Glass transition of one-dimensional molecular chains of *p*-nitroaniline confined in $\text{AlPO}_4\text{-5}$ nanopores revealed by dielectric spectroscopy

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(Received 25 January 1999; accepted 29 July 1999)

The dynamics of molecular chains of hydrogen-bonded *p*-nitroaniline (*p*NA), confined in the one-dimensional pore system of $\text{AlPO}_4\text{-5}$, was studied by broadband dielectric spectroscopy (10^{-2} – 10^6 Hz). Two relaxation processes were observed. A fast process (the α process) shows above 72 °C a Vogel–Fulcher–Tammann behavior typical of glass-forming materials, indicating cooperative dynamics of the “condensed” *p*NA chains. Below the glass temperature the α -relaxation peak broadens significantly and obeys an Arrhenius law. Both observations imply a change in length scale of cooperativity ξ from a temperature-controlled to a chain-length-dependent one. The second relaxation process is tentatively assigned to structural relaxations of the $\text{AlPO}_4\text{-5}$ host lattice itself, since it is also present in calcined (empty) crystals. © 1999 American Institute of Physics. [S0021-9606(99)70437-X]

I. INTRODUCTION

The (dynamic) glass transition observed in many low molecular liquids and in macromolecular systems is an intriguing phenomenon for which many different theoretical concepts have been proposed. These concepts range from free volume approaches¹ to the more recent mode coupling theory² and the fluctuation approach.³ A basic idea of the modern concepts is the assumption of a characteristic length scale of cooperativity or correlation length ξ that increases with increasing relaxation time, i.e., with decreasing temperature. In the last several years many efforts have been made to prove the existence of such a characteristic length scale by confining glass-forming materials to geometries of the order expected for ξ . Such confined geometries are, e.g., present in nanoporous glasses,^{4,5} porous membranes,⁶ or channel structures of zeolite host systems.^{7,8}

The main expectation for such confined geometries is that the cooperative dynamics, manifested by a Vogel–Fulcher–Tammann (VFT) dependence of the mean relaxation time, changes when ξ approaches the typical length of a molecular ensemble. As a result, the glass transition may either shift,⁹ or the liquidlike behavior characterized by a (VFT) dependence may change to single molecule dynamics

as expressed by an Arrhenius-type temperature dependence of the relaxation time.⁸

The present study is focused on the dynamics of molecular chains of *p*-nitroaniline (*p*NA) adsorbed in the one-dimensional channels of the molecular sieve $\text{AlPO}_4\text{-5}$ (structure code AFI). This host–guest system is of particular interest since the highly polar (and hyperpolarizable) *p*NA molecules will be adsorbed in a preferred direction, leading to a macroscopic polarization which gives rise to a second-harmonic generation activity¹⁰ and to pyroelectricity.^{11,12} Owing to the small channel diameter of 0.73 nm, the *p*NA molecules can neither pass each other nor flip around their short molecular axis. Infrared measurements revealed a high molecular orientation with a mean deviation angle of the long molecular axis from the channel direction of less than 15° at 273 K.¹³ Another important feature of the aligned *p*NA molecules is their ability to form single or even double hydrogen bonds, the probability of which is temperature dependent.

Recently, the observation of a relaxation process in (dynamic) pyroelectric experiments was reported, which was assigned to cooperative motions of the one-dimensional *p*NA chains.¹² In the present paper we want to address the relaxational behavior of $\text{AlPO}_4\text{-5/pNA}$ by dielectric spectroscopy.

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II. SAMPLE PREPARATION AND EXPERIMENTAL SETUP

Large $\text{AlPO}_4\text{-5}$ crystals were hydrothermally synthesized in TeflonTM-lined autoclaves with triethylamine as a template according to recipes from the literature.¹⁴ Crystallization was performed at 180 °C for 25 min using microwave heating. The reaction mixture used had the molar composition 1 Al_2O_3 : 2.18 H_3PO_4 : 1 Et_3N : 1 HF: 300 H_2O (mixture 2 in Ref. 15). To remove the organic template, the crystals were calcined at 700 °C for 48 h. The removal of the template was verified with Fourier transform infrared (FTIR) spectroscopy, the crystal structure was validated by x-ray diffraction. Freshly calcined crystals were filled with *p*NA from the vapor phase at 155 °C for several hours. The degree of filling with *p*NA molecules was determined with FTIR and thermogravimetric analysis and amounted to about 1%.¹⁶ A detailed description of the loading procedure is given in Ref. 12. FTIR, pyroelectric and SHG experiments confirm the alignment of the *p*NA molecules and the formation of chainlike structures.

