

Relaxation dynamics of a polymer in a 2D confinement

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(Received 7 July 2003; accepted 22 December 2003)

The molecular dynamics of oligomeric poly(propylene glycol) (PPG) liquids ($M_w = 1000, 2000,$ and 4000 g/mol) confined in a two-dimensional layer-structured Na-vermiculite clay has been studied by broadband dielectric spectroscopy. The α -relaxation and the normal mode relaxation processes were studied for all samples in bulk and confinement. The most prominent experimental observation was that for the normal mode process: the relaxation rate in the clay is drastically shifted to lower frequencies compared to that of the bulk material. This slowing down is probably caused by the strongly reduced number of accessible chain conformations in two dimensions. Also the temperature dependence of the relaxation time for the normal mode process is strongly affected by the confinement. In contrast, for the α -relaxation of the confined polymers we observed only a slight increase of the relaxation rate at high temperatures compared to the corresponding bulk samples, and a decrease of its relaxation strength relative to the β relaxation. Thus, the glass transition is unaffected by the 2D confinement, suggesting that the underlying phenomena responsible for the glass transition is the same as in bulk. Moreover, in the clay the intensity of the normal mode is stronger than that of the α -process, in contrast to the bulk samples where the opposite behavior is observed. © 2004 American Institute of Physics. [DOI: 10.1063/1.1650289]

I. INTRODUCTION

During recent years the dynamics of molecules in confined geometries has gained a growing interest.¹⁻⁹ The influence of finite size effects on the structure and dynamics of matter is important both from a fundamental and an applied point of view. Of special interest is to understand the nature of the glass transition which is an unsolved problem of condensed matter physics.¹⁰⁻¹⁴ The most prominent experimental feature of the glass transition is the rapidly increasing viscosity or the related relaxation time of the main (or α -) relaxation as temperature is decreased towards the glass transition temperature, T_g . By confining molecules in very small spaces, one hopes to learn more about the underlying physics such as the possible existence of a length scale associated with molecular motions responsible for the glass transition.

For polymers, both the α -relaxation, which is associated with local segmental dynamics, and the normal mode process, which is related to the diffusional properties of the whole chains, can be studied by dielectric spectroscopy.³⁻⁵ The normal mode process is only seen for polymers having a dipole moment component parallel to the chain. This gives a total dipole vector which is proportional to the end-to-end vector and the overall chain dynamics can thus be determined.

Various liquids in different types of confinements have been studied in recent years. Schüller *et al.*¹ found, for poly(propylene glycol)(PPG) confined in nanoporous glasses, a positive shift of T_g ($\Delta T_g = T_{g,Conf} - T_{g,Bulk}$). This shift decreases as the molecular weight (M_w) increases. They also observed an additional relaxation process which they associated with a layer of molecules adsorbed at the pore surface.

Huwe *et al.*⁶ have studied the dynamics of ethylene glycol confined to zeolitic host systems of different topologies and pore sizes. They observed a transition from a non-Arrhenius behavior, for large pore sizes as well as the bulk liquid, to an Arrhenius one for single (or few) isolated molecules. The segmental dynamics of polymer films intercalated in polymer/silicate nanocomposites has also been investigated.⁷ The authors found, for the polymer in the confinement, a new mode which is much faster than the segmental α -relaxation of the bulk polymer and with a much weaker temperature dependence. The physical meaning of this new mode is still under discussion.

The monomer and 7-mer of propylene glycol confined in the same kind of vermiculite clay as used here have been studied by quasielastic neutron scattering.⁹ The results showed that the methyl group rotation speeds up by the confinement whereas the diffusive motions become slightly slower. However, as far as we know there are no experimental studies on longer chain-lengths of PPG in a two-dimensional confinement like the vermiculite clay used in this work. This kind of confinement presents several interesting advantages: (a) a very weak, or negligible, interaction between polymer and clay platelets; (b) thousands of two-dimensional monolayers in a macroscopic piece of material; (c) the possibility to separate and identify different relaxation processes due to their different sensitivities to confinement.

The aim of this work is to analyze how α - and normal mode relaxations are affected by the two-dimensional confinement of a vermiculite clay. By means of dielectric spectroscopy the temperature dependence of the relaxation time, the relaxation strength and the shape of the relaxation function are analyzed and discussed for each process. The results are also compared with studies of molecular dynamics in other kinds of confinements.

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II. THEORETICAL BACKGROUND

A. α - or segmental relaxation

Despite the fact that glasses are materials which have been available since the rise of mankind and despite the fact that they play an essential role in modern technology, the physical understanding of the phenomenon remains an unsolved problem of condensed matter physics.¹⁵ The most prominent features observed when a glassforming liquid or polymer melt cools down is the rapid increase of the characteristic relaxation time and the strong non-Debye behavior of the relaxation function. This has been observed using many different experimental methods including mechanical spectroscopy, ultrasonic attenuation, light and neutron scattering, NMR spectroscopy, and especially broadband dielectric spectroscopy.

In the high temperature limit the α -relaxation time has a typical value of about $\tau_0 \cong 10^{-13}$ s. In this range the viscosity of the liquid has a value of about 10^{-3} – 10^{-2} Pa s. With decreasing temperature both the relaxation time and the viscosity increase strongly. The temperature dependencies of the relaxation times for the α - (and normal mode) processes are normally found to closely follow the Vogel–Fulcher–Tammann (VFT) (Ref. 16) equation

$$\tau = \tau_0 \exp(DT_0 / (T - T_0)), \quad (1)$$

where τ_0 is the relaxation time at infinite temperature, D the fragility parameter (giving the curvature of the function), and T_0 the temperature where τ goes to infinity.

