

Coupling of Caged Molecule Dynamics to JG β -Relaxation: Polymers II

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Abstract

At temperatures below the nominal glass transition temperature $T_{g\alpha}$, the structural α -relaxation and the Johari-Goldstein (JG) β -relaxation are too slow to contribute to susceptibility measured at frequencies higher than 1 GHz. This is particularly clear in the neighborhood of the secondary glass transition temperature $T_{g\beta}$, which can be obtained directly by positronium annihilation lifetime spectroscopy (PALS) and adiabatic calorimetry, or deduced from the temperature at which the JG β -relaxation time τ_β reaches 1000 s. The fast process at such high frequencies comes from the vibrations and caged molecules dynamics manifested as the nearly constant loss (NCL) in susceptibility measurements, elastic scattering intensity, $I(Q, T)$, or the mean-square-displacement, $\langle u^2(T) \rangle$, in quasielastic neutron scattering experiment. Remarkably we find for many different glass-formers that the NCL, I or $\langle u^2 \rangle$ measured in the glassy state change its temperature dependence at temperature T_{HF} near $T_{g\beta}$. In paper I [S. Capaccioli et al., *J.Phys. Chem. B* **2015**, *119* (28), pp 8800–8808] we have made known this property in the case of the polyalcohols and a pharmaceutical glass former, flufenamic acid studied by THz dielectric spectroscopy, and explained it by the coupling of the NCL to the JG β -relaxation, and the density dependence of these processes. In this paper II, we extend the consideration of the high frequency response to broader range from 100

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3 MHz to THz in the glassy state of many polymers observed by quasielastic light scattering,
4 Brillouin scattering, quasielastic neutron scattering, and GHz-THz dielectric relaxation. In all
5 cases, the NCL changes its T -dependence at some temperature, T_{HF} , below $T_{g\alpha}$, which is
6 approximately the same as $T_{g\beta}$. The latter is independently determined by either PALS,
7 adiabatic calorimetry, or low frequency dielectric and mechanical spectroscopy. The property,
8 $T_{HF} \approx T_{g\beta}$, had not been pointed out before by others and in any of the quasielastic neutron and
9 light scattering studies of various amorphous polymers and van der Waal small molecular
10 glass-formers over the past three decades. The generality and fundamental importance of this
11 novel property revitalize the data from these previous publications, making it necessary to be
12 reckoned with in any attempt to solve the glass transition problem. In our rationalization, the
13 property arises firstly from the fact that the JG β -relaxation and the caged dynamics both
14 depend on density and entropy. Secondly, the JG β -relaxation is the terminator of the caged
15 dynamics, and hence the two processes are inseparable or effectively coupled. Consequently
16 the occurrence of the secondary glass transition at $T_{g\beta}$ necessarily is accompanied by
17 corresponding change in the temperature dependence of either the NCL, I or $\langle u^2 \rangle$ of the fast
18 caged dynamics at $T_{HF} \approx T_{g\beta}$.

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1. Introduction

In the recent past, we and our collaborators as well as others have demonstrated the fundamental properties and role played by the secondary relaxation of a certain class in glass transition by experiments¹⁻¹³ and simulations.¹⁴ Such secondary relaxations have been called by us^{1,2,11-13,15-18} the Johari-Goldstein (JG) β -relaxation¹⁹⁻²¹ in order to distinguish them from the intramolecular secondary relaxations of no connection to the structural α -relaxation. At the same time the nomenclature serves to honor Johari and Goldstein for their important discovery of the existence of a secondary relaxation in a totally rigid molecular glassformer, which belongs to this important class. The JG β -relaxation like its precursor, the primitive relaxation of the Coupling Model^{1,2,7-13}, bears many strong connections with the slower structural α -relaxation, and therefore it is impossible to discuss the latter and the associated glass transition without considering the former. These connections *in toto* can be found in several reviews^{11,12}, and some in paper I²² of this series. Here we mention only few essential examples that are critical for this paper. First is the approximate co-invariance of frequency dispersion of the α -relaxation²³, and the separation of the JG β -relaxation from α -relaxation, measured by the ratio $\tau_{\alpha}(T,P)/\tau_{\text{JG}}(T,P)$, to variations of pressure P and T ,^{4,7-12} where $\tau_{\alpha}(T,P)$ and $\tau_{\text{JG}}(T,P)$ are their relaxation times. Second is that τ_{α} and τ_{JG} both are approximately functions of the same product variable ρ^{γ}/T where ρ is the density and γ is a material constant.^{12,13} The immediate implication from this property is not only the α -relaxation but also the JG β -relaxation depends on density and entropy (the conjugate variables to pressure and temperature). Moreover, since the JG β -relaxation is the precursor of the α -relaxation, causality implies that the ρ^{γ}/T -dependence originates from the JG β -relaxation, and it is passed

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3 on to the α -relaxation and becomes magnified because of the many-body cooperative nature
4 of the α -relaxation^{11-13,16,24,25}. The two connections in the above and in particular the ρ'/T -
5 dependence of the JG β -relaxation are sufficient for us to expect the existence of a secondary
6 glass transition at temperature T_β on cooling the glass below the primary glass transition
7 temperature T_g . At T_β and below the $\tau_{JG}(T)$ becomes too long for the JG β -relaxation to
8 equilibrate the structure, resulting in secondary vitrification and concomitant change of the
9 Arrhenius T -dependence of $\tau_{JG}(T)$ above T_β to a weaker one below it. The secondary glass
10 transition from the JG β -relaxation at T_β shows up experimentally in heat capacity
11 measurements by various techniques of calorimetry²⁶⁻³⁰, and in hole volume from positronium
12 annihilation spectroscopy.³¹⁻³³

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27 In paper I²² we addressed the dielectric losses $\epsilon''(\nu)$ at $\nu=0.6$ and 1 THz of glycerol,
28 threitol, xylitol, and sorbitol in the polyalcohols family, obtained by terahertz time-domain
29 spectroscopy³⁴. On heating the glasses, the dielectric losses, $\epsilon''(\nu)$ at $\nu=1$ THz, increase
30 monotonically with temperature but the temperature dependence changes at two temperatures,
31 first deep in the glassy state at a sub- T_g temperature, T_{HF} , and second at the nominal T_g or $T_{g\alpha}$
32 in the current paper. The change of $\epsilon''(\nu=1$ THz) at $T_{g\alpha}$ is not new and the same as that found
33 in susceptibility measurements by dynamic light scattering in the GHz regime³⁵⁻³⁹, and
34 neutron scattering⁴⁰⁻⁴⁷ with resolution ranging from 10 ps to 1 ns in many glass-formers. The
35 change of $\epsilon''(\nu=1$ THz) at $T_{HF}<T_{g\alpha}$ is novel and drew our attention to its origin. By plotting τ_α
36 and τ_{JG} from low frequency dielectric measurements against temperature of the four
37 polyalcohols, we obtained $T_{g\alpha}$ and $T_{g\beta}$ defined respectively as the temperatures at which
38 $\tau_\alpha(T_{g\alpha})=100$ s and $\tau_{JG}(T_{g\beta})=100$ s. The values of $T_{g\beta}/T_{g\alpha}$ compares very well with the value of
39 $T_{HF}/T_{g\alpha}$ for each of the four polyalcohols. The good correspondence found indicates that the
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change of $\varepsilon''(\nu=1 \text{ THz})$ at $T_{HF} < T_g$ is somehow related to the secondary glass transition at $T_{g\beta}$. Notwithstanding, at $T_{HF} \approx T_{g\beta}$ the value of $\tau_{JG}(T_{\beta LF})$ is about 100 s, which is more than 14 decades longer than the time corresponding to the probe frequency of 1 THz. Thus the JG β -relaxation itself is not directly observed by the terahertz time-domain spectroscopy. The $\varepsilon''(\nu=1 \text{ THz})$ measured comes from the response of the nearly constant loss (NCL) associated with the caged molecule dynamics at high frequencies that precede the JG β -relaxation. The caged dynamics is not a normal relaxation process^{2,11,16,17,24,25,40,48}. It has no characteristic time, and hence the loss is a power law, $\chi''(f) = A(T)f^c$ with $c \ll 1$ in the susceptibility spectrum, or the NCL. $A(T)$ has the weak temperature dependence of $A_{ref} \exp(T/T_{ref})$ for $T < T_{ref}$. The NCL persists until the cages are dissolved by the onset of the primitive relaxation of the Coupling Model (CM), a local relaxation of the entire molecule with primitive relaxation time τ_0 . The primitive relaxation is followed by the spatially and dynamically heterogeneous relaxation processes (collectively considered as the JG β -relaxation), which involves participations of increasing number of molecules with increase of time. Thus, $\tau_{JG}(T) \approx \tau_0(T)$ in order of magnitude, and the JG β -relaxation is spatially and dynamically heterogeneous as well as to some extent cooperative, consistent with results from experiments⁴⁹ and simulations.^{50,51} Observed by dielectric spectroscopy, the application of high electric field increases the loss from the JG β -relaxation, while there is no change of the NCL^{16,52}. After the JG β -relaxation finally come the terminal α -relaxation having the maximum length-scale and the Kohlrausch time dependence,

$$\phi(t) = \exp[-(t/\tau_\alpha)^{1-n}] \quad (1)$$

for its correlation function. In order of magnitude, the relaxation time, $\tau_{JG}(T) \approx \tau_0(T)$, is an upper bound or terminator of the NCL time regime, a prediction of the CM verified by

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3 experimental data and molecular dynamics simulations in many molecular
4 glassformers^{2,16,17,24,25}, and ionic conductors^{2,8,53-57}. In the case of an ionic liquid⁵⁷, the electric
5 modulus data show the termination of the NCL by the primitive ion relaxation analogous to
6 molecular liquids and glasses. It is from this relation between the NCL and the JG β -
7 relaxation that the change of T -dependence of $\tau_{JG}(T)$ at $T_{g\beta}$ is reflected by the corresponding
8 change of NCL observed as $\epsilon''(\nu=1 \text{ THz})$.
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10 The interpretation of the THz data in paper I is sufficiently general that it implies the
11 same features in the dynamics should be observed by other high frequency spectroscopy
12 including, GHz dielectric relaxation, quasielastic light scattering, Brillouin spectra, and
13 neutron scattering. Motivated by this possibility, we reexamine this wealth of experimental
14 data in the literature to look for sub- T_g change in susceptibility data from these high frequency
15 spectroscopies at T_{HF} . After finding it, we compared with the secondary glass transition
16 temperature, $T_{g\beta}$, independently obtained by positronium annihilation lifetime spectroscopy
17 (PALS), adiabatic calorimetry, or low frequency dielectric and mechanical measurements, to
18 see if it is the same as T_{HF} within experimental uncertainty. The results presented in the
19 following sections show in several glass-formers that $T_{HF} \approx T_{g\beta}$, verifying that the coupling of
20 the caged dynamics (NCL) to the JG β -relaxation is fundamental and general. This property
21 of the JG β -relaxation together with its well established property of its coupling with the α -
22 relaxation are indisputable evidences of the fundamental importance of the JG β -relaxation,
23 without which the evolution of dynamics from short times to terminal flow cannot be realized.
24 The data also bring out once more the idea that the dependence of molecular mobility on
25 density and entropy actually starts at the primitive relaxation/JG β -relaxation level. This
26 experimental fact refutes any theory that are based on the conventional view^{58,59} that only the
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3 dependence of the structural α -relaxation on density and entropy is needed to solve the glass
4 transition problem.
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8 In the following sections we introduce the collection of data, one polymer at a time.
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10 Although all data are taken from the published literature, the relation of the key feature of the
11 fast process to the primitive relaxation/JG β -relaxation has not been pointed out and its
12 significance made evident. With the new insights and impacts on research on glass transition
13 gained from this study, the values of the tremendous amount of experimental data published
14 by others are considerably enhanced.
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22 23 24 25 **2. Poly(methyl methacrylate)**

26 27 **(a) Dielectric Relaxation at 10GHz**

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29 A literature search led us to find that the nearly constant loss (NCL) has been found nearly
30 fifty years ago by Amrhein and Mueller⁶⁰ in dielectric relaxation studies of polymers
31 including poly(methyl methacrylate) (PMMA) and poly(vinylchloride) (PVC) at 10 GHz, and
32 even at lower frequencies from 1 to 100 kHz at temperatures low compared to T_g such as 100
33 K. The weak temperature and frequency dependences of $\tan\delta$ ($\equiv \epsilon''/\epsilon'$) data are well described
34 by AT^λ and f^c with $c \ll 1$. Called the dielectric background loss and interpreted as due to the
35 anharmonic coupling of the electric field to acoustic modes by Amrhein and Mueller, it is
36 exactly the NCL of cage dynamics. Since $\tan\delta$ has the power law temperature dependence
37 AT^λ , Amrhein and Mueller showed their data in plot of $\log(\tan\delta)$ vs. $\log T$. Their 10 GHz data
38 are reproduced in the inset of Fig.1 and a break at 244 K found by them is evident. The data
39 are re-plotted as $\tan\delta$ vs. T in the main part of Fig.1. A change to a stronger T -dependence of
40 $\tan\delta$ occurs at $T_{HF} = 246$ K. More recently direct observation of the NCL in PMMA and other
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3 polymers by dielectric spectroscopy at frequencies from 100 MHz to 20 GHz and at
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5 temperatures from 293 to 353 K were reported by Nozaki and coworkers⁶¹. Although
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7 temperature dependence of the NCL was not reported in any detail to find the crossover and
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9 determine $T_{\beta, HF}$, the relevant data helps to show the existence of the NCL up to 20 GHz.
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12 13 14 15 **(b) Quasielastic Light Scattering and Neutron Scattering**

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17 Duval, Mermet and collaborators^{37,38} studied the fast process in glassy PMMA by quasielastic
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19 light scattering and neutron scattering at time-scales of about 4×10^{-12} s and of the order of
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21 10^{-11} s respectively. PMMA specimen has number-averaged molecular weight of 58 000
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23 g/mol and the DSC T_g is about 390 K.
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27 Measured over temperatures from deep in the glassy state to the glass transition
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29 temperature, the intensity of quasielastic scattering, $I(\omega, T)$, increases monotonically with
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31 temperature. Shown in Fig.2 are the quasielastic light scattering (QELS) intensity data^{37,38} as a
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33 function of temperature. The lines are drawn to indicate there is a change of the intensity on
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35 crossing T_{HF} of about 240 K. It is important to note that this crossover in T -dependence at
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37 about 240 K had not been pointed out before. The $T_{HF}=240$ K from QELS is also in
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39 approximate agreement with $T_{HF}=246$ K determined from 10 GHz dielectric $\tan\delta$ in Fig.1 and
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41 $T_{HF}=243$ K in the inset. Positron annihilation lifetime spectroscopy (PALS) measurements, in
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43 the temperature range 110-480 K were made on a commercial-grade PMMA ($M_w = 280\ 000$
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45 g/mol) by Hristov et al.³³ From these measurements, a method was proposed by Hristov et al.
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47 to evaluate the hole volume in the amorphous polymer. The results given in terms of the hole
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49 volume fraction, ΔF_h , are shown as a function of temperature in Fig.2. Remarkably, there are
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51 good overall agreements in the temperature dependence of the QELS intensity and that of
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3 ΔF_h . More importantly, ΔF_h changes to a stronger temperature dependence on crossing a
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6 temperature, $T_{\beta,PALS}$, nearly the same as $T_{HF}=240$ K. Note that $T_{\beta,PALS}$ is a direct measure of
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8 $T_{g\beta}$, and thus we have $T_{g\beta}\approx T_{HF}$. Although this coincidence will be discussed collectively with
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10 other experimental data and glass-formers in the Discussion section, we hasten to remind the
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12 reader that in Paper I we have attributed the change at $T_{\beta,HF}$ to secondary glass transition at
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14 $T_{HF}\approx T_{g\beta}$ reflected on the NCL via its coupling to the JG β -relaxation. Therefore the fact that
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16 $T_{\beta,PALS}\approx T_{HF}$ is direct confirmation of the vitrification of the JG β -relaxation at these nearly
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21 same temperatures.