For the dielectric measurements, *p*NA loaded $\text{AlPO}_4\text{-5}$ crystals were slightly pressed between circular brass electrodes of 20 mm in diameter. This procedure resulted in a moderately packed layer (~ 40 vol % packing density) with a thickness of ~ 85 μm of preferentially planar-oriented crystals. The dielectric experiments were performed using a combination of a Schlumberger SI 1260 impedance gain-phase analyzer with a dielectric electrometer (developed by TNO) for frequencies between 10^{-2} and 10^3 Hz, and a Hewlett-Packard 4284A precision LCR meter for frequencies between 10^3 and 10^6 Hz. The sample was placed in a nitrogen cryostat (Novocontrol), the temperature of which was controlled with a stability better than ± 50 mK.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Dielectric experiments were carried out isothermally in steps of 5 or 2.5 K in the following sequence: (i) heating from 25 to 195 °C, (ii) cooling down to -150 °C, and (iii) heating again to 25 °C. As expected, during the first heating irreversible changes in the dielectric spectra occurred due to the desorption of adsorbed water, mainly around 50 °C. Subsequent repeated cooling and heating revealed a highly reproducible relaxation behavior that was hardly dependent on the direction of temperature variation. Typical spectra are shown in Fig. 1. Two well-separated relaxation processes show up, a fast α relaxation and a slow process (II), which peak frequency is more than four decades lower.

For a quantitative analysis we fitted the loss spectra by two Havriliak–Negami functions (HN) according to

$$\varepsilon'' = - \sum_{k=1}^2 \text{Im} \left\{ \frac{\Delta \varepsilon_k}{(1 + (i\omega\tau_k)^{a_k})^{b_k}} \right\}, \quad (1)$$

where $\Delta \varepsilon_k$ and τ_k denote the relaxation strength and the mean relaxation time of the k th process. The two peak shape parameters a_k and b_k , which determine the slope of the low frequency tail $m=a$ and the high frequency tail $n(-ab)$, depend on the underlying distribution in relaxation times.

FIG. 1. Dielectric loss spectra of $\text{AlPO}_4\text{-5/pNA}$ (with 1% *p*NA) measured for eight different temperatures during cooling from 195 °C. Inset: The same spectra normalized to peak frequency f_{peak} and peak maximum $\varepsilon''_{\text{peak}}$ (master plot).

The peak relaxation frequencies of both relaxation processes versus the inverse temperature are shown in Fig. 2.

The most striking result is the behavior of f_α [or $\tau_\alpha = (2\pi f_\alpha)^{-1}$], which temperature dependence at high temperatures ($75^\circ\text{C} < T < 160^\circ\text{C}$) can be described quite well by a Vogel–Fulcher–Tammann (VFT) equation (2) with the parameters $\log(\tau_\infty)[s] = -5.8$, $E_V = 3.4$ kJ/mol and $T_V = 296$ K

$$\tau(T) = \tau_\infty \exp \left[\frac{E_V}{R(T - T_V)} \right]. \quad (2)$$

Such a VFT behavior is typical for a dynamic glass transition and indicates cooperative rearrangements of the participating (*p*NA) molecules on a temperature dependent, cooperativity length scale $\xi(T)$. At $T \sim 72^\circ\text{C}$ the relaxation time τ_α departs markedly from the VFT law, indicating a change in the cooperative dynamics, which usually defines the glass transition temperature T_g . This temperature coincides with the maximum in the apparent activation energy

FIG. 2. Activation plot of the peak relaxation frequency f_{peak} for $\text{AlPO}_4\text{-5/pNA}$ vs $1/\text{temperature}$. In the case of process II a symmetric relaxation function ($0 < a < 1$, $b = 1$) was at high temperatures assumed (closed triangles). The low-temperature fits (open triangles) were performed using fixed values for $\Delta \varepsilon_2$ and a_2 .