B. Normal mode relaxation

In contrast to low molecular weight molecules, where the dipole moment can be well represented by a rigid vector, there are for long chain molecules different possibilities for the orientation of a molecular dipole vector with respect to the polymer backbone. According to Stockmayer¹⁷ macromolecules with molecular dipoles fixed parallel to the backbone are called type A polymers (see Fig. 1 in Ref. 3). For these polymers the dipole moment for the whole chain is given by a summation over the individual dipole moments parallel to the chain backbone. For type B polymers the dipole moment is rigidly attached perpendicular to the chain skeleton. There is no correlation between the dipole moment and the chain contour for these molecules. Most of the synthetic macromolecules are of type B. Finally, chain molecules having the dipoles in a more or less flexible side chain like the poly(n -alkyl methacrylates) are denoted type C. For type B and C polymers only the α -relaxation, and possible secondary relaxations, appear in the dielectric spectrum.

For type A polymers, like poly(propylene glycol), the time correlation function of the dipole moment for a whole chain is proportional to the fluctuation of the end-to-end vector $\langle r^2 \rangle^{1/2}$ of the chain, and can be measured by dielectric spectroscopy.³ The corresponding relaxation process, called normal mode relaxation, can be observed at lower frequencies than for the α -relaxation. The dielectric strength of this process is given by¹⁸

$$\Delta \epsilon = \frac{4\pi N \mu^2 F_{\text{Onsager}} \langle r^2 \rangle}{3kTM}, \quad (2)$$

where N is the Avogadro number, μ the dipole moment parallel to the polymer chain per monomer unit, $F_{\text{Onsager}} (\cong 1)$ is the internal field factor, and M the molecular weight.

The global motion of the chain is described by the time correlation function Φ_{Ch} of the end-to-end vector \mathbf{r} which is given by¹⁵

$$\begin{aligned} \Phi_{\text{Ch}}(t) &= \frac{\langle r(0)r(t) \rangle}{\langle r^2 \rangle} \\ &= \frac{8}{\pi^2} \sum_{p=1}^N \frac{1}{p^2} \exp(-t/\tau_p), \end{aligned} \quad (3)$$

where τ_p is the relaxation time of the mode p . The Rouse model gives

$$\tau_p = \frac{\zeta N^2 b^2}{3\pi^2 kTp^2}, \quad p = 1, 3, \dots, \quad (4)$$

where N is the number of beads, b describes the average distance between the beads, and ζ is the monomeric friction coefficient. From Eq. (3) it is clear that only the first mode contributes significantly to the dielectric relaxation.

III. EXPERIMENT

PPG ($\text{H}[\text{OCH}(\text{CH}_3)\text{CH}_2]_n\text{OH}$) of different molecular weights ($M_w = 1000, 2000, \text{ and } 4000$ g/mol) have been used for this study as these are polymers showing a dielectrically active normal mode relaxation, and do not crystallize in the supercooled regime. The polymers were purchased from Aldrich Chemical Company, Inc., and opened and manipulated inside a glove-box under a controlled argon atmosphere.

As confining host material, vermiculite clays provided by Askania, Sweden, were used. Vermiculites are unique in the sense that they are able to provide two-dimensional geometries with extremely thin and well-defined layer thickness. The clays were washed and then treated for about six months with 1 M NaCl solution at room temperature, with regular changes of solution, to produce pure Na-vermiculite.

Totally dry Na-vermiculite clays were obtained by drying at 150 °C in a vacuum oven for 48 h. After the drying we carefully weighted the clay pieces and they were thereafter submerged in the respective polymers. The clays were left in bottles, at 70 °C for two weeks. Filling was carefully monitored by weighing the samples. By comparing the weights of the submerged and vacuum dried clay crystals we were able to estimate the *macroscopic* densities of the intercalated PPG to approximately 0.34, 0.46, and 0.43 g/cm³ for PPG1000, 2000, and 4000, respectively. However, from the x-ray diffraction measurements shown in Fig. 1 it is evident that the molecules are very inhomogeneously distributed. In Fig. 1 the scattering angle θ has been converted to a d -spacing (the distance between consecutive clay platelets) through the crystallographic relation $d = \lambda/2 \sin \theta$, where λ is the wavelength of the incoming x-ray beam. Figures 1(a) and 1(b) show the diffraction data after 1 day, before full equilibrium has been reached, and after two weeks when the maximum