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23 In the neutron scattering experiment of PMMA^{37,38} performed on IN6 at ILL
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25 (Grenoble), the elastic peak intensity $S(Q;\omega=0;T)$ measured at different temperatures is
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27 normalized by $S(Q;\omega=0;0)$, the extrapolated values at $T=0$ K, $S(Q;\omega=0;0)$, and the results
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29 are plotted as a function of Q^2 . The ratio, $S(Q;\omega=0;T)/S(Q;\omega=0;0)$, is proportional to
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31 $\exp[-2W(Q,T)]$, where $W(Q,T)=Q^2\langle u^2(T)\rangle$ and $\langle u^2(T)\rangle$ is the mean square displacement
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33 (MSD). There is a linearly temperature-dependent contribution to the MSD from harmonic
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35 vibrations. Duval et al. subtracted this contribution from $\langle u^2(T)\rangle$, the difference $\Delta\langle u^2\rangle$ comes
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37 from the NCL of caged dynamics in our interpretation except at low temperatures where the
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39 contribution is from the rotational motion of the ester methyl group in PMMA⁶². In Fig. 3,
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41 $\Delta\langle u^2\rangle$ is plotted against temperature and compared with ΔF_h . The initial increase of $\Delta\langle u^2\rangle$ at
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43 low temperatures is due to the motion of the methyl group. Above ~ 100 K, again there is good
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45 agreement in the T -dependence of these two quantities. The change in T -dependence of $\Delta\langle u^2\rangle$
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47 is at T_{HF} approximately equal to 240 K and practically same as $T_{HF}=246$ K from QELS, and
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49 $T_{\beta,PALS}$. Our identification of the fast dynamics seen in the glassy state of PMMA in QENS
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51 and QELS experiments as NCL has support from the direct observation of NCL in high
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3 frequency dielectric measurements in the range from 100 MHz to 20 GHz, and at
4 temperatures from 293 to 353 K all below T_g of PMMA⁶¹. The light scattering experiment
5 also found the NCL in the susceptibility spectrum of PMMA at 350 K in the GHz range³⁶, and
6 in polyisobutylene (PIB) at temperatures 40 K below $T_{g\alpha}$.^{35,36}
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13 Although justified by Hristov et al.³³, the use of ΔF_h to represent hole volume is model
14 dependent. However, the important deduction of crossover of its T -dependence at $T_{\beta,PALS}$ can
15 be checked against the PALS data using more conventional approach by considering the
16 variations of the o-Ps lifetime, τ_3 , in PMMA with temperature. The PALS data of Wang et
17 al.³¹ and Qi et al.³² are presented in Fig. 4. The glass transition temperature $T_{g\alpha}$ and the
18 secondary transition temperature $T_{\beta,PALS}$ determined from the average o-Ps lifetime τ_3 versus
19 temperature are respectively at 355 ± 18 K and 251 ± 28 K³¹ or slightly below it³², in agreement
20 with that deduced from ΔF_h in Fig.3.
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35 ***(c) Brillouin Scattering and Light scattering***

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37 Caliskan et al.³⁹ studied the high frequency dynamics of PMMA using Brillouin scattering at
38 the Brillouin frequency, $\nu_{Br}=17$ GHz, and light scattering from 0.5 to 10^4 GHz. The light
39 scattering data taken at 350 and 200 K show directly the presence of the NCL in some
40 frequency range above 0.5 GHz, ensuring the observation of caged dynamics. From the full-
41 width at half-maximum of the Brillouin peak, Γ , the acoustic attenuation is given in terms of
42 the internal friction factor, $Q^{-1}=\Gamma/\nu_{Br}$, where ν_{Br} is the Brillouin frequency 17 GHz. The
43 temperature dependence of $Q^{-1}(T)$ at $\nu_{Br}=17$ GHz is reproduced in Fig.5 together with the
44 quasielastic light scattering intensity at 17 GHz at four temperatures. The two red lines are
45 drawn to indicate possible change of temperature dependence of both sets of data at $T_{HF}\approx 240$
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3 K, as found by Duval et al.³⁷ by QELS and QENS. This possible change of T -dependence was
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5 not noticed before, and certainly no connection to secondary glass transition was made in
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7 Ref.[39].
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10 11 *(d) $T_{g\beta}$ from Low Frequency Dielectric Spectroscopy*

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14 The secondary relaxation of PMMA observed by dielectric relaxation with large dielectric
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16 strength involves not only a 180° flip of the $-\text{O}-(\text{C}=\text{O})$ -plane of the side group between two
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18 potential energy minima but also the rocking motion of the part of the repeat unit on the main
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20 chain, the amplitude of which increases with temperature.^{63,64} This mechanism actually was
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22 first proposed by Yee and Takemori⁶⁵ from their dynamic bulk relaxation measurements. The
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24 temperature and frequency effects they found indicate that the β -relaxation in PMMA is not a
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26 purely internal motion but is coupled to the bulk. This property of the β -relaxation indicates
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28 its connection to the α -relaxation, and hence it is the JG β -relaxation according to one of the
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30 criteria proposed in literature.¹⁵ Several broadband dielectric relaxation measurements of high
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32 molecular weight PMMA have been published in the literature. However, it is known⁶⁶ that
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34 asymmetric vinylidene polymers like PMMA exhibit large variations in their stereo-regularity
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36 or tacticity. Commercial PMMA has a syndiotactic pair content of about 75%. From 50% to
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38 100% syndiotacticity, the T_g increase is slightly more than 10°C. The tacticity of the samples
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40 used in the QELS and QENS studies, as well as the PALS study by Wang et al.³¹ and Qi et
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42 al.³² have not been specified. Only Hristov et al.³³ mentioned their sample is commercial
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44 grade PMMA, and accordingly we choose the dielectric measurement of syndiotactic PMMA
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46 of Bergman et al.⁶⁷, and not the atactic PMMA data of Jin et al.⁶⁸. The α - and JG β -relaxation
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48 times, τ_α and τ_β , had been determined by these authors. By extrapolating the Arrhenius T -
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50 dependence of τ_β to 100 and 1000 s, the corresponding dielectric secondary glass transition
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3 temperatures $T_{g\beta}$ are 248 and 235 K respectively. These values of $T_{g\beta}$ determined by dielectric
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6 measurements are consistent with the values of $T_{\beta,PALS}=251\pm 28$ K from PALS
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9 measurements³¹. Either the dielectric or the PALS value of $T_{g\beta}$ is consistent with the broad
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11 crossover at $T_{HF}\approx 246$ K detected by the high frequency dielectric $\tan\delta$ data at $\nu=10$ GHz, and
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13 by the QELS, and QENS measurements. Thus the observed changes of temperature
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15 dependence of the dielectric $\tan\delta$ at 10 GHz, the QELS intensity, and the $\Delta\langle u^2 \rangle$ from QENS
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17 at T_{HF} are related to the secondary glass transition at $T_{g\beta}$.
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21 Note that at $T_{g\beta}=248$ or 235 K, τ_{β} is more than ten orders of magnitude longer the time-
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23 scales of these high frequency measurements, and it is inconceivable that the JG β -relaxation
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25 is directly probed at such high frequencies. Actually the depolarized light scattering
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27 susceptibility spectra of PMMA obtained by Caliskan et al.³⁹ show that the NCL was
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29 observed at frequencies from above 0.5 GHz to 15 GHz at 350 K and at 200 K below $T_{g\alpha}$. The
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31 same was found in polyisobutylene^{25,35,36} over a much broader range of temperatures below
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33 $T_{g\alpha}$, and in the polyalcohols in Paper I. Hence there is no doubt that the process actually
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35 probed at high frequencies is the NCL of caged dynamics. The sensitivity of the NCL to the
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37 secondary glass transition is caused by the connection of the NCL to the JG β -relaxation,
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39 coming from the fact that the caged dynamics regime is terminated by the primitive/JG β -
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41 relaxation. Furthermore, the size of the cage depends on density, and the change of
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43 temperature dependence of density at the secondary glass transition is naturally reflected in
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45 the same way by the NCL.
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3 The experimental methods applied to PMMA and revisited in Section 2 are remarkably
4 varied. Several high frequency techniques have been employed to measure the NCL of caged
5 dynamics and to observe the crossover in temperature dependence of the NCL at T_{HF} deep in
6 the glass state. The hole volume fraction measured by PALS also exhibits a crossover in T -
7 dependence at $T_{\beta,PALS}$, which indicates occurrence of the JG β -relaxation glass transition at
8 this temperature. Low frequency dielectric measurements of the JG β -relaxation times τ_{β} also
9 enable the dielectric secondary glass transition temperature $T_{g\beta}$ to be determined.

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There are high and low frequency measurements in other glass-formers like those
considered for PMMA. However, in some cases the samples of the glass-former have
significantly different tacticity and the values of T_{HF} , $T_{\beta,PALS}$, and $T_{g\beta}$ cannot be exactly the
same. In other cases, not all high and low frequency measurements are available, and not all
the main points can be verified. Nevertheless, the data of these other glass-formers presented
in the subsections below support the results established in the case of PMMA.

(A) Polystyrene

The most complete QENS data measurements of atactic polystyrene (PS) fully hydrogenated
and partially deuterated had been made by Frick et al.⁴¹ on the backscattering spectrometers
IN10 and IN13 at the ILL, Grenoble. The energy resolutions are about 1 μeV for IN10, and 8
 μeV for IN13. The samples were measured at different momentum transfers. The data of the
normalized elastic scattering intensity $I_{el}(Q,T)$ on IN10 or IN13 plotted logarithmically
against temperature show linear temperature dependence at lower temperature but for
momentum transfers larger than $Q=0.8 \text{ \AA}^{-1}$, slight deviations from a linear temperature
dependence were already observed at temperatures as low as $T=200 \text{ K}$ in the sample PS-d5

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3 which has the phenyl group deuterated. The fast process, observed far below $T_{g\alpha} = 375$ K
4 and with time scale of neutron scattering measurements, is interpreted here as caged molecule
5 dynamics. The change in its T -dependence at $T_{HF} = 200$ K is due to coupling of caged
6 dynamics to JG β -relaxation, consistent with the interpretation of QENS data of PMMA given
7 before. The elastic scattering data of the protonated atactic polystyrene, PS-h8, are similar to
8 the results for PS-d5. Again, the logarithm of the elastic scattering intensity shows deviations
9 from a linear temperature starting in the region around $T=150-200$ K. The deviations from a
10 linear temperature decrease are more pronounced in PS-h8 than for PS-d5. This was taken as
11 indication that the phenyl ring is involved in this fast process with the onset at in the range
12 from 150 to 200 K from the data of Frick et al.⁴¹.

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27 An independent QENS study of atactic PS was made by Kanaya and coworkers⁴²⁻
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44 using two spectrometers with different energy resolutions of 25 μeV and 0.80 μeV
comparable to IN13 and IN10 respectively. We are interested in their MSD data of bulk PS in
Ref.[42]. Reproduced as Fig.6, the $\langle u^2 \rangle$ of bulk PS shows a change of T -dependence at T_{HF}
slightly above 200 K. The elastic scattering intensity $I_{el}(Q, T)$ collected at $Q=1.64 \text{ \AA}^{-1}$ and at
20 μeV resolution were reported in another publications^{43,44}. Plotting $I_{el}(Q, T)$ logarithmically
against temperature, $\log I_{el}(Q, T)$ starts to deviate from linear dependence starting at about 200
K, consistent with the results of Frick et al.⁴¹

The presence of the NCL of PS in the QENS measurements is assured by the high
frequency dielectric measurements from 100 MHz to 20 GHz and at temperatures below $T_{g\alpha}$
from 293 to 353 K.⁶¹ Temperature dependence of the NCL was not reported for us to find the
change and determine T_{HF} . Since 20 GHz corresponds to a timescale of 10^{-10} s, the high
frequency dielectric measurement overlaps with the time scales of IN10 used in the neutron

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3 scattering experiments, which supports our interpretation that elastic scattering intensity as
4 well as $\langle u^2 \rangle$ from neutron scattering is contributed by the NCL of caged dynamics.
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8 Electron paramagnetic resonance studies of small paramagnetic molecules (spin probe)
9 in glassy polystyrene at Larmor frequencies of the order of a few hundred GHz have found
10 fast dynamics in glassy high molecular weight polystyrene⁶⁹⁻⁷¹. The evidence was deduced
11 from the reorientation of the spin probe which exhibit different dynamic regimes in two
12 different temperature regimes separated by a crossover region^{69,70}. Below 180 K the rotational
13 times are nearly temperature independent with no apparent distribution. In the temperature
14 range of 180-220 K a large increase of the rotational mobility is observed accompanied by the
15 broadening of the distribution of correlation times. The increase of the rotational mobility of
16 the spin probe at 180 K is ascribed to the onset of the fast dynamics detected by neutron
17 scattering in the range from 180 to 200 K by neutron scattering^{41,42} (see for example Fig.7).
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19 Furthermore, another EPR study also found that the oriented spin probes in PS lose their
20 alignment above 200 K.⁷¹ The spin probe used in refs.[69] and [70] is 2,2,6,6-tetramethyl-1-
21 piperidinyloxy (TEMPO) similar in structure to the phenyl group of PS, but smaller in size
22 compared to the repeat unit of PS. Nevertheless, the motion of TEMPO will likely be
23 restricted by the caged repeat units of PS in the glassy state at time-scale of the order of 10^{-12} s
24 corresponding to 200 GHz of the EPR experiments. Therefore the change of dynamics of
25 TEMPO exhibited on crossing 180-200 K reflects to some extent the change of NCL from
26 caged repeat units of PS, corroborating the neutron scattering observations.
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30 To further support our interpretation of the change of temperature dependence of either
31 the elastic scattering intensity or $\langle u^2 \rangle$ at T_{HF} more than 170 K below T_g , the JG β -relaxation
32 times of PS in the glassy state is needed to show its secondary glass transition occurs near
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3 $T_{\beta, HF}$ in the neighborhood of 180-200 K. Despite PS being perhaps the most studied polymer,
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6 the JG β -relaxation has not been identified in the glassy state⁷²⁻⁷⁷. The microwave power
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8 saturation method also was able to determine a β -relaxation glass transition temperature T_{β} .⁷⁸
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10 However, for the quenched PS, the value of $T_{\beta}=319$ K is much higher than T_{HF} . Another
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12 support can come from PALS study if the secondary relaxation at around 200 K were detected
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14 directly. Unfortunately we cannot find PALS data of PS at low temperatures⁷⁹ in the literature
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16 showing this, possibly due to the unusually weak relaxation strength of the JG β -relaxation.
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18 Dielectric relaxation⁷⁶ measurements of PS have found a secondary relaxation called β^* . Its
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20 relaxation frequency f_{β^*} has activation energy $E_A=68.5$ kJ/mol and the pre-exponential factor
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22 1.58×10^{13} Hz. The JG β -relaxation of PS has eluded identification by dielectric spectroscopy,
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24 and it is not certain if the β^* -relaxation is the JG β -relaxation or its shadow. Nevertheless, by
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26 extrapolating the Arrhenius T-dependence of the β^* -relaxation time τ_{β^*} to lower temperatures,
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28 the β^* glass transition temperature $T_{g\beta^*}$ is determined. Its value of 212 K is remarkably close
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30 to T_{HF} from QENS. This coincidence suggests the NCL observed by QENS in the glassy state
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32 of PS is coupled to the JG β -relaxation, lying close to the β^* -relaxation and not resolved,
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34 probably being obscured by the latter. Evidence of the existence of the JG β -relaxation in PS
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36 comes from the application of several NMR techniques⁸⁰ whereby its relaxation times were
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38 determined only above $T_{g\alpha}$. The secondary relaxation from NMR turned out to be less than
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40 one order of magnitude slower than the β^* -relaxation at 385 K. This close relation supports
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42 the possibility that indeed the JG β -relaxation in PS is obscured by the β^* -relaxation.
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53 The best evidence of the secondary glass transition attributable to the JG β -relaxation of
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55 PS comes from the other NMR study of the dynamics of the phenyl rings in glassy PS^{81,82}.
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3 The motion involves complex 180° flips and librational motions with relaxation times
4 covering several decades⁸³. These properties resemble JG β -relaxation in the glassy state, and
5 thus the dynamics of the phenyl rings in glassy PS observed⁸¹⁻⁸³ likely reflects the JG β -
6 relaxation, particularly because the phenyl ring is attached to the main chain in PS. Moreover,
7 the 180° flips of the phenyl rings become frozen at about 190 K.^{84,85} This result from NMR
8 study is equivalent to finding the secondary glass transition at $T_{g\beta}=190$ K that originates from
9 the JG β -relaxation of PS. This $T_{g\beta}=190$ K from NMR is nearly the same as T_{HF} determined
10 from neutron scattering data and deduced from the dynamics of spin probes in EPR studies.
11 The near coincidence supports our interpretation that the fast dynamics of PS observed by
12 high frequency probes is caged dynamics, and the change of temperature dependence at T_{HF}
13 is connected to the secondary glass transition at $T_{g\beta}$.

32 **(B) Poly(vinylchloride)**

34 Dielectric relaxation measurements of poly(vinylchloride) (PVC) at the high frequency of 10
35 GHz by Amrhein and Mueller⁶⁰ found a change of the T -dependence of $\tan(\delta)$ deep in the
36 glassy state at $T_{HF}=177.6$ K in addition to another change at $T_{g\alpha}\approx 350$ K. The experimental
37 data are shown in Fig.7. The inset shows the data in a log-log plot as done in the original
38 article. We supplement this by the semi-log plot of the same data. In both representations, the
39 two changes are evident. To check if the change at sub- $T_{g\alpha}$ is related to the secondary glass
40 transition, we employ the published dielectric relaxation data of PVC⁴⁵. By extrapolating the
41 Arrhenius T -dependence of the JG β -relaxation time τ_β to reach long times of 100 and 1000 s,
42 the secondary glass temperature $T_{g\beta}$ is estimated to be 170 and 165 K respectively. The
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3 approximate agreement between T_{HF} and $T_{g\beta}$ is indication that the change of T -dependence of
4 NCL probed at 10 GHz at T_{HF} is responding to the vitrification of the JG β -relaxation at $T_{g\beta}$.
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8 The NCL in PVC at frequencies from 100 MHz to 20 GHz and at temperatures from
9 293 to 353 K had been directly observed Nozaki and coworkers in their dielectric study⁶¹. The
10 dielectric $\tan(\delta)$ of the PVC at three temperatures in the glassy state, 293, 323, and 353 K has
11 the weak temperature dependence at any frequency, characteristic of the NCL. These 20 GHz
12 dielectric data of PVC verify that that fast dynamics observed in PVC by incoherent neutron
13 scattering are the caged molecule dynamics.
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22 Incoherent neutron scattering measurements were performed by Soles and coworkers⁸⁶
23 on bulk PVC with $M_w=233$ kg/mol, using high flux backscattering spectrometer (HFBS) at
24 NIST. The mean square displacements $\langle u^2(T) \rangle$ were determined from the plots of elastic
25 scattering intensity $I_{el}(Q, T)$ against Q^2 . With emphasis on the data in the glassy state, the
26 results are shown in Fig.8, where a change of T -dependence of $\langle u^2(T) \rangle$ at $T_{HF} \approx 170$ K is
27 suggested by the two lines. This value of T_{HF} from neutron scattering is consistent with that
28 from dielectric $\tan\delta$ at 10 GHz by Amrhein and Mueller⁶⁰, and in agreement with secondary
29 glass transition temperature $T_{g\beta}$ estimated to lie between 170 and 165 K. Furthermore, the
30 direct observation of NCL in dielectric measurements at 10 GHz supports that the NCL is
31 identifiable with the fast dynamics detected in the glassy state of PVC by incoherent neutron
32 scattering experiment.⁸⁶
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51 **(C) 1,4 Polybutadiene**

