with molecular weight Mw > 466 g/mol are strongly increase with increasing the molecular weight M_w. At M_w > 4000 g/mol, they are still increasing but relatively very small and seem to be saturation starting from M_w = 56500 g/mol. These means the Rouse dynamics are limited to the chain segments between the two entanglements. The critical molecular weight M_c ~ 4000 g/mol is found two times larger than the entangled molecular weight M_e ~ 2000 g/mol obtained by theoretical calculation from the Rouse theory as well as from the experimental results obtained by DS (S. Kariyo, et al.: 2006), (S. Kariyo, et al.: 2008), (S. Kariyo, et al.: 2008). This factor of two, $M_c = 2M_e$, is found also for the case of viscosity and modulus data (T. C. B. McLeish: 2002).

The maximum value of the dynamic order parameter *S* found from the polymer spectra of PB melts is 0.34. The value for relative magnitude *f* is then 0.11. This value seems to be much higher than that reported in the literature (T. Dollase, R. Graf, A. Heuer, and H. W. Spiess: 2001). However, it is not the case since the value reported in the literatures comes from the investigation for the reptation dynamics alone. The field cycling relaxometry, however, provides the polymer spectra contributed from both the Rouse and the reptation dynamics. The main contribution of the dynamic order parameter *S* here is from the Rouse dynamics because a small increase shown in Fig. 8, *S* ~ 0.02, is found for PB melts with 4000 g/mol < M_w < 56500 g/mol (S. Kariyo, et al.: 2008). Instead, the value of such a small increase, *S* ~ 0.02, could be used for a comparison with the other works (T. Dollase, R. Graf, A. Heuer, and H. W. Spiess: 2001)

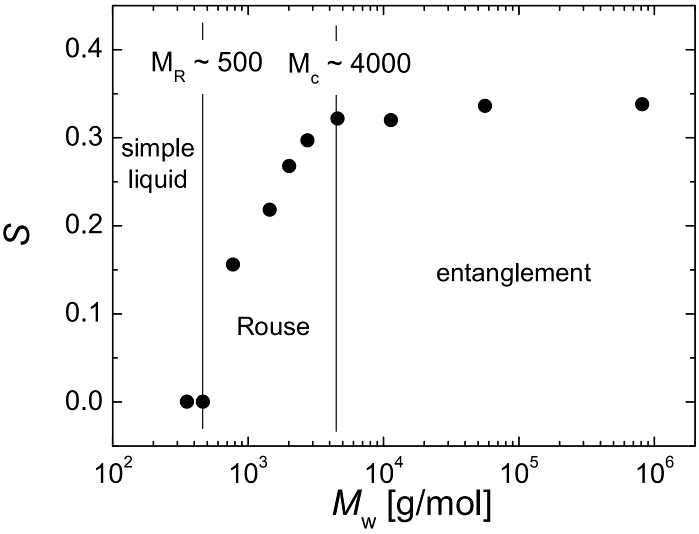


Figure 8: Dynamic order parameter *S* as a function of molecular weight M_w; solid lines distinguish the regions for simple liquid, Rouse, and entanglement dynamics. (S. Kariyo, et al.: 2008).

Conclusions and suggestions

Field cycling relaxometry is a suitable technique for characterizing the polymer dynamics. The master curves obtained by applying frequency temperature superposition provide relaxation spectra of about 8 decades in frequency. An alternative interpretation of the experimental data in terms of the susceptibility instead of the T_1 relaxation dispersion as a function of frequency gives a possibility to compare the results with those obtained by other techniques. In order to probe the polymer dynamics of polymer melts, the segmental dynamics need to take into account. Purely polymer specific dynamics obtained for PB melts is a good example to start with the field cycling relaxometry since many persons have been reported in the literatures and those can be used as a comparison. The results for NR or for polyisoprene PI melts investigated by the field cycling relaxometry are found to be different from those reported for PB melts (S. Kariyo, S. Stapf: 2004), (S. Kariyo, S. Stapf: 2004), (S. Kariyo, S. Stapf: 2005), (S. Kariyo, S. Stapf: 2005), (S. Stapf, S. Kariyo: 2005). According to the interpretation on the PB melts (S. Kariyo, et al.: 2006), (S. Kariyo, et al.: 2008), (S. Kariyo, et al.: 2008), (A. Herrmann, V. N. Novikov, and E. A. Rössler: 2009), (A. Herrmann: 2009), (D. Kruk, A. Herrmann, and E. A. Rössler: 2012), one may expect the same results for PI and PB melts after taking the segmental dynamics into account. Another interesting study is to apply the power law dependences of the T_1 relaxation time on the Larmor frequency (R. Kimmich, E. Anoardo: 2004), (R. Kimmich: 2004), on the measurements represented in term of NMR susceptibility. However, within the frequency window of the commercial field cycling relaxometer, the T_1 relaxation time down to 100 Hz – 1 kHz need to be measured. It is still possible with the help of the stray field compensation. An alternative way to get the results represented the reptation dynamics of polymer melts is to measure the T_1 relaxation times at much higher temperatures but should not reach the melting point of the sample.

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