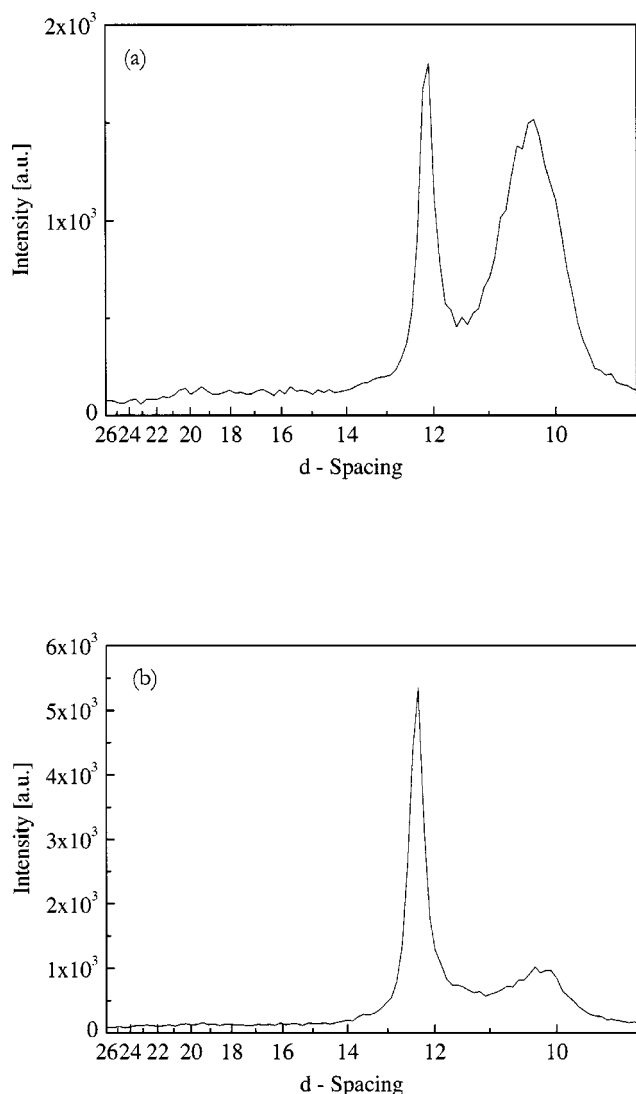


FIG. 1. X-ray diffraction data of PPG4000 intercalated in Na-vermiculite clay after (a) one day intercalation time and (b) two weeks intercalation time, when full equilibrium had been reached. The scattering angle θ has been converted to a crystallographic d -spacing, as described in the text.

amount of PPG had been intercalated between the clay platelets. Two typical d -spacings can be observed; one at about 10.3 Å, which corresponds to the interplatelet distance for dry Na-vermiculite clay¹⁹ containing only the interlayer Na⁺ ions (having a diameter of 2 Å), and one at 12.3 Å corresponding to polymer filled layers with an effective thickness of 4.0 Å for the polymer layer (i.e., a flat monolayer). By comparing the intensities of the two peaks in Fig. 1(b) it is evident that most of the interplatelet spacings are at least partly filled with PPG, but since some layers remain unfilled even at equilibrium it is likely that even the “filled” layers contain unfilled regions of different sizes. Unfortunately, this makes it difficult to accurately estimate the effective *microscopic* densities, which are of interest for the present results of the intercalated liquids. The reason for the inhomogeneous distribution of the molecules is most likely that the clay crystals are naturally occurring minerals with an inhomogeneous distribution of different ions (and therefore also of the charge density) in the clay layers.

TABLE I. Molecular characteristics of the poly(propylene glycol) samples.

Sample	M_w (g/mol)	ρ_{Bulk}^a (g/cm ³)	$T_{g,\text{Bulk}}$ (K)	$T_{g,\text{Clay}}$ (K)
PPG1000	1000	1.005	200.7±0.1	200.7±0.1
PPG2000	2000	1.005	201.5±0.1	201.9±0.1
PPG4000	4000	1.004	203.9±0.1	203.8±0.1

^aData from manufacturer.

Flat pieces of clay were selected for both calorimetric and dielectric measurements. After taking them from the bottles their outer surfaces were carefully dried with tissue paper to eliminate the surface polymer. There was no evidence of residual or surface polymer in the measurements. Furthermore, previous studies with water (not discussed here) have shown that only 3%–4% of the intercalated liquid is located in clay defects and therefore does not contribute significantly to the total calorimetric or dielectric signal.

Calorimetric glass transition temperatures (T_g) were measured with a Q1000TA Instruments Differential Scanning Calorimetry (DSC) at a constant heating rate of 20 K/min using helium as transfer gas. From the heat flow/temperature curves, T_g values were calculated as the onset point. Standard aluminum pans were used for both bulk PPG and clay pieces with confined PPG. Results are shown in Table I.

The dielectric measurements were performed on a high resolution Novocontrol dielectric analyzer covering the broad frequency range (10^{-2} – 10^7 Hz), and an Agilent RF impedance material analyzer 4291B in the frequency range 10^6 – 10^9 Hz. Isothermal (within ± 0.02 K) frequency scans of the complex dielectric function, $\epsilon^*(f) = \epsilon'(f) - i\epsilon''(f)$, were performed every third degree over the temperature range 120–350 K.

IV. ANALYSIS

To describe the experimental response, i.e., the dielectric permittivity $\epsilon(\omega)$, related to the primary (α) process in supercooled liquids, one of the most common choices in the literature is to use the Kohlrausch–Williams–Watts (KWW) function,

$$\phi_\alpha(t) = f \exp[-(t/\tau)^{\beta_{\text{KWW}}}], \quad 0 < \beta_{\text{KWW}} \leq 1, \quad (5)$$

where τ is the relaxation time and β_{KWW} is the stretching parameter. The amplitude parameter f is a measure of the fraction of the experimental quantity that is relaxed via the α -relaxation. The lower the β_{KWW} value, the more stretched the relaxation function, $\phi(t)$, becomes in time. Recently, an empirical response function which is a very good description of the KWW function in the frequency domain has been proposed,²⁰

$$\epsilon''(\omega) = \frac{\epsilon_p''}{\frac{b}{1+b} (b(\omega/\omega_p)^{-1} + (\omega/\omega_p)^b) + (1-b)}, \quad (6)$$