52 1,4-(cis/trans/vinyl)-polybutadiene, $(\text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2)_n$, has no side groups. The
53 specific microstructure, $x\%$ *cis*, $y\%$ *trans* and $(1-x-y)\%$ vinyl, varies from sample to sample.
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3 In the investigation of high frequency dynamics of 1,4 PBD by QENS using IN10 with energy
4 resolution of 14 μeV by Frick et al.⁴⁶, the microstructure is 47% *cis*, 46% *trans* and 7% vinyl,
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6 and the DSC $T_{g\alpha}$ is 185 K. The elastic scattering intensity, $I_{el}(Q)$, was obtained for fixed
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8 window scans performed on IN10 for several momentum transfers Q . The plot of $I_{el}(Q)$
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10 against T shows deviation from the seemingly linear dependence at lower temperatures
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12 starting somewhere within the range from 120 to 130 K, which we take as T_{HF} .
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18 On the other hand, Kanaya et al.⁴⁷ studied also by QENS a sample with 95.7% *cis*, 2.0%
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20 *trans*, and 2.3% vinyl, and the DSC $T_{g\alpha}$ is at 170 K. The energy resolution evaluated from the
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22 full width of the elastic peak is 0.2 meV. The data of $\langle u^2 \rangle$ from the two QENS measurements
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24 had not been obtained on sufficiently number of temperatures below $T_{g\alpha}$ to clearly identify
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26 change of T -dependence at the secondary glass transition temperature. The presence of the
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28 fast process, which is the NCL of caged dynamics in our interpretation, is present in the sub-
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30 T_g region. This property is shown better by the elastic scattering intensity $I_{el}(Q)$, obtained by
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32 integrating the dynamic scattering within the energy resolution. Plotting $\log(I_{el}(Q))$ as a
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34 function of temperature T for several Q values, the quantity is linearly proportional to T in the
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36 low temperature range below ~ 120 K.⁴⁷ There is rapid decrease of $I_{el}(Q)$ with increasing
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38 temperature above ~ 120 K. In parallel to the deviation of $\langle u^2 \rangle$ from the linear temperature
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40 dependence starting at $T_{HF} \sim 120$ to 130 K. These changes come from the fast caged dynamics
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42 in the glassy state. The $\langle u^2 \rangle$ reported by Frick et al.⁴⁶ shows the same behavior.
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49 Existence of the secondary glass transition in 1,4 polybutadiene is assured by the
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51 change of T -dependence of τ_3 in PALS measurement of at $T_{g\beta} \sim 109$ K.⁸⁷ The composition of
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53 the sample studied has 52% *cis*-, 41% *trans*- and 7% vinyl, and the $T_{g\alpha}$ from DSC is 173 K.
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55 Low frequency dielectric relaxation measurements⁸⁷ provide the Arrhenius T -dependence of
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3 $\tau_{\beta}(T)$ in the glassy state. By extrapolating this Arrhenius dependence to lower temperature, the
4 dielectric $T_{g\beta}$ determined by the condition, $\tau_{\beta}(T_{g\beta})=1000$ s, is about 106 K nearly the same that
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6 from PALS. Thus the existence of the secondary glass transition is ascertained, and the values
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8 of $T_{g\beta}$ determined by two techniques are consistent. This PALS and dielectric value of $T_{g\beta}$
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10 ~ 106 -109 K of this sample is 11 to 24 degrees below $T_{HF} \sim 120$ to 130 K from the high
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12 frequency QENS studies of Frick et al and Kanaya et al. This difference is likely due to the
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14 different microstructure of this sample from those investigated by QENS.
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21 Fortunately, also published is the PALS study⁸⁸ of the *same* cis-PBD sample
22 investigated by QENS⁴⁷. The data of the relative intensity, I_3 , of o-Ps exhibit onset of a
23 decrease at $T_{g\beta} \sim 120$ K.⁸⁸ This property of I_3 was explained by part of the holes excluded for
24 o-Ps localization due to some local motion, which is identified here with the NCL observed
25 by QENS on the same sample.
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35 **(D) BPA-Polycarbonate**

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37 Soles and coworkers⁸⁹ performed incoherent elastic neutron scattering measurements of bulk
38 and thin films of polycarbonate of bisphenol A (BPA-PC) with $M_w=36.3$ kg/mol. The
39 calorimetric glass transition temperature $T_{g\alpha}$ of the bulk PC is 423 K. We are interested in the
40 data on bulk PC with better quality than the supported thin films. The elastic scattering
41 intensities are normalized by their 40 K values, thereby setting the mean square displacement
42 $\langle u^2 \rangle$ equal to 0 at 40 K. The energy resolution of spectrometer is 0.8 μ eV, which implies that
43 dynamics with time scale longer than approximately a nanosecond are considered static and
44 not observed. The data of $\langle u^2 \rangle$ supplied digitally by Soles are plotted against temperature in
45 Fig.9. The strong increase in the slope of $\langle u^2 \rangle$ observed at $T_{g\alpha}$ at 423 K is that usually found
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3 in all glass-formers.⁴⁰ In the glassy state also present is another change in the temperature
4 dependence of $\langle u^2 \rangle$ at $T_{HF} \approx 190$ K, as suggested by the intersection of the two dashed lines.
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6 The value of $T_{HF} \approx 190$ K we determine from Soles and coworkers⁸⁹ is in remarkably good
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8 agreement with an earlier determination of T_{HF} by Colmenero and Arbe⁹⁰ (denoted by T_f in
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10 this reference) from the temperature dependence of the elastic intensity measured on BPA-PC
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12 at $Q=1.83 \text{ \AA}^{-1}$ using IN16. In this paper⁹⁰, the fast dynamics in the glassy state of BPA-PC and
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14 other amorphous polymers is attributed to the short-time regime (i.e. $t < t_c$ where $t_c \approx 1$ to 2 ps)
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16 of the segmental α -relaxation. The latter was found experimentally in several polymers⁴⁵ and
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18 had been identified^{45,90} with the primitive relaxation of the Coupling Model^{1,2,11}. It has the
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20 time dependence, $\exp(-t/\tau_D)$, for the relaxation part of the intermediate scattering function
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22 at times shorter than t_c . Argument was given in ref.[90] that T_f can be defined as the
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24 temperature at which $1 - \exp[-\frac{t}{\tau_D(T_f)}]$ is equal to ξ , a value that can be detected by a time of
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26 flight (TOF) instrument. The result is eq.(5) in ref.[90], but it had not been used to deduce
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28 quantitatively the value of T_f for any polymer. The fast dynamics in the glassy state of
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30 proposed by the authors of ref.[90] is obviously different from the caged molecules dynamics
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32 by us. Moreover, while we link T_{HF} to the secondary glass transition temperature $T_{g\beta}$, which
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34 can be independently determined, the value of T_f in ref.[90] has not been identified as such for
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36 any polymer. Notwithstanding, presented in ref.[90] is the fast dynamics in the glassy state of
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38 BPA-PC detected by energy-resolved elastic neutron scattering experiments using the
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40 backscattering neutron spectrometer IN16 at the ILL with energy resolution $\sim 0.5 \text{ \mu eV}$
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42 (HWHM). The temperature dependence of the elastic intensity at $Q=1.83 \text{ \AA}^{-1}$ reproduced as
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44 Fig.S1 in Supplementary Information shows the onset of fast dynamics at T_f or $T_{HF}=193$ K, in
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3 good agreement with what we found in Fig.9 from the neutron scattering data of Soles and
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5 coworkers.
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8 The JG β -relaxation of BPA-PC is not easy to observe by dielectric and mechanical
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10 spectroscopy due to the presence of a prominent γ -relaxation^{91,92}, which is very fast and
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12 dominates the high frequency response. Its relaxation time at $T_{g\alpha}$ is too short to be considered
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14 as the JG β -relaxation. To resolve the JG β -relaxation, the special technique of thermally
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16 stimulated depolarization currents (TSDC) was used by Laredo et al.⁹³. The TSDC spectrum
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18 of amorphous BPA-PC presented in the inset of Fig.9 resolves two peaks. The more intense
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20 low frequency peak is the γ -relaxation, while the high frequency shoulder is the JG β -
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22 relaxation we are looking for. The results from Laredo et al. are consistent with the earlier
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24 TSDC measurements by Sauer et al.⁹⁴. The time-scale of TSDC measurement was not
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26 specified in the paper by Laredo et al. but is of the order of about 100 to 1000 s in the
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28 experiment of Sauer et al. Thus, the temperature where the shoulder in the inset of Fig.9 is
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30 located can be taken as an estimate of $T_{g\beta}$, the secondary glass transition temperature.
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32 Indicated by the arrow in the inset, $T_{g\beta} \approx 190$ K is close to T_{HF} , the crossover temperature of
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34 the T -dependence of $\langle u^2 \rangle$.
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37 PALS data of BPA-PC (MW = 3.2×10^4 g/mol and $T_{g\alpha} = 423$ K) were presented by
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39 Kristiak et al.⁹⁵ and Xie et al.⁹⁶ over the range of temperatures from 50 to 310 K. Novikov et
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41 al.⁹⁷ have compared the PALS data with the intensity, $g(T)$, of the fast relaxation process seen
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43 by quasielastic light scattering (QELS) in the frequency interval 100–1000 GHz is measured
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45 in some polymers including BPA-PC. The PALS data expressed as the fractional free volume,
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47 V_f/V by Novikov et al.⁹⁷ are compared with $g(T)$ and reproduced here in Fig.10. There are
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49 significant uncertainties in the data of the lifetime τ_3 and the relative intensity I_3 of o-Ps
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3 measured in the lower temperature regime and reflected in V_f/V . In spite of the uncertainties,
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5 the data are consistent with a possible change of temperature dependence of V_f/V at about 180
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7 to 190 K, which may be considered as the value of $T_{g\beta}$ of the secondary glass transition. On
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9 the other hand, derived from the model based on the damping of the boson peak vibrations by
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11 the dynamic hole volume fluctuations by Novikov et al., $g(T)$ is proportional to the fractional
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13 dynamic hole volume. This result from the model analysis of the QELS data seems to be
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15 verified for BPA-PC in Fig.10 and other polymers⁹⁷. The temperature dependence of $g(T)$
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17 supports better a change at 180 – 190 K in the figure. Thus, from the proportionality between
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19 $g(T)$ and fractional hole volume, we have another evidence that $T_{g\beta} \approx 180 - 190$ K in BPA-PC
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21 in agreement with T_{HF} from neutron scattering^{89,90}.
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30 **(E) Poly(vinylpyrrolidone)**

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32 Differential scanning calorimetry (DSC) measurements of pure poly(vinylpyrrolidone) by
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34 Karabanova et al.⁹⁸ have found two thermal transitions. The upper transition at 149°C or 422
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36 K is the nominal glass transition temperature, $T_{g\alpha}$, commonly reported in the literature, The
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38 lower one was observed at about 43°C or 316 K, and can be identified with the secondary
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40 glass transition at $T_{g\beta}$. Complex mechanical modulus E^* at 1 Hz also find a loss peak at about
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42 50 C or 323 K, confirming that this secondary relaxation is present and responsible for the
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44 thermal transition at 316 K. This secondary relaxation was also found by dielectric relaxation
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46 measurements⁹⁹ of dry PVP but was called the γ -relaxation. Likely motion of the pyrrolidone
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48 rings attached to the main chain of PVP is involved in the γ -relaxation. The dispersion of the
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50 γ -relaxation is extremely broad, and the dielectric loss peak is very flat. Actually in the glassy
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52 state, the high frequency flank of the γ -relaxation loss peak has frequency dependence $\varepsilon''(f) \propto$
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3 f^c with $c \approx 0.16$, which is effectively the NCL. This is evidence of the γ -relaxation acting as the
4 terminator of the NCL, and hence^{2,16} is identified as the JG β -relaxation of PVP.
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8 Above $T_{g\alpha}$, the γ -relaxation merges with the slower relaxation and d.c. conductivity⁹⁹.
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10 Nevertheless, some of the γ -relaxation times τ_γ were obtained in ref.[99] by fits at
11 temperatures above $T_{g\alpha}$. The data of τ_γ below and above $T_{g\alpha}$ were combined in fitting to a
12 single Arrhenius dependence with prefactor and activation energy equal to of 0.013 ps and
13 0.85 eV respectively. The results are shown in Fig.11 here. Since secondary relaxation time
14 usually change from Arrhenius T -dependence below $T_{g\alpha}$ to a stronger one above it, therefore
15 one must bear in mind of some uncertainty of τ_γ determined by extrapolating the Arrhenius fit
16 from ref.[99] to longer times of 100 or 1000 s as done here in Fig.11.
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28 Quasielastic neutron scattering have been performed on poly(vinylpyrrolidone) on
29 IN16.¹⁰⁰ The mean square displacements $\langle u^2 \rangle$ determined are reproduced in Fig.11. Like the
30 other polymers shown in previous subsections, $\langle u^2 \rangle$ changes to a stronger temperature
31 dependence near the secondary glass transition temperature $T_{g\beta} = 316$ K (location indicated by
32 the arrow) determined by Karabanova et al.⁹⁸ using DSC. The dielectric spectra of PVP show
33 the NCL is present throughout the experimental frequency window from 10^{-1} and up to 10^6
34 Hz. It should continue to the ns and shorter times to overlap the time-scales probed by the
35 IN16 also of the ns range. Thus the $\langle u^2 \rangle$ in Fig.11 comes from the NCL of fast caged
36 dynamics.
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52 **(F) Poly(ethylene terephthalate)**

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54 Incoherent quasielastic neutron scattering (QENS) measurements were made on amorphous
55 poly(ethylene terephthalate) (PET) at the backscattering spectrometer IN10, at the ILL
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(Grenoble, France) by Sanz et al.¹⁰¹. The amorphous sample has $M_w=45$ kg/mol and $T_{g\alpha}=345$ K. Following the standard procedure to obtain the mean square displacement, $\langle u^2 \rangle$, from the elastic scattering intensity, the results are shown as a function of temperature in the lower panel of Fig.12. The presence of change of T -dependence of $\langle u^2 \rangle$ at $T_{HF}=173$ K is suggested by intersection of the red and blue dashed lines, which are linear regressions that optimize the data in the temperature ranges from 0 K to 178 K and above 178 to above 345 K respectively. In the upper panel of Fig.12 we reproduce the dielectric relaxation times of the α -relaxation and the slowest secondary relaxation of PET from the study of Nogales et al¹⁰² and additional dielectric relaxation times¹⁰³ for an amorphous PET with $M_w=25$ kg/mol. The JG β -relaxation involving the motion of the entire repeat unit of polymer is the slowest one compared with the other intramolecular secondary relaxations revealed by dielectric spectroscopy¹⁰², and which is responsible for the secondary glass transition at $T_{g\beta}$. In agreement, dynamic mechanical data¹⁰⁴ on PET reported the existence of only one secondary relaxation, with activation energy and timescale very similar to the slowest one found by means of dielectric spectroscopy: such results confirm the assignment done by of Nogales et al¹⁰² according to which this is the JG relaxation. The Arrhenius T -dependence of its relaxation time τ_{JG} enables us to determine $T_{g\beta}$ by the condition $\tau_{JG}(T_{g\beta})=10^3$ s. The secondary glass transition temperature $T_{g\beta}$ determined is 178 K from dielectric data¹⁰² and 171 K from dynamic mechanical data¹⁰⁴, nearly the same as $T_{HF}=173$ K, and both are well below $T_{g\alpha}=345$ K.

(G) Poly(ethylmethacrylate)

Meier and Frick¹⁰⁵ made QENS measurements of poly(ethylmethacrylate) on a partially deuterated sample (PEMAd5) to suppress the contribution from the methyl group to elastic

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3 scattering intensity. The primary glass transition temperature $T_{g\alpha}$ is 338 K. The onset of fast
4 caged dynamics in the glassy state by neutron scattering experiment was found at $T_{HF}=200$ K,
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6 which was cited in ref.[90]. Dielectric relaxation measurements by Beiner¹⁰⁶ provide the
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8 dielectric relaxation times, τ_{α} and τ_{JG} , of the α -relaxation and the JG β -relaxation. The values
9
10 of τ_{JG} in the glass state are insensitive to difference in molecular weight and tacticity. The
11
12 calorimetric glass transition temperature $T_{g\alpha}$ of the high molecular weight sample studied by
13
14 Beiner is 343 K, not far from $T_{g\alpha}=338$ K of PEMAd5 studied in QENS. Therefore it is safe to
15
16 use the dielectric τ_{JG} of PEMA from Beiner to obtain an estimate of $T_{g\beta}$. Extrapolation of the
17
18 Arrhenius T -dependence of the dielectric τ_{JG} to 10^3 s gives $T_{g\beta} \approx 214$ K, which is higher than
19
20 $T_{HF}=200$ K. However, the difference is not large and can be due to difference in samples, and
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22 errors in the extrapolation of τ_{JG} to longer times.
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33 **(H) Poly(vinyl methylether)**

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35 Bartos et al.¹⁰⁷ measured the temperature dependence of the lifetime of the ortho-positronium,
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37 τ_3 , in amorphous poly(vinylmethylether) (PVME) from positron annihilation lifetime
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39 spectroscopy (PALS). They found τ_3 changes its T -dependence in the glassy state due to
40
41 secondary glass transition at $T_{g\beta}=190$ K, and also at $T_{g\alpha}=250$ K. On the other hand, the
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43 authors of ref.[90] reported from QENS study the onset of fast dynamics, which is caged
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45 dynamics in our interpretation, of PVME at $T_{HF}=188$ K. The near coincidence of T_{HF} with $T_{g\beta}$
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47 is remarkable.
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55 **(I) Polypropylene**