FIG. 3. Schematic drawing of ensembles of *p*NA molecules in the pores of AlPO₄-5. This only gives an “artistic” view, the size and shape of the clusters are arbitrarily chosen.

which can be derived directly from the dielectric constant $\epsilon''(f, T)$ by an activation energy fine structure analysis.^{17,18} Further lowering of the temperature reveals a clear Arrhenius-like behavior of τ_α which can be studied conveniently, since the relaxation rate at T_g is unusually high ($f_{T_g} = 24$ Hz). The Arrhenius parameters of the α relaxation as well as those of process II are given in Fig. 2.¹⁹

The observation of a glass transition in one-dimensional molecular chains of *p*NA is not self-evident. Recently, Huwe *et al.*^{7,8} studied the relaxational behavior of ethylene glycol (EG) confined to zeolitic host systems with different pore sizes. These authors found that already in ensembles of at least 6 EG molecules cooperative (liquidlike) dynamics exists as manifested by a VFT behavior of the relaxation time. By contrast, zeolitic hosts with smaller pores or cages, resulting in arrangements of EG molecules with a lower average number of neighboring molecules (< 6), showed a drastically increased relaxation rate which followed an Arrhenius law.

In the case of AlPO₄-5/*p*NA the number of directly interacting neighbors is only 2, making the assumption unlikely that the adsorbed *p*NA molecules behave like simple glass-forming liquids. Another complication follows from statistical mechanics, which proposes that genuine one-dimensional systems of molecules having only short-range intrachain interactions are not able to undergo phase transitions of any kind.²⁰ However, Leike and Marlow²¹ have shown by model calculations that in particular *p*NA molecules adsorbed in the straight channels of AlPO₄-5 might undergo a first order phase transition when intra- and interchannel dipole-dipole interactions are considered.

Supposing that both *intrachannel* (H bonding, van der Waals and electrostatic forces) and *interchannel* interactions (only electrostatic interactions) contribute to the observed glass transition, one could speculate about the individual role of intra- and interchannel interactions, cf. Fig. 3. A first hint comes from the shape of the α -relaxation peak presented in Fig. 4. While the low frequency slope m was found to be around 0.5 regardless of the temperature, which possibly indicates the presence of a hidden weak additional relaxation process, we recognize a high frequency slope n close to unity for temperatures well above T_g . Such a high n value is typical for low molecular glass-forming liquids, whereas for polymer glasses generally an upper limit of 0.5 is found as is rationalized by the concept of damped intrachain conformational diffusion.²² In other words, *p*NA molecules do not show such a feature characteristic of macromolecular chains. Anyhow, the existence of a glass transition in AlPO₄-5/*p*NA

FIG. 4. The low and high frequency slopes m and n of the α -relaxation peak obtained by a HN fit. The full triangles refer to parameter n .

accompanied by a change in dynamics from VFT to Arrhenius-like implies the existence of a characteristic length scale that limits the correlation length. We think that the length of the molecular chains of the “condensed” *p*NA molecules provides such a geometric limit. Assuming that the correlation length will finally approach the size of the molecular ensemble, which is related to the length of *p*NA-chain sequences, the broadening of the α relaxation around and below T_g might reflect the actual length distribution of the *p*NA sequences. The idea that the cooperative dynamics of *p*NA molecules persists in the sub- T_g region is supported by the Arrhenius parameters themselves. Both the high activation energy ($E_a = 112$ kJ/mol) as well as the low preexponential factor ($\log(\tau_\infty)[s] = -19.3$) are in the range usually found for β processes in side-chain²³ or main-chain liquid crystalline polymers,²⁴ indicating the cooperative nature of such (Arrhenius-type) relaxations.²⁵ Further studies to confirm this relationship are in progress.

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¹⁶The low average degree of loading was caused by the presence of a large number of crystals not filled with *p*NA due to structural imperfections.

These unfilled crystals could not be removed from the “powder” sample, but they surely do not contribute to the dielectric response observed.

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