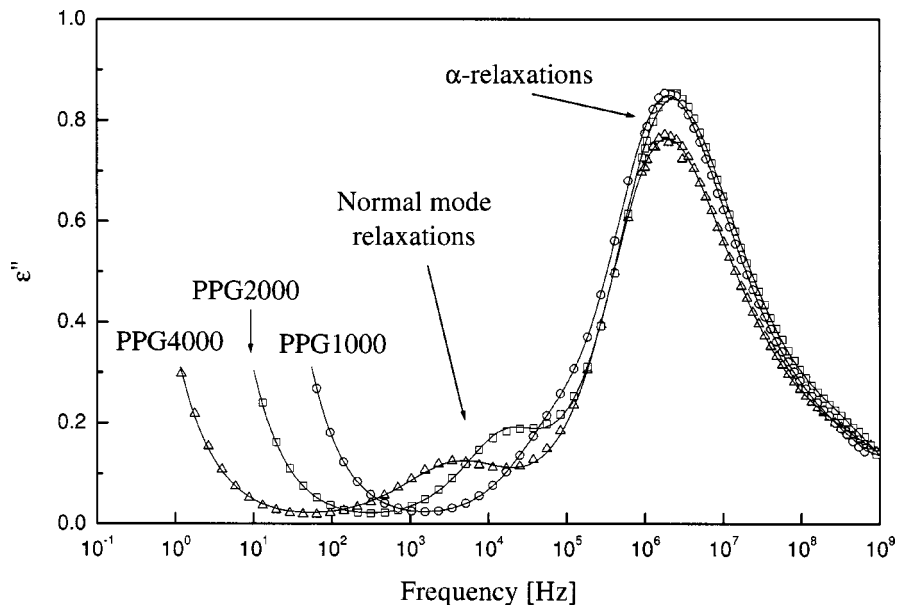


FIG. 2. Imaginary part of the dielectric response $\epsilon''(f)$ for bulk polymers at $T=250$ K. PPG1000 (circles), PPG2000 (squares), and PPG4000 (triangles). Filled lines represent the least square fits to the experimental data.

where ϵ_p'' is the amplitude at the peak maximum, ω_p is the peak frequency, and b is the shape parameter. Equation (6) has only three adjustable fit parameters and has been used in the present study to fit the α -relaxation both in bulk and confined PPG.

An often used alternative to the KWW expression is the so-called Havriliak–Negami (HN) expression,²¹

$$\epsilon^*(\omega) = \epsilon_\infty + (\epsilon_s - \epsilon_\infty) \frac{1}{[1 + (i\omega\tau)^\alpha]^\beta} \quad (7)$$

Here ϵ_∞ is the high frequency limit of the response, and ϵ_s the low frequency limit of the static permittivity ($\Delta\epsilon = (\epsilon_s - \epsilon_\infty)$). τ is the relaxation time and α and β are shape parameters. If β is set to one the symmetrical Cole–Cole (CC) (Ref. 22) function is obtained. This expression is widely used to describe the response of secondary relaxation processes in glassforming materials. We used a CC function

to describe the normal mode in bulk and the β -relaxation both in bulk and confinement. For the normal mode of confined PPG we used the full HN function.

V. RESULTS

In the case of the dry clay only one slow process, apart from a low-frequency dispersion, could be observed, and this was fitted with a Cole–Cole function. The α -parameter was temperature independent ($\cong 0.45$) and the relaxation time follows an Arrhenius temperature dependence with an activation energy of $E_A \cong 0.78$ eV. This process is probably the Maxwell–Wagner interfacial polarization characteristic of inhomogeneous media.²³ However, since it is a very slow and weak process, it does not affect the here studied α - and normal mode main relaxation processes of PPG, and will therefore not be further discussed here.

Figure 2 shows the total dielectric loss for bulk PPG of

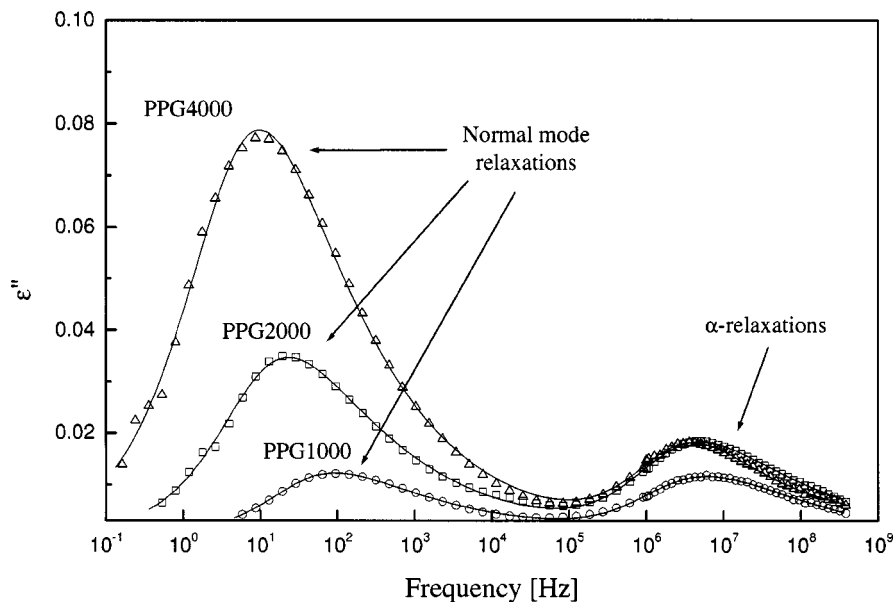


FIG. 3. Imaginary part of the dielectric response $\epsilon''(f)$ for confined polymers at $T=250$ K. Conductivity has been subtracted for clarity. The symbols are the same as in Fig. 2. Filled lines represent the least square fits to the experimental data.

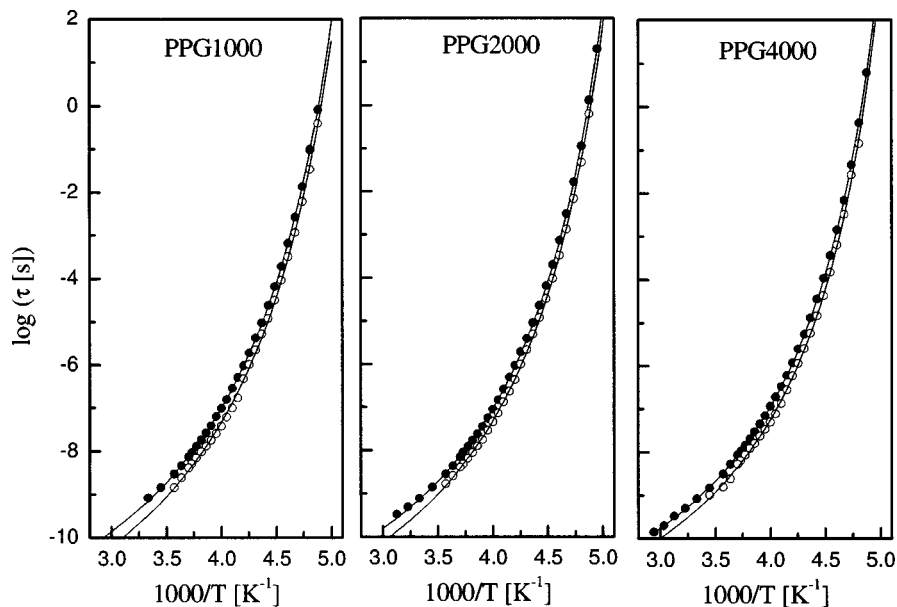


FIG. 4. α -relaxation times vs inverse temperature for the three polymers. Bulk data are presented using filled symbols and confined data with open circles.