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3 Kanaya and coworkers¹⁰⁸ studied the amorphous atactic polypropylene (aPP) with
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5 $M_w=1.02 \times 10^6$ g/mol and calorimetric $T_{g\alpha}=259$ K by quasielastic neutron scattering. The
6
7 time-of-flight (TOF) spectrometers used are LAM-4013 and LAM-80ET14 at the National
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9 Laboratory for High Energy Physics (KEK), Tsukuba, Japan. The energy resolutions of LAM-
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11 40 and LAM-80ET are 0.2 and 0.02 meV respectively. The QENS measurements detected the
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13 fast process of in the picosecond time range in the glassy state below $T_{g\alpha}$ and above $T_{g\alpha}$. Same
14
15 as that found in other amorphous polymers and small molecular glass-formers, the fast
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17 process in aPP is independent of Q and hence is localized. This property and the very weak
18
19 temperature dependence of the fast process are strong evidences that it originates from caged
20
21 molecule dynamics as in our interpretation. Temperature dependence of the elastic scattering
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23 intensity $I_{el}(Q)$ observed at $Q=1.64 \text{ \AA}^{-1}$ and energy resolution of 0.02 meV is reproduced
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25 together with the corresponding MSD, $\langle u^2 \rangle$, in the lower panel of Figure 13. The logarithm of
26
27 $I_{el}(Q)$ decreases and $\langle u^2 \rangle$ increases linearly with increasing temperature at lower temperatures
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29 but starts to decrease more steeply after crossing $T_{HF}=190$ K due to the onset of the fast caged
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31 dynamics.
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39 Parallel to the QENS study was the measurements of the macroradical decay rate by an
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41 ESR technique in a-PP. Using the second-order kinetic model for the decay reaction of alkyl
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43 tertiary macroradicals, the effective second-order decay rate constant, k_{eff} , was obtained at
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45 temperatures below and above $T_{g\alpha}=259$ K. The results of k_{eff} are reproduced as a function of
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47 temperature in the upper panel of Fig.13. On increasing temperature, change to a more rapid
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49 increase with temperature of k_{eff} occurs at ~ 190 K and at ~ 250 K. The change of k_{eff} at ~ 190
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51 K coincides with $T_{HF}=190$ K of QENS, and the change at 250 K can be identified with
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53 $T_{g\alpha}=259$ K at the primary glass transition. The latter indicates that k_{eff} is determined by
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3 density, and hence the change at ~ 190 K reflects the secondary glass transition with $T_{g\beta} \approx 190$
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6 K. Thus, the QENS data and the macroradical decay rate measurements on aPP once more
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8 support the general findings by us that the fast caged dynamics in the ns-ps time range
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10 respond to the secondary glass transition at $T_{HF} \approx T_{g\beta}$.
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14 15 16 **(J) Polymers with insufficient data**

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18 There are two experimental findings that we linked together to reveal their connection. One is
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20 the change of the temperature dependence at T_{HF} of the intensity of the fast caged dynamics in
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22 the glassy state of glass-formers. The other is the secondary glass transition at $T_{g\beta}$ in the
23
24 glassy state. While the first finding transpires at time-scales from ns to ps, the second on
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26 occurs at 100 to 1000 s. Despite the huge difference in time-scales, we find the two
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28 temperatures are nearly the same, i.e. $T_{HF} \approx T_{g\beta}$, in the polyalcohols in Paper I and nine
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30 polymers in this paper. The fast process, identified as the caged dynamics by us, and its onset
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32 or change in T -dependence at some temperature T_{HF} deep in the glassy state is generally found
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34 at high frequencies in glass-formers in general. However there are several other polymers
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36 where the secondary glass transition has not been investigated and $T_{g\beta}$ is unknown or
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38 uncertain. The data are incomplete or insufficient to test the relation, $T_{HF} \approx T_{g\beta}$, as rigorously as
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40 we like. Nevertheless it is worthwhile to mention these cases here to stimulate further studies
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42 for completion of the link.
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50 Several quasielastic neutron scattering (QENS) studies of polymers found the fast caged
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52 dynamics represented by $\langle u^2 \rangle$ or elastic scattering intensity changes temperature dependence in
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54 the glassy state undergo at T_{HF} significantly lower than $T_{g\alpha}$. However either the secondary glass
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56 transition has not been seen and its $T_{g\beta}$ not determined directly by calorimetry, PALS, or
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3 dielectric relaxation, or there are some uncertainty in determining $T_{g\beta}$. These cases include the
4 following polymers discussed in the following subsections (i)-(vi).
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8 (i) QENS studies of trans 1,4 polychloroprene (PCP) with MW= 4×10^5 g/mol and $T_{g\alpha}=228$
9 K performed by Kanaya and coworkers¹⁰⁹ found the fast caged dynamics represented by $\langle u^2 \rangle$
10 changes temperature dependence in the glassy state undergo at $T_{HF} \approx 170$ K.
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14 (ii) Incoherent inelastic neutron scattering studies were carried out on polyisobutylene
15 (MW=53000 g/mol, and $T_{g\alpha} \approx 200$ K) by Frick and Richter¹¹⁰ using the backscattering
16 spectrometer IN10. The natural logarithm of the elastic scattering intensity plotted as a
17 function of temperature shows change of temperature dependence at $T_{HF} \approx 150$ K. Change is
18 exhibited by $\langle u^2 \rangle$ at $T_{HF} \approx 150$ K. The frequency range probed by IN10 is above 0.2 GHz.
19 Additional mean square displacement data on polyisobutylene have been obtained by Kanaya
20 and co-workers¹¹¹ with the instrument LAM40-KENS ($\delta E = 0.02$ meV). The temperature
21 dependence of $\langle u^2 \rangle$ is reproduced in the lower panel of Fig.S2 in Supplementary Information,
22 showing a clear crossover at $T_{HF} \approx 150$ K, common to the two sets of data in spite of the quite
23 different dynamic range probed by the two spectrometers. Sokolov et al. used dynamic light
24 scattering to study the fast dynamics of PIB (MW=10,000 g/mol)^{35,36}. The susceptibility
25 spectra are totally manifested by the NCL in the frequency range, $0.5 < f < 20$ GHz and
26 temperature range $160 \leq T \leq 230$ K. These light scattering data assure that the fast process of
27 PIB observed below $T_{g\alpha}$ by neutron scattering on IN10 above 0.2 GHz is the NCL in
28 susceptibility. However, we find no study showing the secondary glass transition of PIB, and
29 hence $T_{g\beta}$ is unknown from experiment. However, there is a theoretical estimate of the
30 Arrhenius temperature dependence of the slowest secondary relaxation time presented in the
31 paper by Törmälä¹¹². Taken as the JG β -relaxation of PIB and extrapolating its Arrhenius
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3 dependence of its relaxation time to 10^3 s, we determine a plausible value of $T_{g\beta} \approx 141$ K. This
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5 value of this approximate $T_{g\beta}$ is not far from $T_{HF} \approx 150$ K and it is far below $T_{g\alpha}$ determined by
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7 dielectric spectroscopy¹¹³, as shown in Fig.S2 in Supplementary Information.
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11 (iii) Incoherent neutron scattering was employed by Floudas et al.¹¹⁴ to study the
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13 dynamics of solution-chlorinated polyethylene with $T_{g\alpha} \approx 317$ K. The temperature dependence
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15 of the incoherent dynamic structure factor or $\langle u^2 \rangle$ changes on crossing $T_{HF} \approx 239 - 249$ K. We
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17 have no information on $T_{g\beta}$, and the relation $T_{HF} \approx T_{g\beta}$ cannot be verified at this time.
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21 (iv) The methyl groups in 1,4 polyisoprene contribute to neutron scattering at lower
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23 temperatures that can obscure the fast dynamics. In elastic neutron backscattering experiment
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25 on IN10 and IN13, Frick and Fetters¹¹⁵ used three partially deuterated samples (PI-d₃, PI-d₅,
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27 and PI-d₈) and of a fully protonated sample (PI-h₈) to separate out the dynamics of the methyl
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29 group and from the fast process in the glassy state. The PI-d₅ and PI-d₈ samples have the
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31 methyl group protonated, and the methyl group rotation contribution appear at low
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33 temperatures in the first of a two-step process in the elastic intensity $I_Q(T)$ at $Q = 1.95 \text{ \AA}^{-1}$ (see
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35 Fig.2 in ref.115). The second step at higher temperatures is the fast process found in the other
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37 polymers. The samples PI-d₅ and PI-d₈ have the methyl groups deuterated and they make no
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39 contribution to scattering. Hence the first step vanishes, and the fast process in the glassy state
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41 becomes evident in the elastic scattering intensity (Fig.2 in ref.115). All samples exhibit the
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43 usual prominent decrease of $I_Q(T)$ when temperature is increased past $T_{g\alpha}$. The JG β -
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45 relaxation was found in the glassy state of 1,4-polyisoprene of different microstructures^{116,117}.
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47 By extrapolation of its Arrhenius temperature dependence to 1000 s, the value of $T_{g\beta}$ was
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49 determined for mostly cis 1,4-polyisoprene to be ~ 121 K, and ~ 129 K from the data of ref.116
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51 and ref.117 respectively. For trans 1,4-polyisoprene, $T_{g\beta} \sim 115$ K. These values of $T_{g\beta}$ seem to
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3 be near the temperature T_{HF} where possible changes of temperature dependence of $I_Q(T)$ or
4 $\langle u^2(T) \rangle$ occurs in the deuterated methyl group samples. However the data as presented in
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6 ref.[115] are not clear enough for the determination of T_{HF} . Also we are mindful of the
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8 significantly higher calorimetric $T_{g\alpha}=215$ K of the samples studied by neutron scattering
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10 without giving information of the *cis* and *trans* contents, and the lower values of 203 K,¹¹⁶
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12 and 209.9 K from ref.114 for the *cis* samples, 201 K for the *trans* samples¹¹⁷. Thus the
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14 relation $T_{g\beta} \approx T_{HF}$ cannot be verified with certainty. Another indication of T_{HF} is near $T_{g\beta}$ can
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16 be inferred from the model calculations for the first relaxation step of the methyl group
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18 rotation by Frick and Fetters. The calculations show the first step terminates at either 120 or
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20 140 K (see Figs.6a and 6b of ref.115), which can be taken as the onset of increase in
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22 temperature dependence of the caged dynamics at T_{HF} near one of the possible values of $T_{g\beta}$.
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30 (v) Quintana et al.¹¹⁸ performed quasielastic neutron scattering experiment on glassy
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32 polyethersulfone (PES) using the IN16 spectrometer at ILL with resolution between 2 to 5
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34 μeV . Determined by DSC, the glass transition temperature of the sample, $T_{g\alpha}$, is 500 K. They
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36 obtained the T -dependence of the quasielastic intensities, $I(Q,T)$, at Q equal to 0.65, 0.96,
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38 1.33, and 1.76 \AA^{-1} . On increasing temperature, $I(Q,T)$ assumes a stronger temperature
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40 dependence after crossing T_{HF} with values lying between 150 to 200 K depending on Q .
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44 David et al.¹¹⁹ investigated the mechanical relaxation of PES in the glassy state. They
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46 found several secondary relaxations. The β -relaxation has two branches, β_1 and β_2 . The
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48 Arrhenius temperature dependences of their relaxation times, τ_{β_1} and τ_{β_2} , were given¹¹⁹, and
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50 from which the two possible secondary glass transition temperatures, $T_{g\beta_1}=151.5$ K and
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52 $T_{g\beta_2}=215.7$ K are determined. Thus in PES we find $T_{g\beta_1}$ and $T_{g\beta_2}$ are consistent with the
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54 spread in the values of T_{HF} at different Q .
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(vi) Although the main purpose of the quasielastic neutron scattering on poly(vinyl acetate) (PVAc) by Mukhopadhyay et al.¹²⁰ is the study of the methyl group dynamics, the measurements were carried out over a temperature range from 50 to 300 K, below its glass transition temperature ($T_{g\alpha} = 315$ K). A rotation rate distribution model (RRDM) was used to describe the methyl group dynamics in the glassy polymer. In a plot of the logarithm of the width Γ_0 of the most probable Lorentzian component vs $1/T$, the methyl group dynamics are evident from nearly linear dependence. However, $\log(\Gamma_0)$ deviates from this linear dependence on $1/T$, starting at temperatures higher than ≈ 200 K. Thus we identify this temperature as the T_{HF} , as the onset of the fast caged dynamics.

Commonly observed by dielectric and mechanical spectroscopy in the glassy state of PVAc is a fast secondary relaxation commonly called the β -relaxation¹²¹. Its relaxation time at $T_{g\alpha}$ is much shorter than that of the JG β -relaxation estimated by the primitive relaxation time of Coupling Model^{1,15}. The true JG β -relaxation of PVAc is slower and can be identified with the additional very broad secondary relaxation, labeled β' and found by Smith et al.¹²¹ in time scales between segmental α -relaxation and the β -subglass process. Smith et al. speculated that it may be due to *cis-trans* isomerism of the ester groups. We assume this is related to the JG β -relaxation of PVAc. From the Arrhenius dependence of $\tau_{\beta'}$, we estimate $T_{g\beta} \approx 210 \pm 10$ K, which is not far from $T_{HF} \approx 200$ K.

4. Discussion and Conclusion

In our first paper of the series²² we have shown the dielectric loss at THz of the polyalcohols comes from the NCL of caged dynamics. Moreover, the observed crossover in temperature dependence of the NCL at high frequencies deep in the glassy state occurs at the secondary

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3 glass transition temperature $T_{g\beta}$, which can be independently determined by low frequency
4 dielectric relaxation measurements of the JG β -relaxation by the condition $\tau_{\beta}(T_{g\beta})=100$ or
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6 1000 s. Since the β -peak frequency $f_{\beta}(T_{g\beta})=[1/2\pi\tau_{\beta}(T_{g\beta})]$ is about 15 decades lower than 1
7 THz, the observed process cannot be the JG β -relaxation itself, and instead it is the NCL of
8 caged molecules taking place before. Support of this identification comes from the direct
9 observation of the NCL over a broad range of frequencies from 40 Hz to 10 GHz by dielectric
10 spectroscopy of these polyalcohols¹²². Thus, the observed crossover in the T -dependence of
11 the NCL is testimony to the coupling between the NCL to the JG β -relaxation, suggested
12 before in previous studies^{2,16,17,24,25}. Worthwhile to note are the direct observations of the
13 NCL in the time domain from ps to ns range by optically heterodyne detected optical Kerr
14 effect (OHD-OKE) experiments of a variety of small molecular glass-formers including
15 ortho-terphenyl (OTP)¹²³⁻¹²⁵. The secondary glass transition of OTP and several small
16 molecular glass-formers had been detected by adiabatic calorimetry.^{26,126} For OTP, $T_{g\beta}=133$
17 K and $T_{g\alpha}=240$ K. In a separate paper III, where we address van der Waals small molecular
18 glass-formers including OTP and toluene, QENS measurements¹²⁷ are presented to show the
19 change of T -dependence of the mean square displacements, $\langle u^2 \rangle$, near the secondary glass
20 transition temperature $T_{g\beta}$ determined by adiabatic calorimetry.

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In this paper we look for similar effects in amorphous polymers. High frequency
measurements in the glassy state by quasielastic light scattering, Brillouin scattering,
quasielastic neutron scattering, and dielectric measurements from 100 MHz to 20 GHz all
have observed the NCL, and its crossover in temperature dependence at a temperature T_{HF}
below the glass transition temperature $T_{g\alpha}$. The experimental data supporting the existence of
the secondary glass transition $T_{g\beta}$ are provided by PALS data and low frequency dielectric

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3 measurements. The hole volume fraction measured by PALS also exhibits a crossover in T -
4 dependence at $T_{\beta,PALS}$, which indicates occurrence of the JG β -relaxation glass transition at
5 this temperature. Low frequency dielectric measurements of the JG β -relaxation times τ_{β} also
6 enable the dielectric secondary glass transition temperature $T_{g\beta}$ to be determined. The good
7 agreements between T_{HF} , $T_{\beta,PALS}$, and $T_{g\beta}$ found validate the following two main points of this
8 paper. The results of all the polymers considered are summarized in Table 1.
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18 The important advance made here and in the previous paper I²² is the connection
19 between the fast caged dynamics seen in the glassy state by high frequency experiments and
20 the secondary glass transition found at extremely low frequencies. This connection is pointed
21 out by us for the polymers in this paper II, and for the polyalcohols in Paper I²². This
22 connection was not recognized before by the quasielastic neutron scattering and light
23 scattering communities in many studies carried out in the past three decades. The emphasis of
24 most of these high frequency experiments was on the dynamics at temperatures above $T_{g\alpha}$
25 with the purpose of comparing the data with the prediction of Mode Coupling Theory¹²⁸ on
26 critical properties at $T_c > T_{g\alpha}$. The current recognition of the connection between caged
27 dynamics and JG β -relaxation should restore and revitalize the importance of the findings in
28 the glassy state of many different glass-formers by the many experiments carried out at high
29 frequencies in the past.
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46 There are two points in the dynamics of glass-forming substances that are critical and
47 have to be recognized for understanding the origin of this connection. The first point is that
48 the JG β -relaxation time τ_{JG} is coupled to density ρ . There is support of this coupling to
49 density from studies in the equilibrium liquid state at elevated pressures, where it is found
50 that τ_{β} shifts with pressure like τ_{α} ^{7-12,14,18} and the two relaxation times can be scaled by the
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3 same product variable T/ρ^γ where γ is a material constant¹³. On cooling, when τ_β becomes
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5 much longer than the experimental time-scale, the JG β -relaxation and the density it couples
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7 to can no longer be equilibrated, resulting in the secondary glass transition. Furthermore,
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9 recently it has been shown¹²⁹ that freezing of the motions related to JG β -relaxation in well
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11 aged metallic glass contributes to glass entropy and enthalpy.
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15 The second point is the coupling of the NCL of caged dynamics to the JG β -relaxation.
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17 Without the coupling, the NCL would not respond to the secondary glass transition at
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19 $T_{HF} \approx T_{\beta,PALS} \approx T_{g\beta}$ as observed. There are independent evidences of the coupling of NCL to
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21 density from aging experiments performed at the NCL regime in glycerol, propylene
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23 carbonate¹³⁰, xylitol¹³¹, colloidal suspension⁴⁹, and metallic glasses¹³². The coupling brings
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25 out the fundamental importance of the JG β -relaxation in its connection to the NCL from
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27 caged dynamics in the glassy state and manifested as the fast dynamics in the THz to GHz
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29 range. The fast dynamics at temperatures above $T_{g\alpha}$ have attracted a lot of attention in the past
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31 three decades due to the influence of Mode Coupling Theory (MCT)¹²⁸. Notwithstanding, the
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33 focus of this paper is on the fast dynamics of caged molecules in the glassy states, which
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35 cannot be addressed by MCT because the validity of which is confined to the liquid state.
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41 Although this paper is focused on the change of temperature dependence at $T_{g\beta}$ of the
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43 fast caged dynamics manifested as NCL in susceptibility, and elastic intensity or mean square
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45 displacement in neutron scattering, one should not forget similar change occur at $T_{g\alpha}$ ⁴⁰. The
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47 change of temperature dependence of caged dynamics at $T_{g\alpha}$, as well as at $T_{g\beta}$, happens
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49 because the fast caged dynamics depend on density and couple to both the α -relaxation and
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51 the JG β -relaxation. Because of these properties, the changes of temperature dependence of
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53 density on crossing $T_{g\alpha}$ and $T_{g\beta}$ are passed on to the caged dynamics that transpires at much
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3 shorter times (or higher frequencies). The fast process (identified with the caged dynamics in
4 here) had been seen in the glassy states below $T_{g\alpha}$ of a variety of polymers and small
5 molecular van der Waals glass-formers by quasielastic neutron and light scattering
6 experiments in the past three decades. However, no one before had pointed out that the
7 temperature T_{HF} below $T_{g\alpha}$, at which change of its T -dependence is observed, can be
8 identified with the secondary glass transition temperature $T_{g\beta}$. This identification is done for
9 the first time for the polyalcohols and a pharmaceutical in Paper I, and in this Paper II for the
10 polymers. Paper III follows up the present paper to show the same property in the glassy
11 states of small molecular van der Waals glass-formers including *o*-terphenyl and toluene from
12 quasielastic neutron scattering, Brillouin scattering, and Mössbauer spectroscopic
13 experiments. Thus, the novel property we find is general and fundamental, and it needs to be
14 addressed in any serious attempt to solve the glass transition problem.
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37 data of amorphous PET and BPA-PC respectively, and Giulio Monaco and Tullio Scopigno
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40 Italian Republic and the People’s Republic of China 2013-2015 (Significant Research Project
41 PGR00137).
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53 **Supporting Information Available**

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3 More mean square displacements and relaxation time data on polymers (BPA-PC and PIB)
4 are provided in the Supporting Information. This information is available free of charge via
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6 the Internet at <http://pubs.acs.org>.
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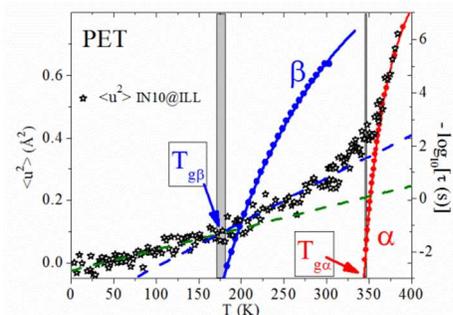
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Table of contents graphic.