different molecular weights. The main peak corresponds to the α -relaxation while the normal mode peak is on the low frequency side of the main peak and moves towards lower frequencies with increasing molecular weight. At this temperature the β relaxation appears as a wing (outside the experimental frequency window) on the right-hand side of the α -peak.

Figure 3 shows the dielectric loss for confined PPG's. The α -relaxation appears at high frequencies close to where the bulk α -peak was observed (see Fig. 2), but the normal mode has drastically shifted towards lower frequencies compared to the bulk. Moreover, a strong increase of the relative amplitude of the normal mode compared to the α -process is observed.

The dielectric relaxation of PPG with different molecular weights have been studied by Schönhals *et al.*³⁻⁵ both in bulk and confined to porous glasses. Our results are in qualitative agreement with theirs. However, some differences were observed and these will be discussed below, where we analyze the characteristic behavior of each process separately.

A. α -relaxation

The temperature dependence of the relaxation time of the α -relaxation as obtained from the analysis can be described by the VFT equation [Eq. (1)]. Figure 4 shows the relaxation time τ versus inverse temperature for the confined and bulk polymers. The VFT parameters obtained from the fitting procedure are given in Table II. From these data it is clear that for all three molecular weights the temperature dependence of the α -relaxation time is, within experimental error, unaffected by the confinement at low temperatures, while only a very slight speeding up in the clay can be observed at high temperatures. This behavior is opposite to that observed for PPG confined to porous glasses^{3,4} and will be discussed later.

From the fitting of the VFT equation to the relaxation time data a dielectric glass transition temperature T_g^{Diell}

$=T(\tau=100\text{ s})$ was estimated (see Table II). There were no appreciable differences (within 1 K) in $\Delta T_g [\Delta T_g = T_g^{\text{Diell}}(\text{clay}) - T_g^{\text{Diell}}(\text{bulk})]$ for the three polymers. This was also confirmed by means of DSC measurements (see Table II). It is interesting to note that Schönhals *et al.*^{4,5} obtained ΔT_g values as high as 10 K for the same polymers confined in porous glasses with pore sizes between 2.5 and 7.5 nm. This fact indicates that the geometry of the confinement has a large influence on how the α -relaxation is affected.

One of the most common ways to define the fragility of a glassformer (using Angell's strong-fragile classification²⁴) is by means of the D parameter resulting from a VFT fit. A low value of D corresponds to a fragile material. We note from Table II that the trend of the D parameter indicates a slightly increasing fragility with increasing M_w for bulk PPG. The same trend is observed for the confined polymers.

We will now analyze how the relaxation strength is affected by the confinement. Since the geometry of the clay pieces and their distribution in the sample cell are not the same for the different samples, it is difficult to determine the absolute value of the dielectric strength for confined polymers. However, a comparison between the relative dielectric strength of different process (i.e., α - and β relaxations) in bulk and clay can be done. For the β relaxation, $\Delta\epsilon_\beta$ is

TABLE II. Parameters obtained from fitting a VFT function to the α -relaxation for the three polymers in bulk as well as in confinement.

Sample	$\log[\tau_0\text{ (s)}]$	D	$T_0\text{ (K)}$	$T_{g,100\text{ s}}\text{ (K)}$	$T_{g,\text{DSC}}\text{ (K)}$
Bulk					
PPG1000	-12.7 ± 0.1	6.4 ± 0.1	168.1 ± 0.3	199.8 ± 0.1	200.7 ± 0.1
PPG2000	-12.5 ± 0.1	5.8 ± 0.1	170.7 ± 0.3	200.5 ± 0.1	201.5 ± 0.1
PPG4000	-12.4 ± 0.1	5.5 ± 0.1	173.4 ± 0.2	202.3 ± 0.1	203.9 ± 0.1
Confinement					
PPG1000	-13.0 ± 0.2	6.4 ± 0.3	167.7 ± 1.2	198.8 ± 0.8	200.7 ± 0.1
PPG2000	-12.8 ± 0.1	6.0 ± 0.2	169.9 ± 0.6	199.6 ± 0.4	201.9 ± 0.1
PPG4000	-12.5 ± 0.1	5.2 ± 0.2	174.4 ± 0.8	201.7 ± 0.6	203.8 ± 0.1

TABLE III. Relaxation strength for α - and β relaxations for the three polymers in bulk as well as in confinement, at $T=211$ K. Ratio of relaxation strength between α - and β relaxations, and ratio between bulk, and confinement relative amplitudes (see text).

Sample	Condition	$\Delta\epsilon_\alpha$	$\Delta\epsilon_\beta$	$\Delta\epsilon_\alpha/\Delta\epsilon_\beta$	$(\Delta\epsilon_\alpha/\Delta\epsilon_\beta)_{\text{Bulk}}/(\Delta\epsilon_\alpha/\Delta\epsilon_\beta)_{\text{Clay}}$
PPG1000	Bulk	1.54 ± 0.02	0.65 ± 0.02	2.37 ± 0.10	1.74 ± 0.16
	Clay	$14.4\pm 0.2\text{E-}3$	$(10.6\pm 0.4)\text{E-}3$	1.36 ± 0.07	
PPG2000	Bulk	1.37 ± 0.02	0.60 ± 0.05	2.28 ± 0.22	1.37 ± 0.30
	Clay	$23.6\pm 0.3\text{E-}3$	$(14.1\pm 1.5)\text{E-}3$	1.67 ± 0.20	
PPG4000	Bulk	1.28 ± 0.02	0.55 ± 0.02	2.33 ± 0.12	1.54 ± 0.14
	Clay	$25.4\pm 0.4\text{E-}3$	$(16.8\pm 0.4)\text{E-}3$	1.51 ± 0.06	

obtained directly from the CC expression [Eq. (7)]. For the α -relaxation, however, we obtained the $\Delta\epsilon_\alpha$ value by numerical integration of the fitted dielectric loss, ϵ''_α as

$$\Delta\epsilon_\alpha = \frac{2}{\pi} \int_{-\infty}^{\infty} \epsilon''(\omega) d(\ln \omega). \quad (8)$$

Even if the strength of the β relaxation is hard to determine, especially for confined polymers, it is possible to make a rough estimation of the relative dielectric strength between the α - and β processes. Table III shows the relaxation strengths of the α - and β relaxations for bulk and confined PPG at $T=211$ K where both processes are clearly defined and well separated in our experimental frequency window. Column five shows the ratio $\Delta\epsilon_\alpha/\Delta\epsilon_\beta$, and in the last column the ratio between the relative amplitudes in bulk and clay is presented. From Table III it is clear that the relative intensity of the α -relaxation is reduced in clay by about a factor of 1.5. If we assume that the relaxation strength of the β relaxation is basically unaffected by the confinement, this implies that the α -relaxation is weaker in the clay than in bulk. A similar change in the relative amplitude of the α -process has also been observed for other glassformers in the same confinement.²⁵

Turning to the peak shape, Fig. 5 shows mathematical constructions of the α -peak (based on the fits previously discussed) with normalized intensity and scaled peak frequency,

f_p , for all the investigated samples. There is basically no difference in the peak shape for the bulk polymers. However, in the case of the confined polymers the peak is broader and more asymmetric. The difference compared to bulk increases with decreasing molecular weight. The inset in Fig. 5 shows the temperature dependence of the b shape parameter [Eq. (6)] for PPG2000. Similar weak temperature dependencies were observed also for the other PPGs.

B. Normal mode relaxation

We now turn to the normal mode relaxation and investigate how the confinement affects the motion of the whole chain. Figure 6 shows the relaxation time τ versus inverse temperature for the normal mode of bulk and confined polymer. The VFT-function has been fitted to the data and the resulting values of the VFT parameters are presented in Table IV. Two important features can be observed in Fig. 6. A drastic shift of the relaxation time to lower frequencies for confined polymers and a clear molecular weight dependence of the relaxation time.

Besides the large shift of the relaxation time, the most noticeable effect of the confinement is the strong increase of the relaxation strength of the normal mode compared to the α -relaxation. By comparing Figs. 2 and 3 it is clear that the relative relaxation strength of the normal mode has increased

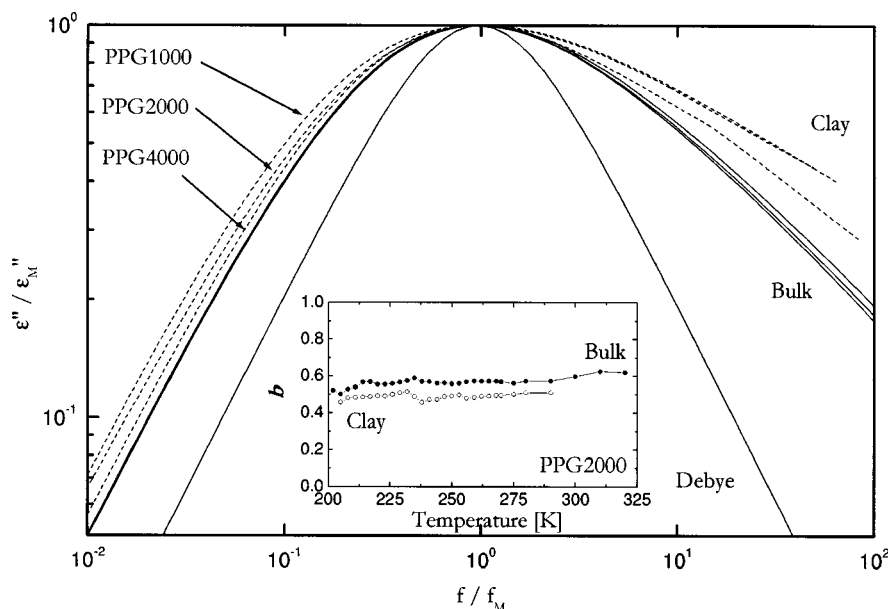


FIG. 5. Mathematical constructions of the normalized dielectric loss of the α -relaxation, based on the fits described in the text, for the three polymers at $T=250$ K. Bulk data are presented using filled lines and confined data with dashed lines. A Debye peak has been added for comparison. The inset shows the temperature dependence of the b shape parameter for both bulk and confined PPG2000.