TOC. Left side: mean square displacement, $\langle u^2 \rangle$, of amorphous PET (open black stars) as measured at the IN10 spectrometer by Sanz and co-workers [101] plotted as a function of temperature. Data are from ref.[101] and redrawn. The arrows indicate the location of $T_{g\beta}$ and $T_{g\alpha}$. Right side: logarithm of the reciprocal of α - (red and blue closed circles) and JG β -relaxation time from dielectric spectroscopy.

Table I. Values of the characteristic temperature, T_{HF} , from high frequency measurements of caged dynamics, the secondary glass transition temperature, $T_{g\beta}$, and the primary glass transition temperature, $T_{g\alpha}$, of the polymers considered in this article.

Polymer	T_{HF} (K) $T_{g\beta}$ (K) $T_{g\alpha}$ (K)	$T_{HF}/T_{g\alpha}$	$T_{g\beta}/T_{g\alpha}$
PMMA	240 -246 refs.[37-39] 250 refs.[31,32,60] 390	0.615 – 0.63	0.64
PS	200 ref.[42] 190 refs.[84,85] 373	0.54	0.51
PVC	177.6 ref.[60]; 170 ref.[86]; 165 – 170 ^a 350	0.51	0.47 – 0.49
1,4 PBD	120 -130 ref.[46] ^b 109 ref.[87] ^c 185 ref.[46] ^b ; 174 ref. [87] ^c	0.65 – 0.70	0.63
<i>cis</i> PBD	120 ref.[47] 120 ref.[88] 170	0.71	0.71
BPA-PC	200 ref.[87] 190 ^a 423	0.47	0.45
PVP	316 ref.[100] 316 ref.[98] 422	0.75	0.75
PET	173 ref.[101] ^a 172.4 ref.[102] ^a 345	0.50	0.50
PEMA	200 ref.[105] 214 ref.[108] ^a 338	0.59	0.63
PVME	188 ref.[90] 190 ref.[107] 250	0.75	0.76
aPP	190 ref.[108] 190 ref.[108] 259	0.73	0.73
trans 1,4 polychloroprene	170 ref.[109] <i>d</i> 228	0.75	<i>d</i>
PIB	150	0.75	0.70

	140 ref.[112] ^a 200		
solution-chlorinated polyethylene	239 – 249 ref.[114] <i>d</i> 317	0.75 – 0.79	<i>d</i>
PES	150 – 200 ref.[118] 151.5 – 215.7 ref.[119] ^a 500	0.30 – 0.40	0.3 – 0.43
PVAc	200 ref.[90, 120] 210±10 ref.[121] ^a 315 ref.[120]	0.63	0.63-0.70

^a and from this work

^b microstructure of sample: cis: trans: vinyl = 47: 46: 7

^c microstructure of sample: 52% cis- , 41% trans- and 7% vinyl

^d value of $T_{g\beta}$ not available

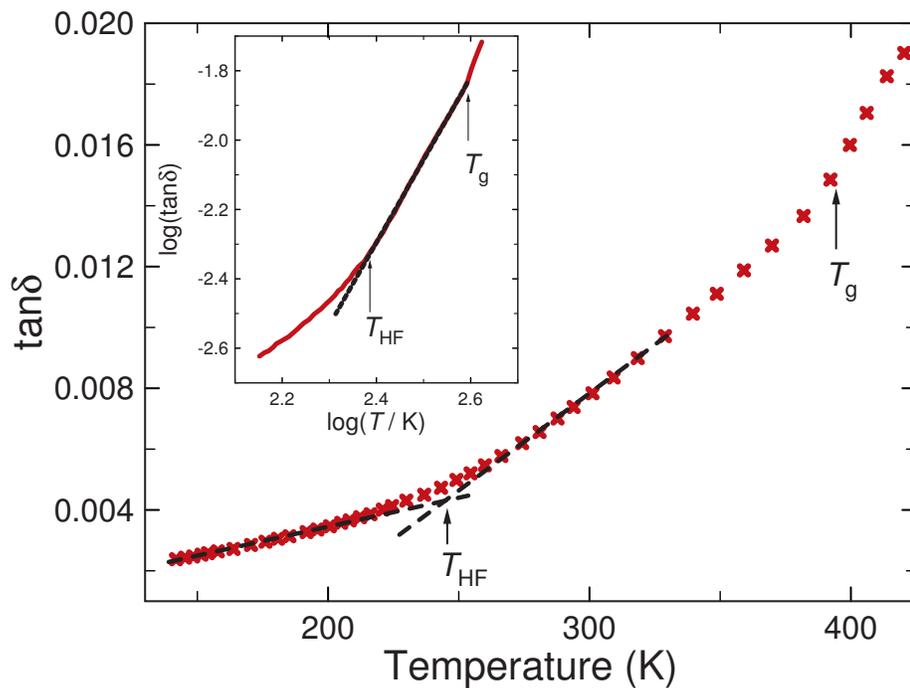


Fig.1. Dielectric loss of PMMA at 10 GHz as a function of temperature, and as a function of $\log(\text{temperature})$ in the inset. Data are from ref.60, and redrawn. The arrows indicates T_{HF} .

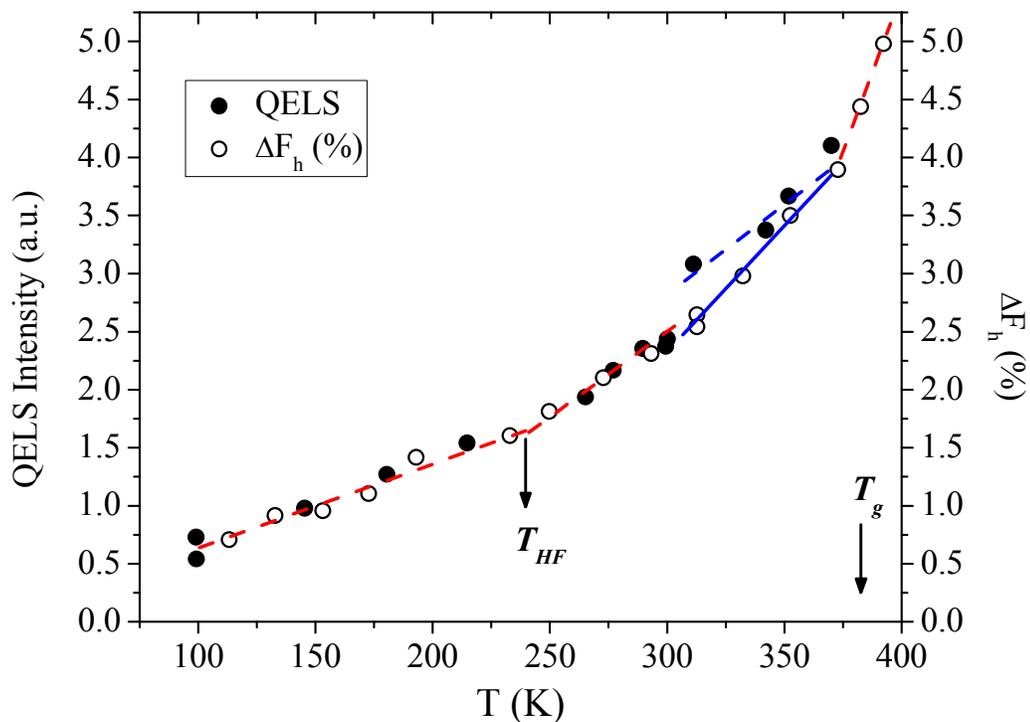


Fig.2. Comparison between the QELS intensity in arbitrary units (a.u.) and the dynamic hole volume fraction, ΔF_h , of PMMA. Data from ref.37 are redrawn. The arrow indicates T_{HF} which is practically the same as the secondary glass transition temperature $T_{g\beta}$ determined by PALS.

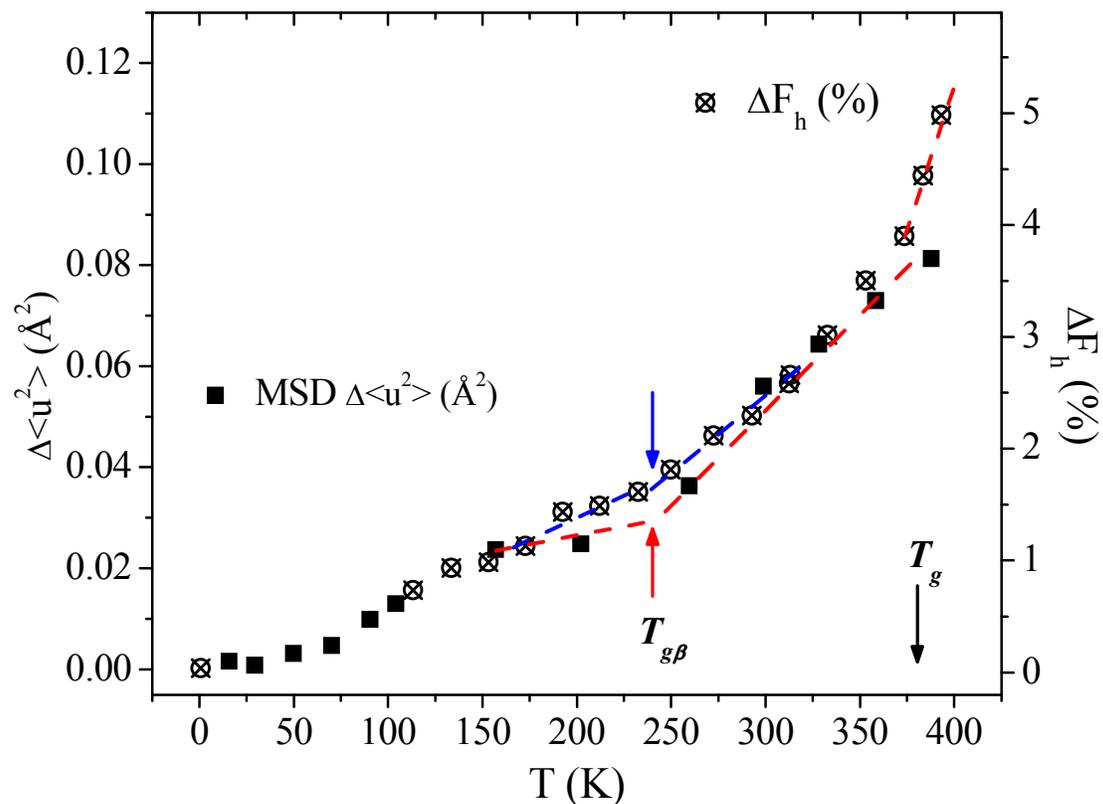


Fig.3. Comparison between the MSD, $\Delta\langle u^2 \rangle$, and the dynamic hole volume fraction, ΔF_h , of PMMA. Data from ref. 37 are redrawn. The arrows indicate the secondary and primary glass transition temperatures $T_{g\beta}$ and T_g .

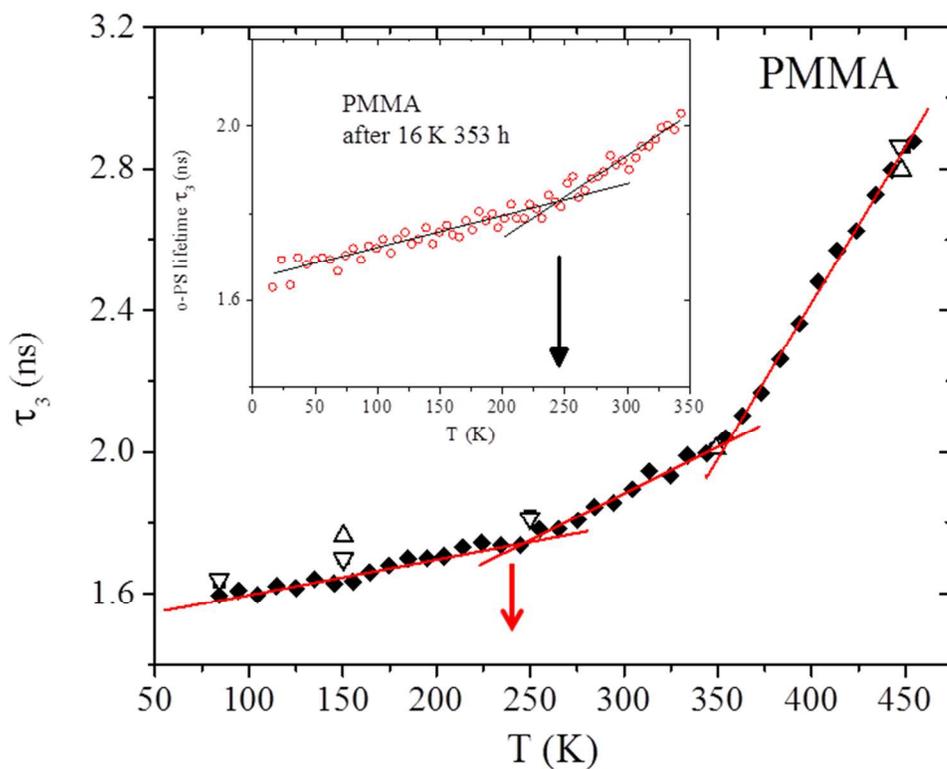


Fig.4. The average o-Ps lifetime τ_3 versus temperature for PMMA. Data in the main figure and in the inset are from ref.31 and ref.32 respectively, and are redrawn. The arrows indicate the secondary glass transition temperature $T_{g\beta}$.

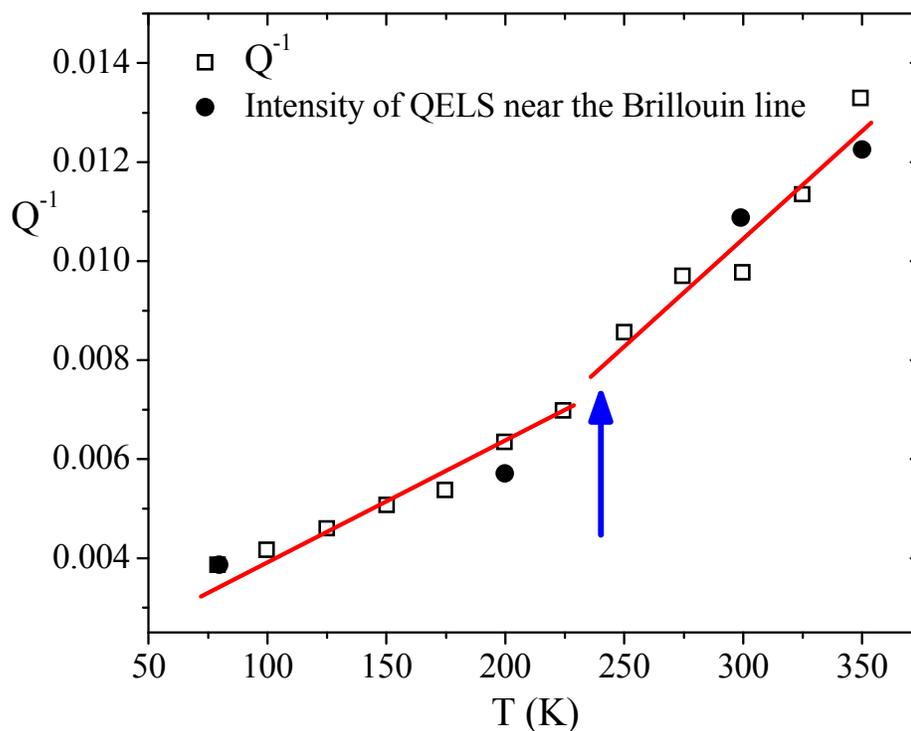


Fig.5. The internal friction of PMMA obtained from the width of the Brillouin line (open squares), and compared with the quasielastic light scattering intensity at 17 GHz (solid circles). The two red lines are drawn to indicate possible change of temperature dependence of both sets of data at $T_{HF} \approx 240$ K. Data are from ref.39 and redrawn. The arrow indicate the secondary glass transition temperature $T_{g\beta}$ determined by PALS.