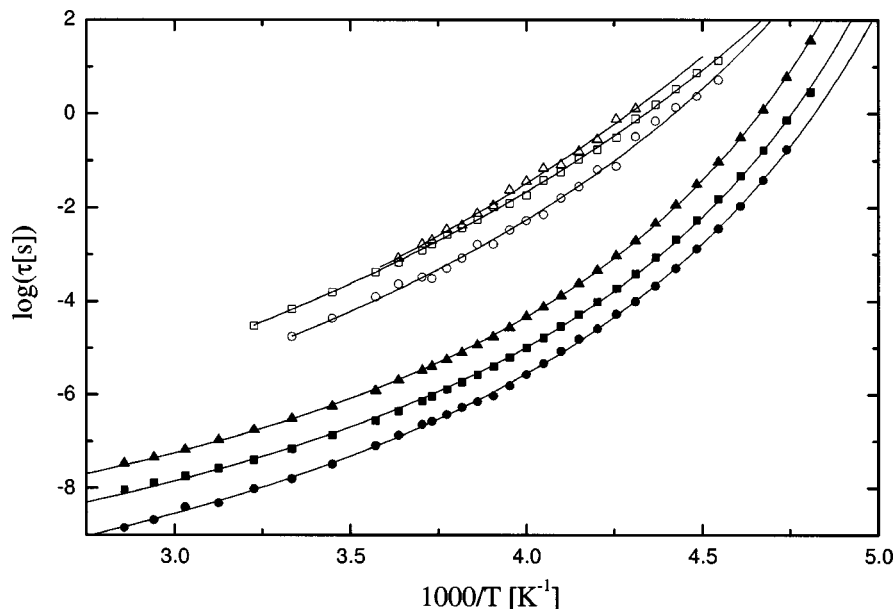


FIG. 6. Normal mode relaxation times vs inverse temperature for the three polymers. Bulk data are presented using filled symbols and confined data with open symbols [PPG1000 (circles), PPG2000 (squares), and PPG4000 (triangles)]. Lines represent the least square fits to the VFT equation.

in the clay compared to bulk, for all three molecular weights. In bulk the α -process is the main relaxation, whereas in the present confinement the normal mode peak is as high as, or even higher than, the α -peak.

Finally, mathematical constructions of the normalized dielectric loss for the normal mode are shown in Fig. 7 for both bulk and confined PPG. The data have, as in Fig. 5, been scaled with the peak frequency, f_p , and normalized to the peak amplitude. For the bulk samples a CC (symmetric) function was used to fit the data, whereas for the confined polymers a HN (asymmetric) function had to be used. The inset in Fig. 7 shows the temperature dependence of the shape parameters (α and β) for both bulk and confined PPG2000. A similar behavior was observed for PPG1000 and PPG4000.

VI. DISCUSSION

A. α -relaxation

Contrary to the findings for PPG confined in porous glasses,⁴ we observed basically no effects of our 2D confinement on the relaxation time and T_g for the α -process. The only noticeable difference is a slight speeding up of the α -relaxation for confined polymers, which occurs at high temperatures rather than at low temperatures as usually is the case for 3D confinements⁴ (see Fig. 4). The unaffected T_g indicates that the underlying phenomena responsible for the dynamic glass transition must be the same in bulk and in our confined system. In contrast, a lowering of T_g , up to more than 10 K, was observed by Schönhals and Stauga⁴ for the same polymers confined to porous glasses. The different behaviors can be explained using the cooperativity concept of the glass transition. In porous glasses the characteristic length ξ is limited by the pore size, whereas in our 2D confinement there is no restriction for ξ in two of the three dimensions. Recent studies²⁶ have shown that the characteristic length ξ in molecular liquids is unaffected by the present confinement.

Another interesting finding for the α -process is the reduction of its relaxation strength (see Table III). One possible explanation is adsorption effects which should reduce the relaxation strength by immobilizing segments of the polymer chain. However, since this should also reduce the relaxation rate and increase T_g , which is not observed, this does not seem to be the correct explanation. It is then more likely that some configurations are frozen due to geometrical restrictions. This will be further discussed in the next section.

B. Normal mode relaxation

For type A polymers the normal mode is generally observed as a separate relaxation process at frequencies below the α -process. Since the overall chain dynamics is reflected by this process its properties strongly depend on molecular weight. Our results show that the normal mode is drastically shifted to lower frequencies in our 2D confinement (see Fig. 6). A shift of the normal mode to lower frequencies has also been observed for PPG confined to porous glasses,^{3,4} however some differences are worth to discuss. For PPG in 3D confinement the shift is not so drastic as in our 2D system and the relaxation time at high temperatures, i.e., the τ_0 value, does not coincide with the bulk value (see Table I in Ref. 3). This is not the case for our confined polymers, where τ_0 values for bulk and confined polymers are basically the same (see Table IV), which supports the idea that this relaxation process is in fact the normal mode. Moreover, τ_0 for the α -relaxation is also about the same for bulk and confined PPG (see Table II). This indicates that the origin of the relaxation process may be unaffected by the present 2D confinement. However, we observe a difference in τ_0 between α - and normal mode, in agreement with previous results on bulk PPG.³

Previous results have shown that the normal mode is only weakly influenced by the confinement when the interaction between the polymer and the walls of the porous glass is reduced.^{3,4} However, although the interaction of the poly-

TABLE IV. Parameters obtained from fitting a VFT function to the normal mode relaxation for the three polymers in bulk as well as in confinement.

Sample	$\log[\tau_0 \text{ (s)}]$	D	$T_0 \text{ (K)}$
Bulk			
PPG1000	-11.8 ± 0.1	8.1 ± 0.2	160.0 ± 0.7
PPG2000	-10.8 ± 0.1	7.0 ± 0.2	164.0 ± 0.7
PPG4000	-10.2 ± 0.1	6.7 ± 0.1	166.7 ± 0.3
Confinement			
PPG1000	-9.9 ± 0.5	12.4 ± 2.3	146.5 ± 6.7
PPG2000	-10.2 ± 0.3	17.7 ± 1.5	131.0 ± 3.5
PPG4000	-11.1 ± 2.1	23 ± 15	123 ± 27

mer with the clay platelets is very weak, as indicated from the results of the α -relaxation time, the retardation of the relaxation rate can be understood in terms of geometrical restrictions. One should take into account that the number of allowed conformations, for a given chain, is much more restricted in 2D than in 3D. A reduction of the configuration space thus gives the chain less opportunities to move and, therefore, it needs more time to relax. Additionally, the possibilities of having frozen configurations in parts of the chain are much higher in a two-dimensional confinement.²⁷ These frozen arrangements not only delay the relaxation of the whole chain, but also prevent the α -process to take place in such regions. It is possible that at least a part of the observed reduction in the relaxation strength of the α -process is due to these geometrical restrictions.

The molecular weight dependence of the relaxation time for the normal mode process is also affected by the confinement. For bulk samples this dependence is described by the Rouse theory.²⁸ For bulk PPG, at these present low molecular weights, we observe a $\tau \propto M^{2.06 \pm 0.09}$ dependence which agrees with the theoretical prediction ($\tau \propto M^2$) and with previous experimental data on PPG (Ref. 29) and polyisoprene (PI).³⁰ On the other hand, for the confined polymer we found

that $\tau \propto M^{1.44 \pm 0.20}$, which may only be valid for this low molecular weight range and is most likely related to the reduced dimensionality.

Most of the experimental observations discussed here for PPG are in good agreement with the findings of Jeon and Granick³¹ for *cis*-polyisoprene confined to thin films. Although their films ($\cong 100$ nm) are much thicker than ours, they also observed a retardation of the normal mode relaxation time and a broadening of the peak shape in the confinement. Moreover, as in our case the temperature dependence of the α -relaxation time was basically unaffected by the confinement.

We finally discuss the strong confinement induced increase of the relaxation strength of the normal mode. This behavior has also been observed by Schönhal and Stauga^{3,4} for PPG confined to porous glasses. From Fig. 8 in Ref. 3 it appears that the increase of the relaxation strength is of the same order of magnitude in both types of confinement. Moreover, the reason for the increase of the relaxation strength is the same in both systems: the increase of the end-to-end vector. According to Adachi and Kotaka,^{18,30} the dielectric strength of the normal mode process is proportional to the end-to-end vector $\langle r^2 \rangle^{1/2}$ of the chain [see Eq. (2)]. From the self-avoiding random walk theory we know that $\langle r^2 \rangle \propto M^{2\nu}$, with the exponent $\nu \cong 0.592$ in three dimensions and $\nu = \frac{3}{4}$ for two dimensions. Therefore, for a given molecular weight we expect a longer end-to-end distance in a 2D confinement and therefore also a stronger relaxation process according to Eq. (2). The experimental data show a noticeable increase of the molecular weight dependence of the relaxation strength for confined polymers compared to bulk. This fact supports the previous reasoning and confirms the strong effect of the 2D confinement on the polymer chain conformations.

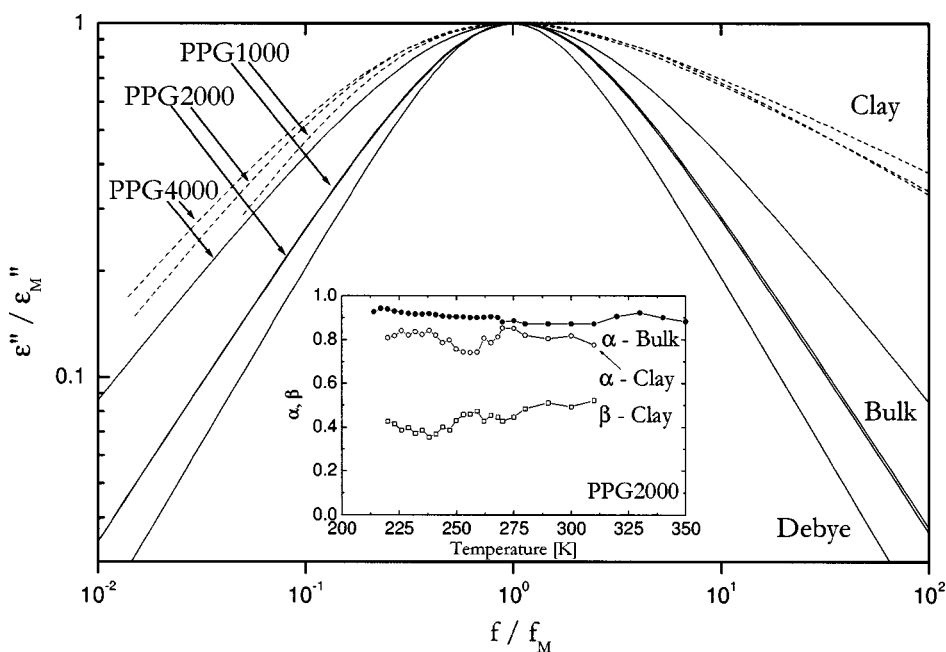


FIG. 7. Mathematical constructions of the normalized dielectric loss of the normal mode relaxation, based on the fits described in the text, for the three polymers at $T=250$ K. Bulk data are presented using filled lines and confined data with dashed lines. A Debye peak has been added for comparison. The inset shows the temperature dependence of the α and β shape parameters for both bulk and confined PPG2000.

VII. CONCLUSIONS

In this work we have used broadband dielectric spectroscopy to study the α - and the normal mode relaxations both in bulk and confined PPG of different molecular weights.

It was found that the relaxation time of the α -process is basically unaffected by the confinement, whereas its relaxation strength decreases in the clay.

In contrast, the normal mode relaxation is strongly affected by the confinement. The shift to lower frequencies and the increase of its relaxation strength in the clay was shown to be directly related to the reduced number of accessible chain conformations and on the average more extended chains in the two-dimensional confinement.

ACKNOWLEDGMENTS

J.S. is a Royal Swedish Academy of Sciences Research Fellow supported by a grant from the Knut and Alice Wallenberg Foundation. The Swedish Research Council and Swedish Foundation for Strategic Research are acknowledged for financial support.

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