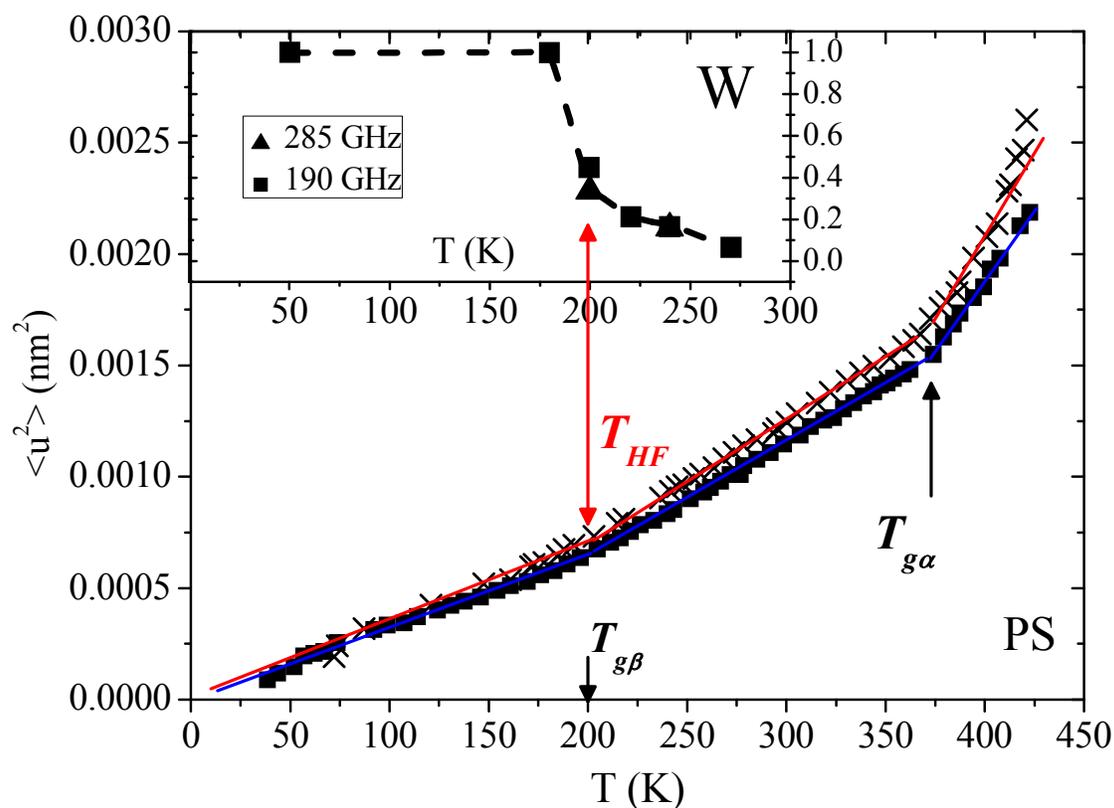


Fig.6. Temperature dependence of mean-square displacement $\langle u^2 \rangle$ from neutron scattering measurements by means of instrument OSIRIS, $\delta E=25 \mu\text{eV}$, (crosses) and HFBS, $\delta E=0.8 \mu\text{eV}$, (solid squares) for a-PS. Data are from refs.[42-44] and redrawn. The red and blue lines are drawn to indicate change of temperature dependence of both sets of data at T_{HF} and at $T_{g\alpha}$. The inset shows W , the fraction of ESR active probes (TEMPO) trapped in PS, measured by the ESR at two different frequencies (data from ref.[70]).

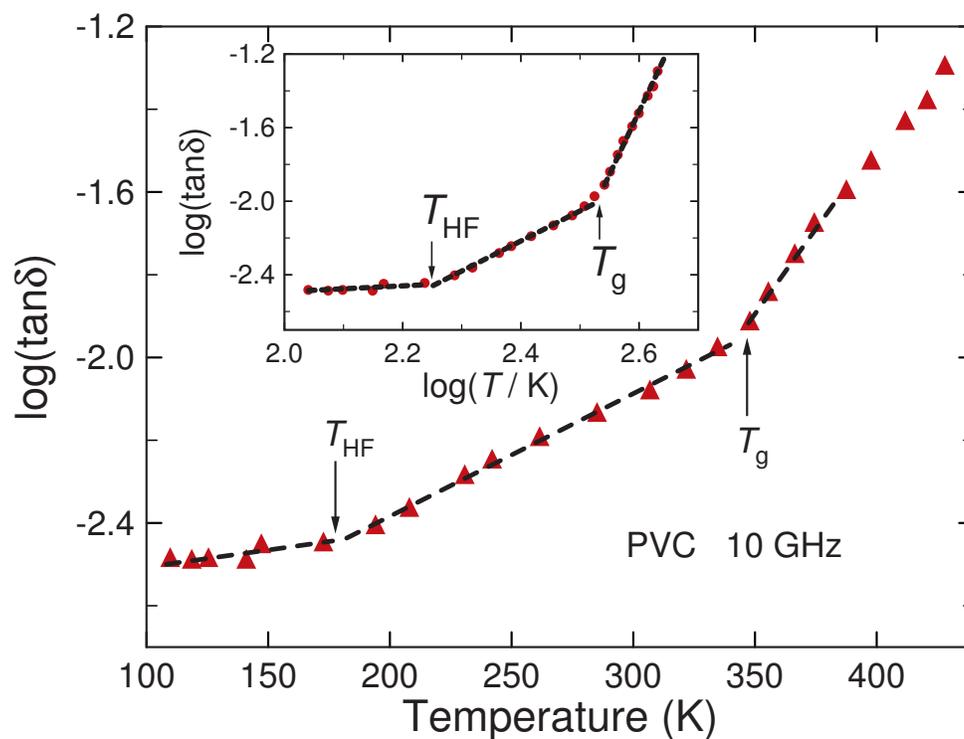


Fig.7. Dielectric loss of PVC at 10 GHz as a function of temperature, and as a function of $\log(\text{temperature})$ in the inset. Data are from ref.60, and redrawn.

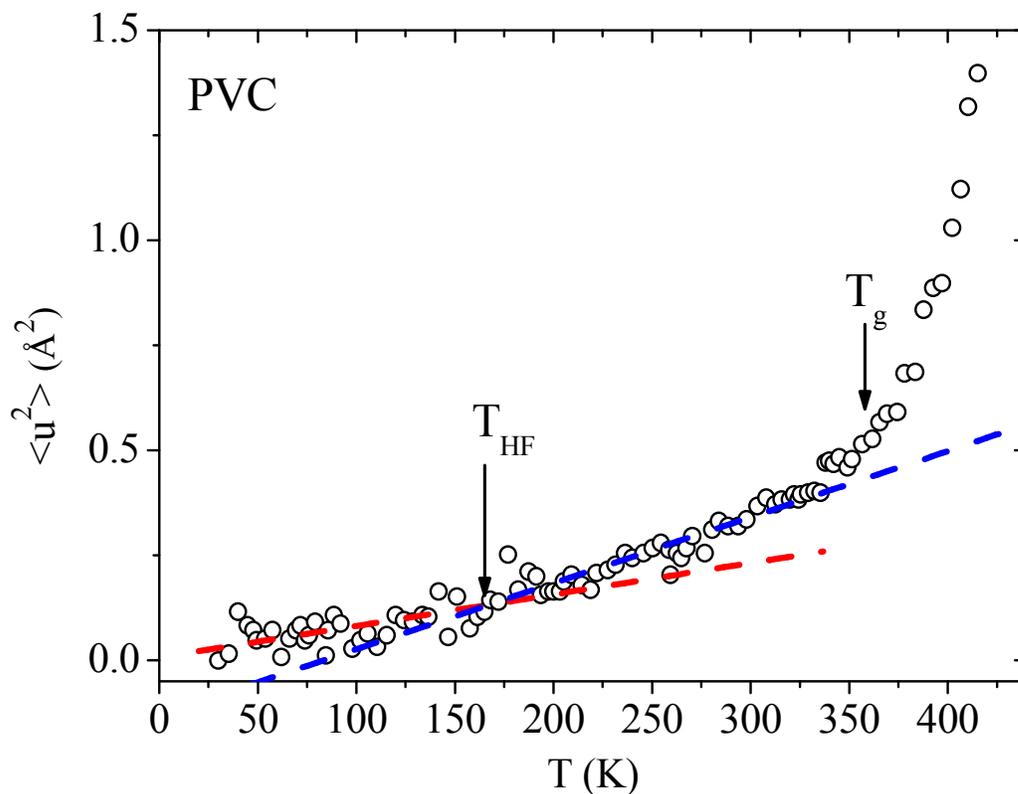


Fig.8. Mean-square atomic displacements (open circles) plotted as a function of temperature for a bulk film of PVC. Data are from Soles and coworkers in ref. [86], and replotted here. Red and blue dashed lines are linear regressions to data trying to optimize a linear behavior over the widest temperature range starting from below (0 K) and from above (350 K). The value of T_{HF} is that reported in table I, the value of T_g is that reported by Soles and coworkers.

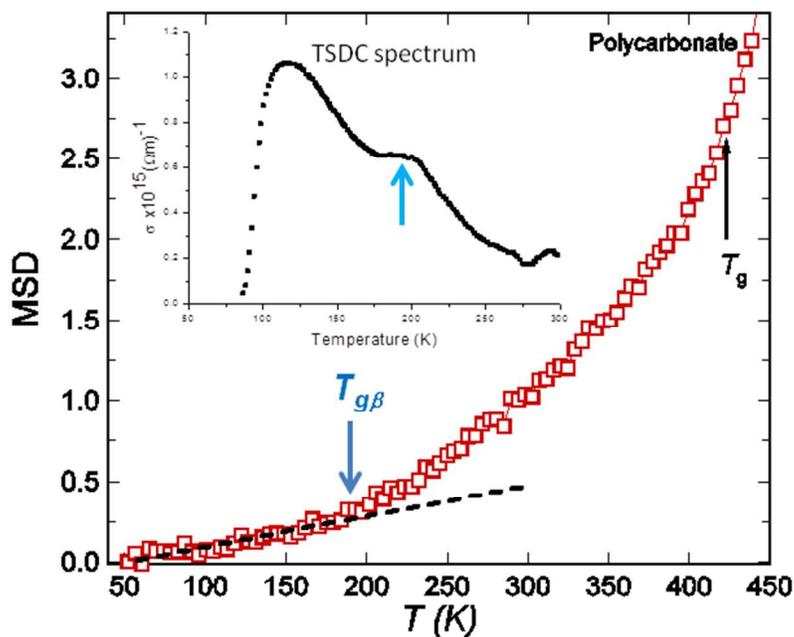


Fig.9. Mean square displacement (MSD) as a function of temperature for bulk PC. Neutron scattering data are from ref.[89] and redrawn. The inset are TSDC data of PC are from ref.[93] and redrawn. The arrows indicate the secondary glass transition temperature $T_{g\beta} \approx 190$ K determined by the shoulder in the TSDC spectrum.

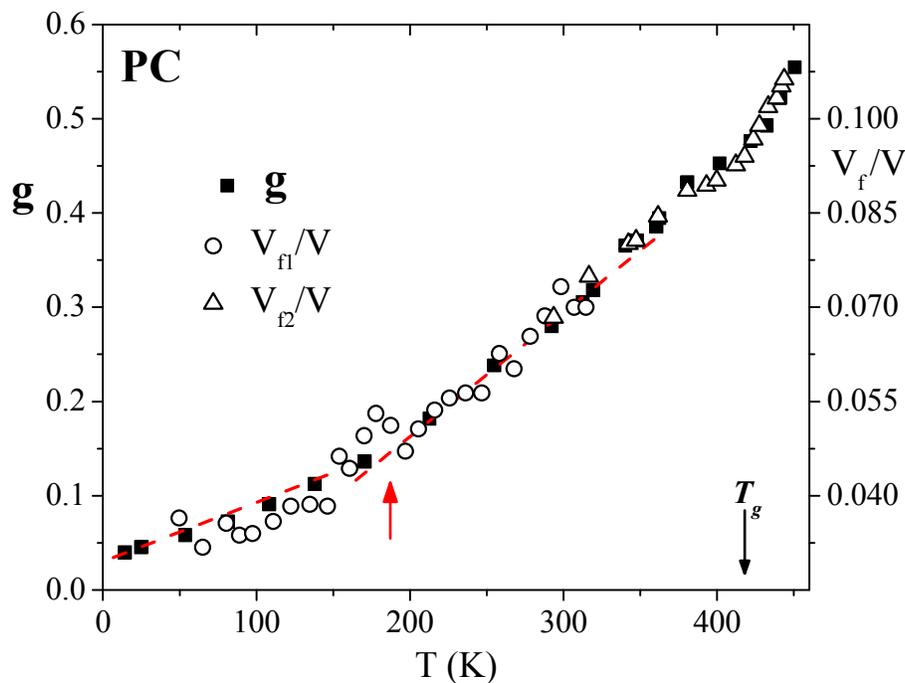


Fig.10. Comparison of fractional free volume, V_f/V , and relaxation strength or intensity, $g(T)$, of the fast relaxation process in polycarbonate seen by quasielastic light scattering (QELS) in the frequency interval 100–1000 GHz of PC. Data are from ref.[97], and redrawn. The upward pointing arrow indicates $T_{g\beta} \approx 190$ K.

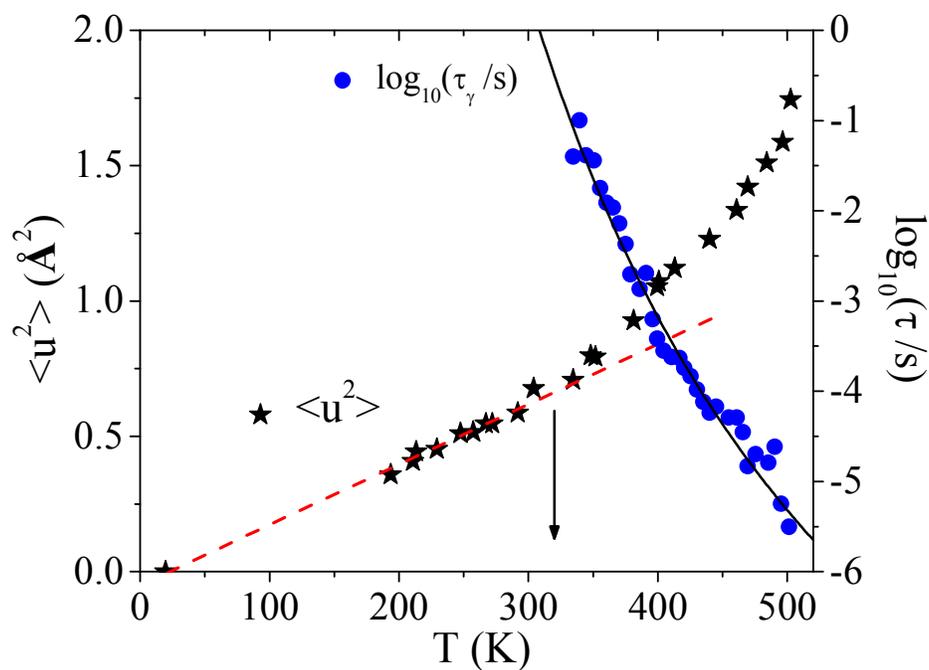


Fig. 11. Mean square displacement, $\langle u^2 \rangle$ of PVP (closed black stars), and the logarithm of the JG relaxation time of PVP (closed blue circles) plotted as a function of temperature. Data are from refs.[99-100] and redrawn. The arrow indicates the location of the secondary glass transition temperature, $T_{g\beta}=316$ K, determined by Karabanova et al.⁹⁸ using DSC.

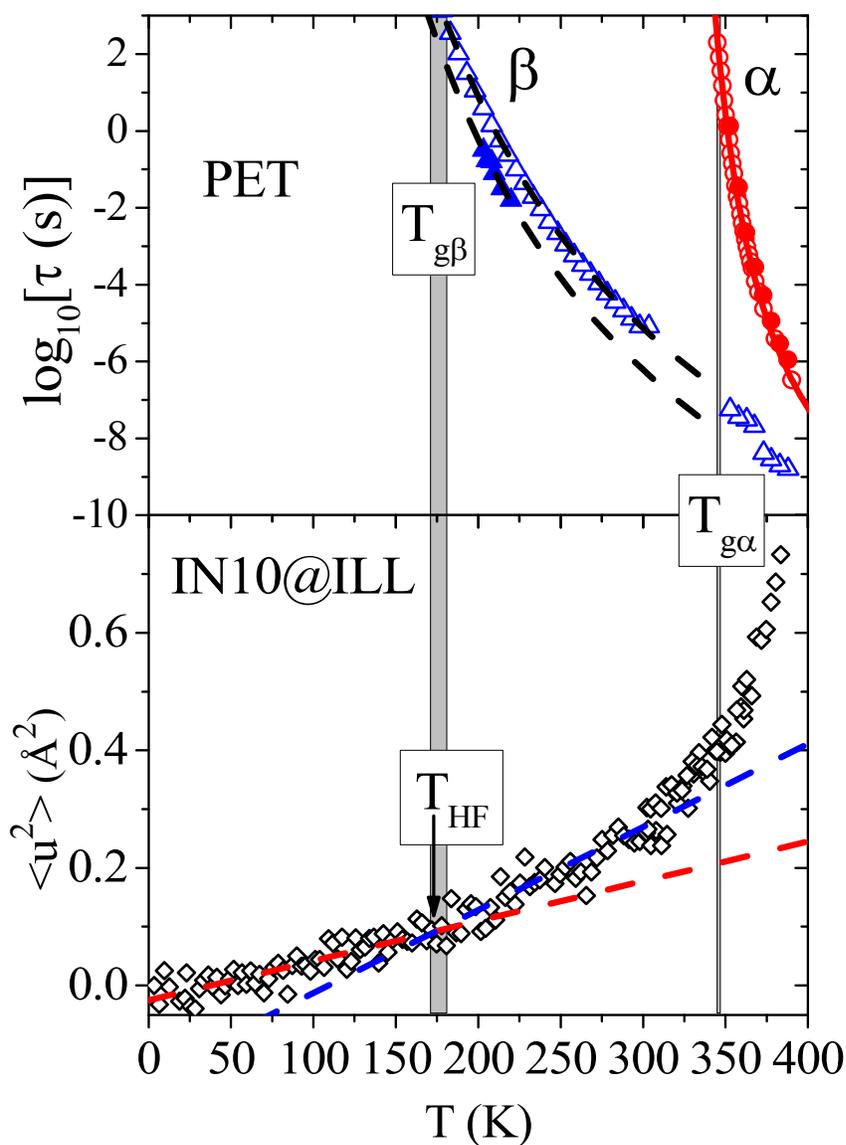


Fig.12. Upper panel: logarithm of the α - (red closed¹⁰² and open¹⁰³ circles) and JG β -relaxation time (blue open and closed triangles, from dielectric¹⁰²⁻¹⁰³ and dynamic mechanical spectroscopy¹⁰⁴ data respectively) of PET plotted as a function of temperature. The low temperature gray shaded area is bracketed from the $T_{g\beta}$ values obtained when $\tau(T_{g\beta})=10^3$ s for dielectric and dynamic mechanical data. The narrow high temperature shaded area marks the

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3 interval for the values of $T_{g\alpha}$ obtained from the two sets of data from ref.[102] and ref.[103].
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6 The solid curve is a Vogel Fulcher Tammann fit to the α -relaxation. The dashed lines are
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8 Arrhenius fits for the β -relaxation times. **Lower panel:** mean square displacement, $\langle u^2 \rangle$, of
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10 amorphous PET (open black diamonds) as measured at the IN10 spectrometer plotted as a
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12 function of temperature. Data are from ref.[101] and redrawn. Data above 383 K are not
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14 shown, being potentially affected by cold crystallization. The two dashed lines are linear
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16 regressions optimized in the low and intermediate temperature region. The arrow indicates the
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18 location of T_{HF} as obtained from the crossing of the two linear regressions.
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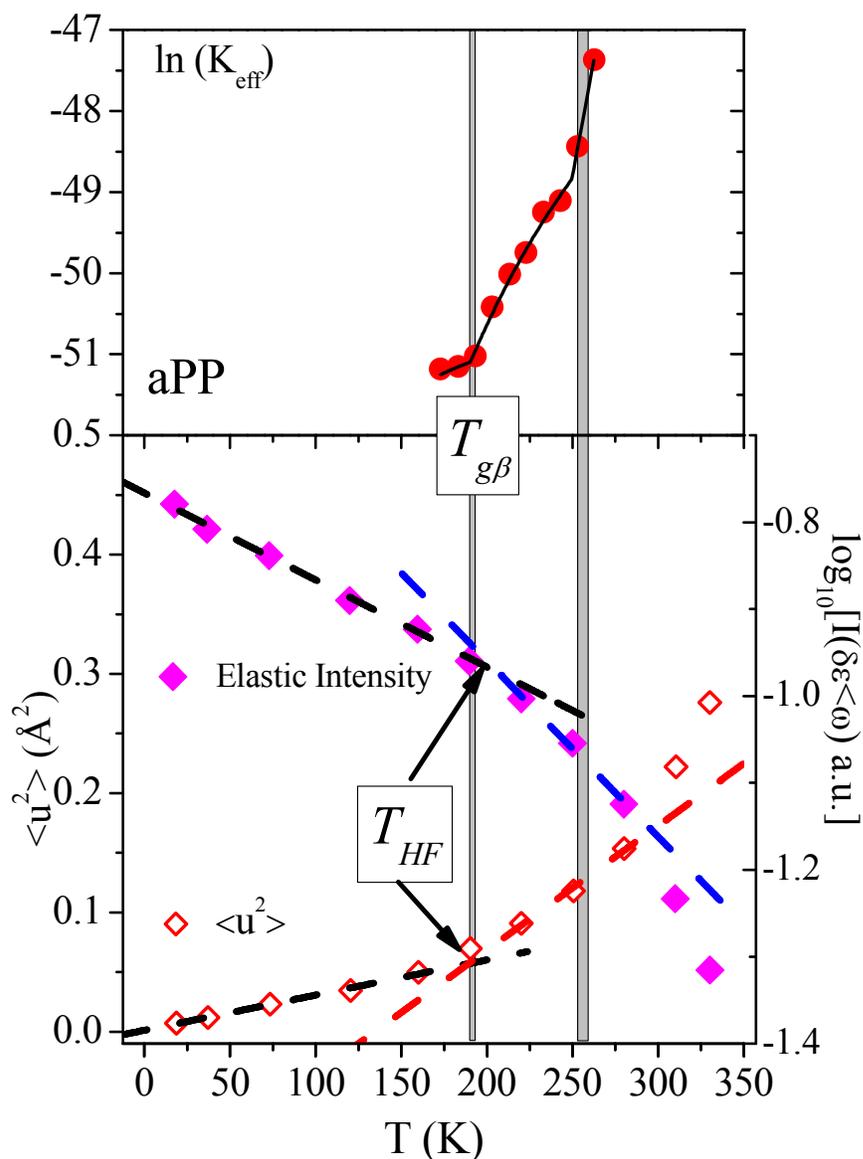
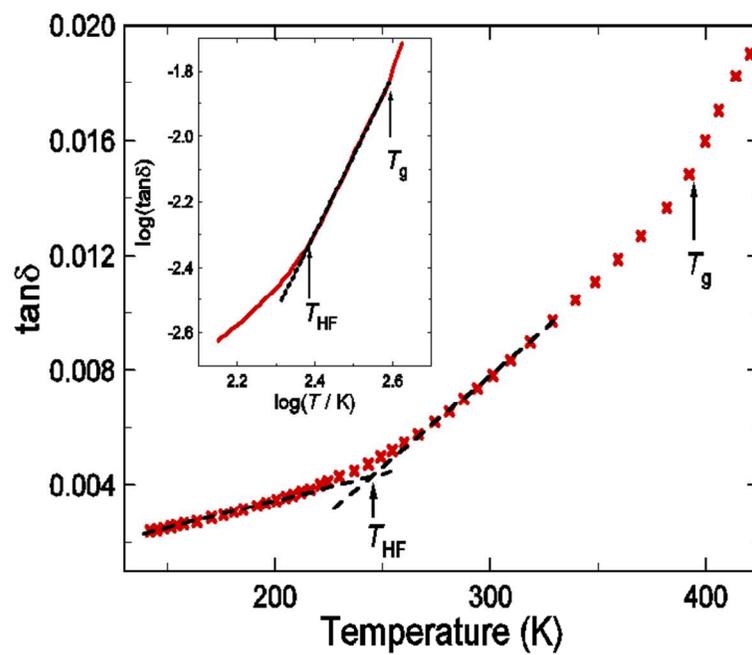


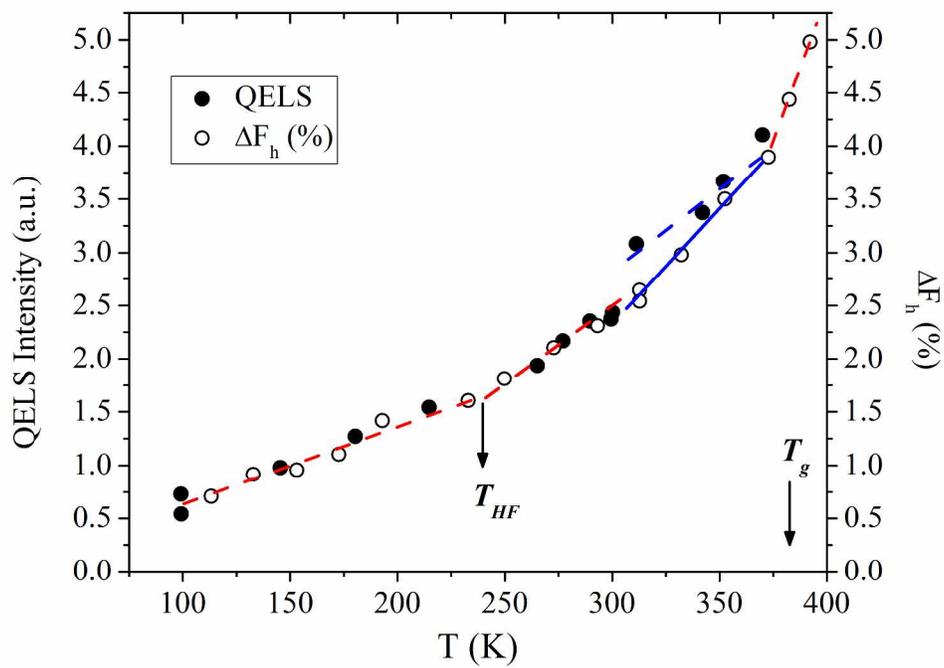
Fig.13. Upper panel: logarithm of effective second-order macroradical decay rate constant, k_{eff} , obtained from ESR technique¹⁰⁸ plotted versus temperature for amorphous atactic polypropylene (aPP). The grey shaded areas mark respectively the transition from trapped regime and the glass transition temperature, $T_{g\alpha}=259$ K as determined in ref.[108]. The width of the area reflect the experimental uncertainty. **Lower panel:** mean square displacements (red open diamonds) and logarithm of elastic intensity (closed magenta diamonds) from

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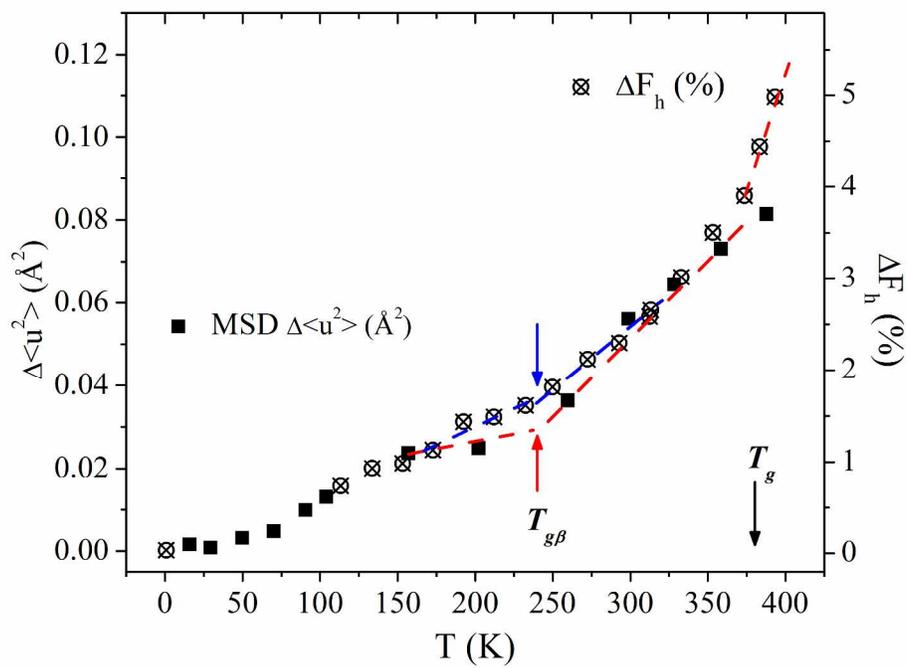
quasielastic neutron scattering data ($\delta E=0.02$ meV) of amorphous atactic polypropylene (aPP)¹⁰⁸ plotted versus temperature. Dashed lines are linear regressions optimized in the low and intermediate temperature region. The arrow indicates the location of T_{HF} as obtained from the crossing of the linear regressions from the two temperature ranges.



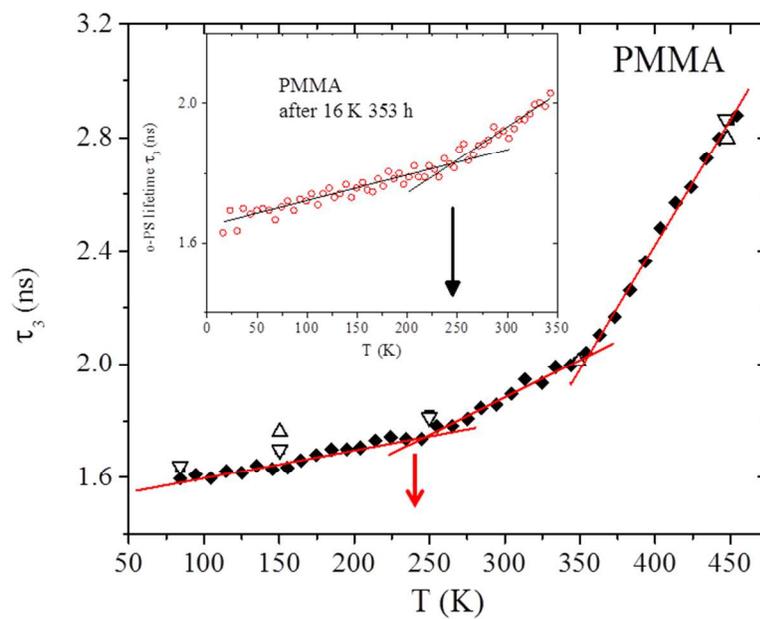
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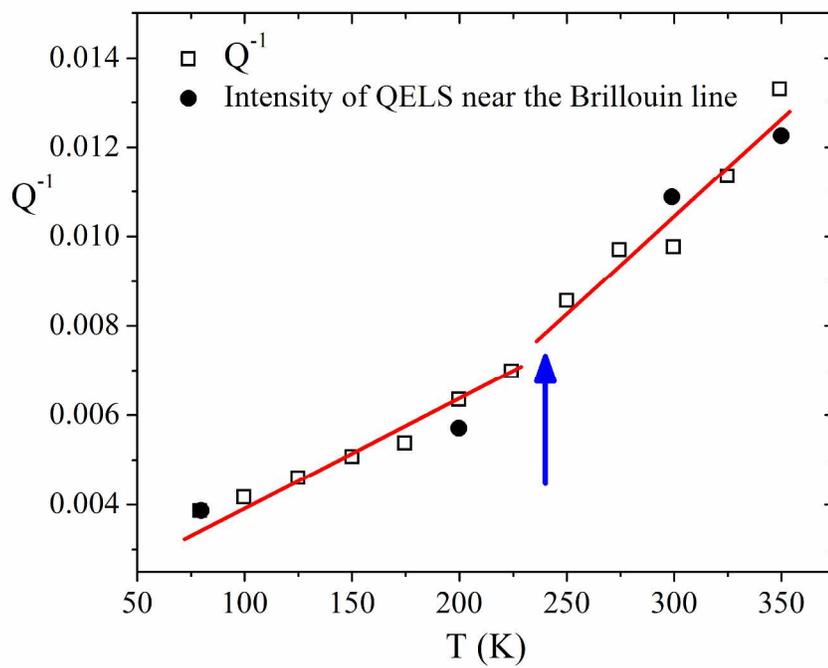


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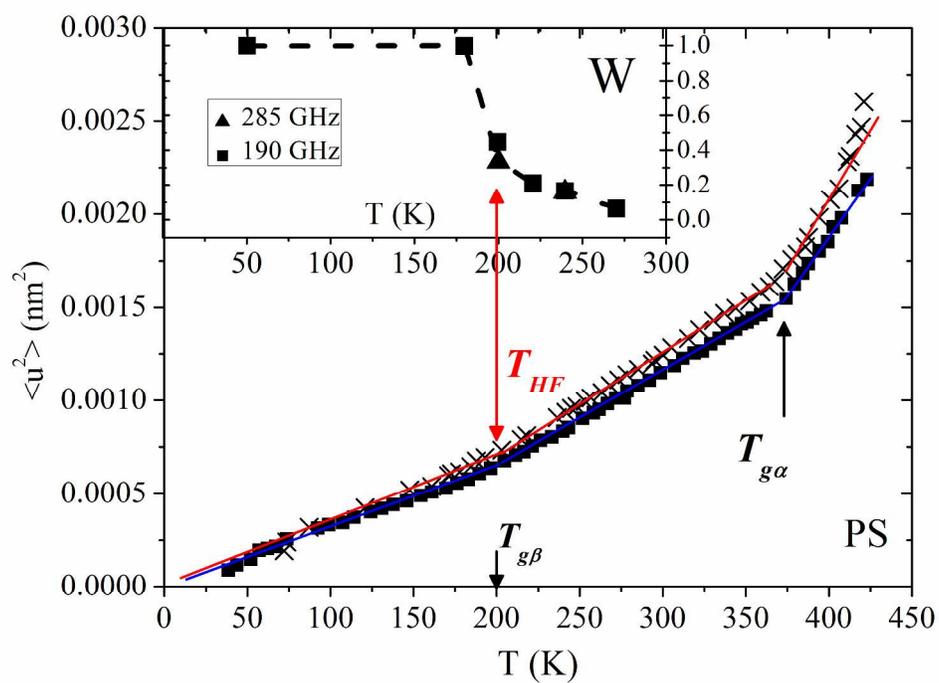


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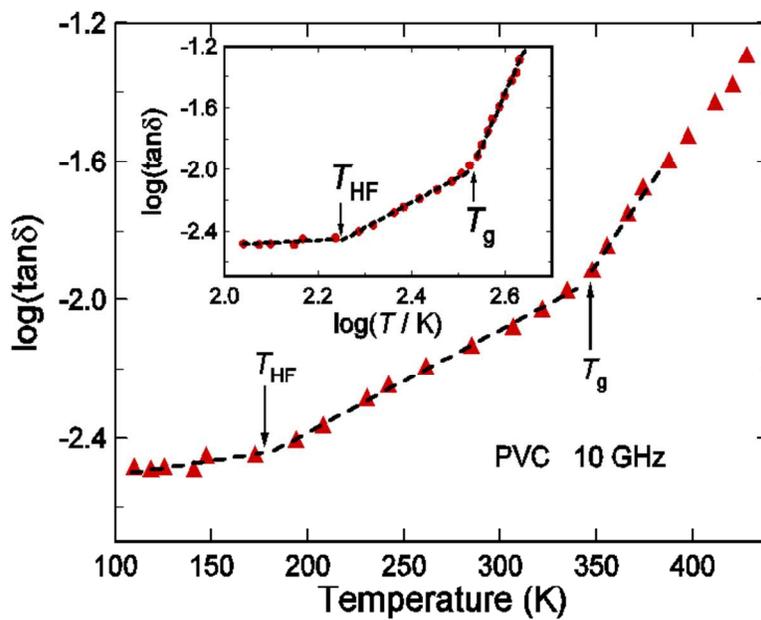




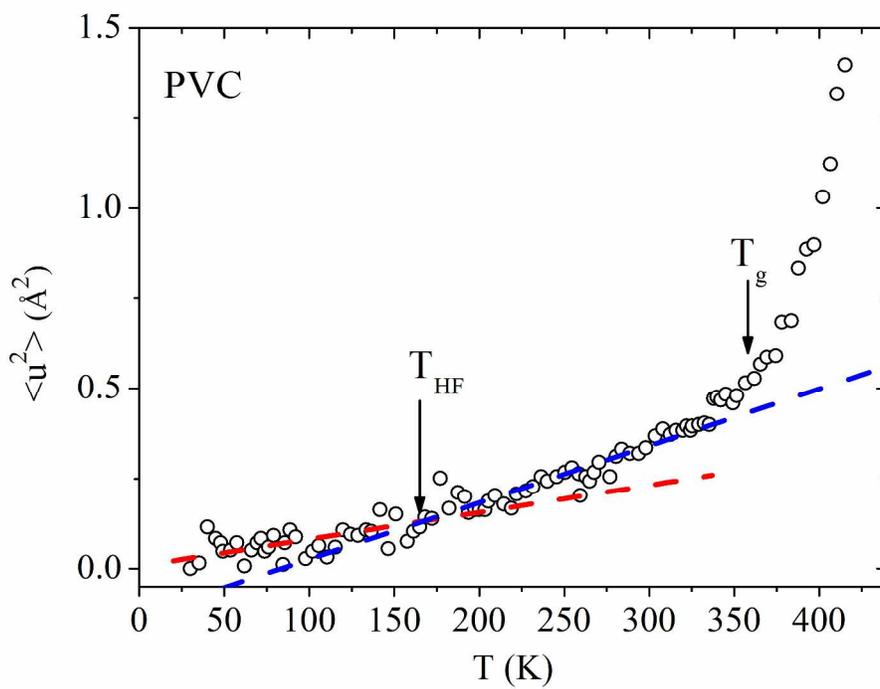
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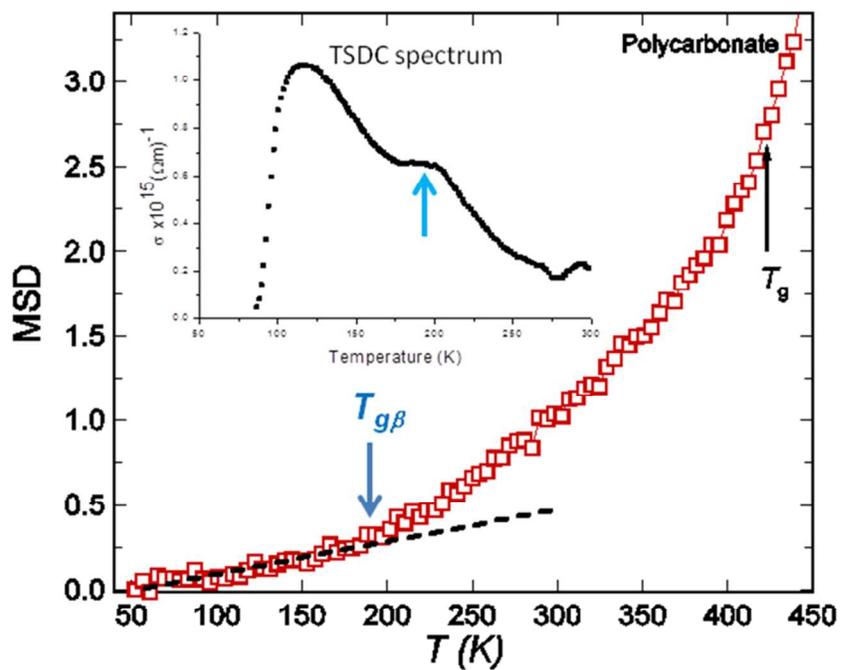
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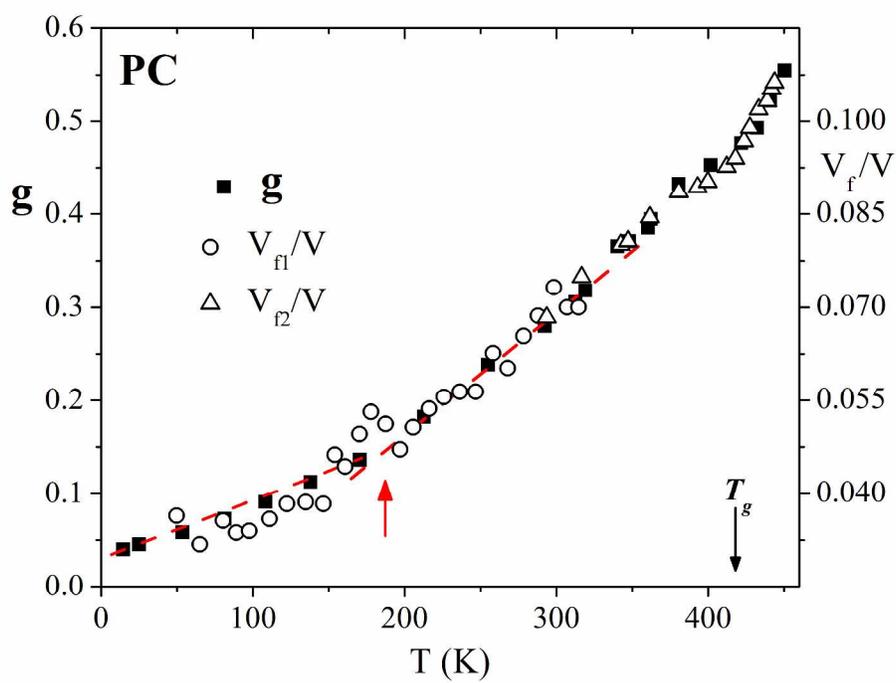
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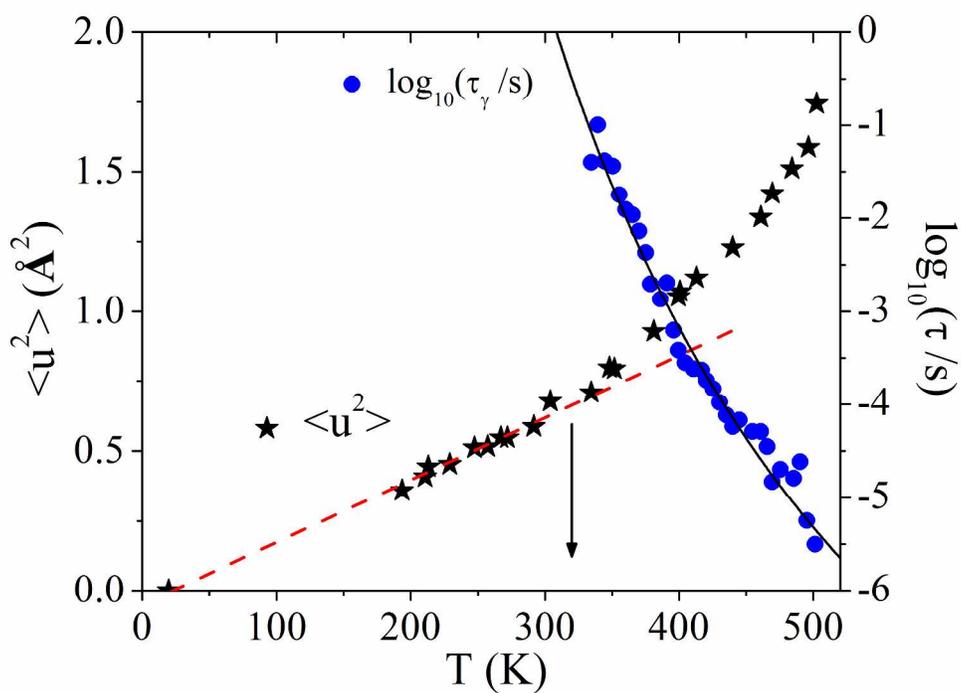
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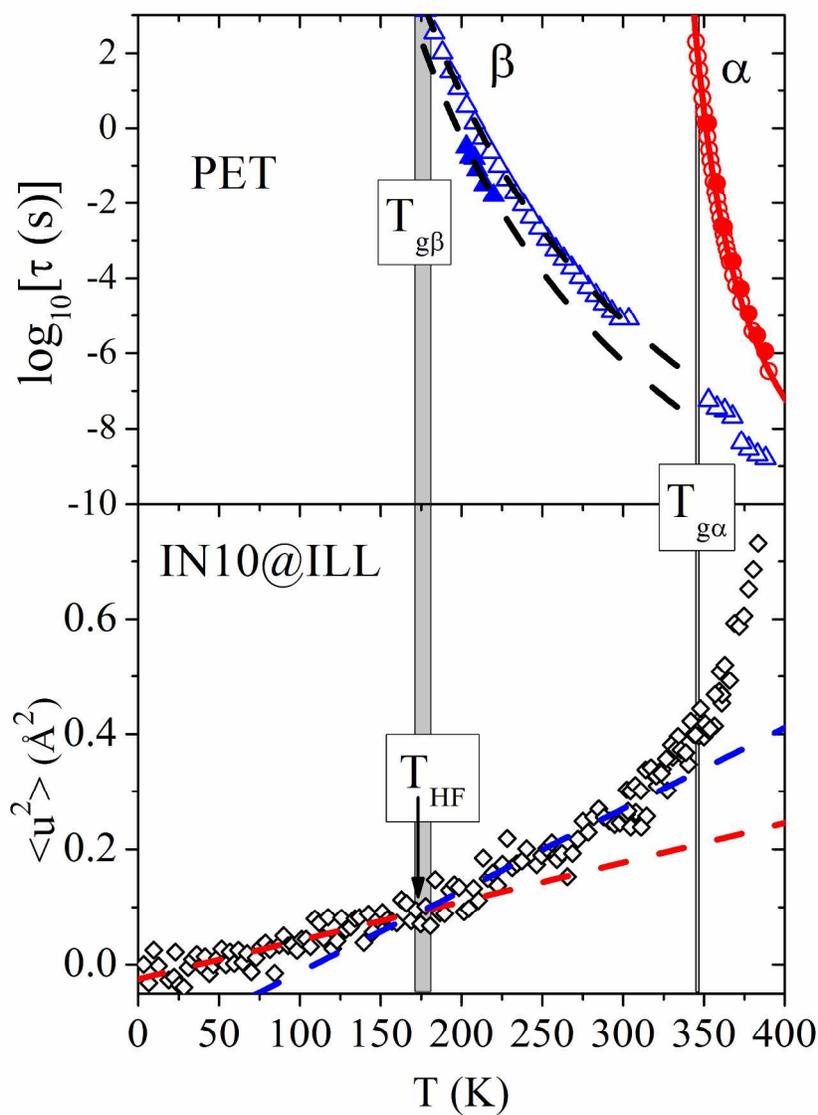
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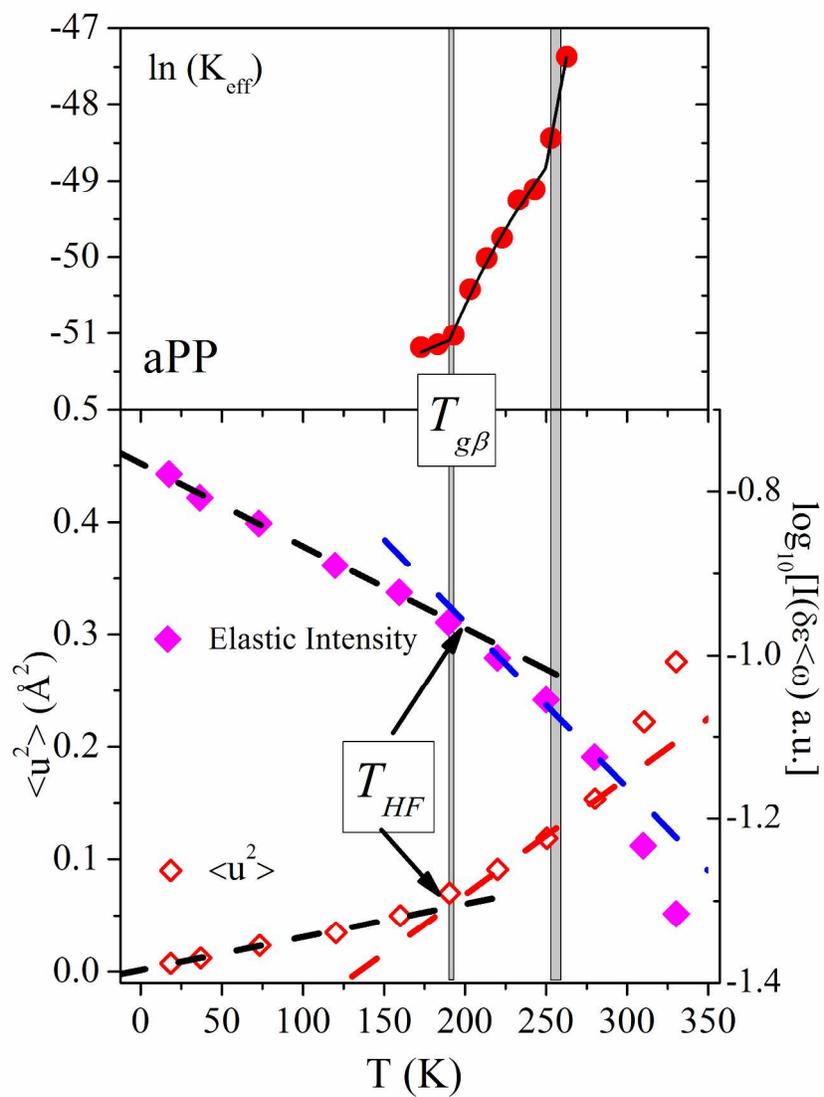
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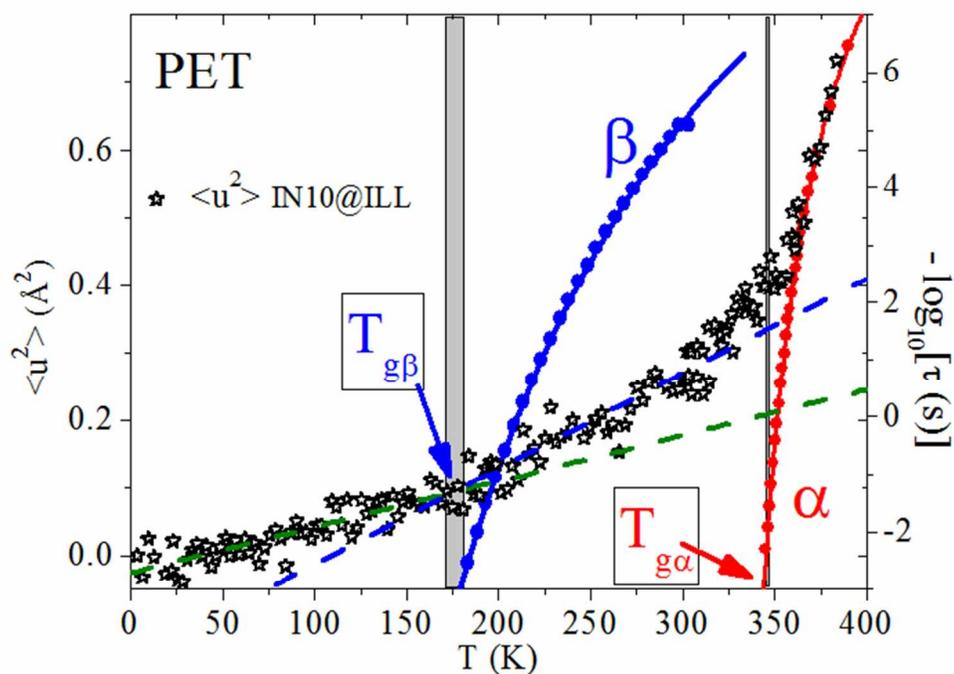
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TOC. Left side: mean square displacement, $\langle u^2 \rangle$, of amorphous PET (open black stars) as measured at the IN10 spectrometer by Sanz and co-workers [101] plotted as a function of temperature. Data are from ref.[101] and redrawn. The arrows indicate the location of $T_{g\beta}$ and $T_{g\alpha}$. Right side: logarithm of the reciprocal of α - (red and blue closed circles) and JG β -relaxation time from dielectric spectroscopy. $\beta\alpha\alpha$
60x42mm (300 x 300 DPI)

Coupling of Caged Molecule Dynamics to JG β -Relaxation II: Polymers

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^b*State Key Lab of Metastable Materials Science and Technology,
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Supplementary Information

Additional neutron scattering data on the temperature dependence of the fast caged dynamics of the polymers, BPA-polycarbonate and poly-isobutylene, are shown in Fig.S1 and Fig. S2 respectively.

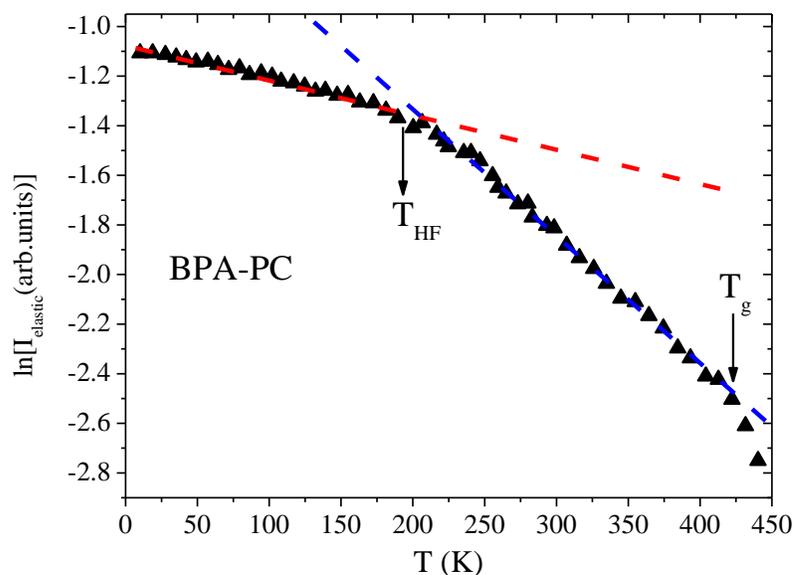


Fig. S1. The temperature dependence of the elastic intensity at $Q=1.83 \text{ \AA}^{-1}$ measured on BPA-PC by using IN16. Data are from ref.[S1] and redrawn. The red dashed line is a fit of the harmonic behavior at low temperature provided in ref. [S1]. The blue dashed line is a linear regression of the data at temperatures below T_g and above T_{HF} .

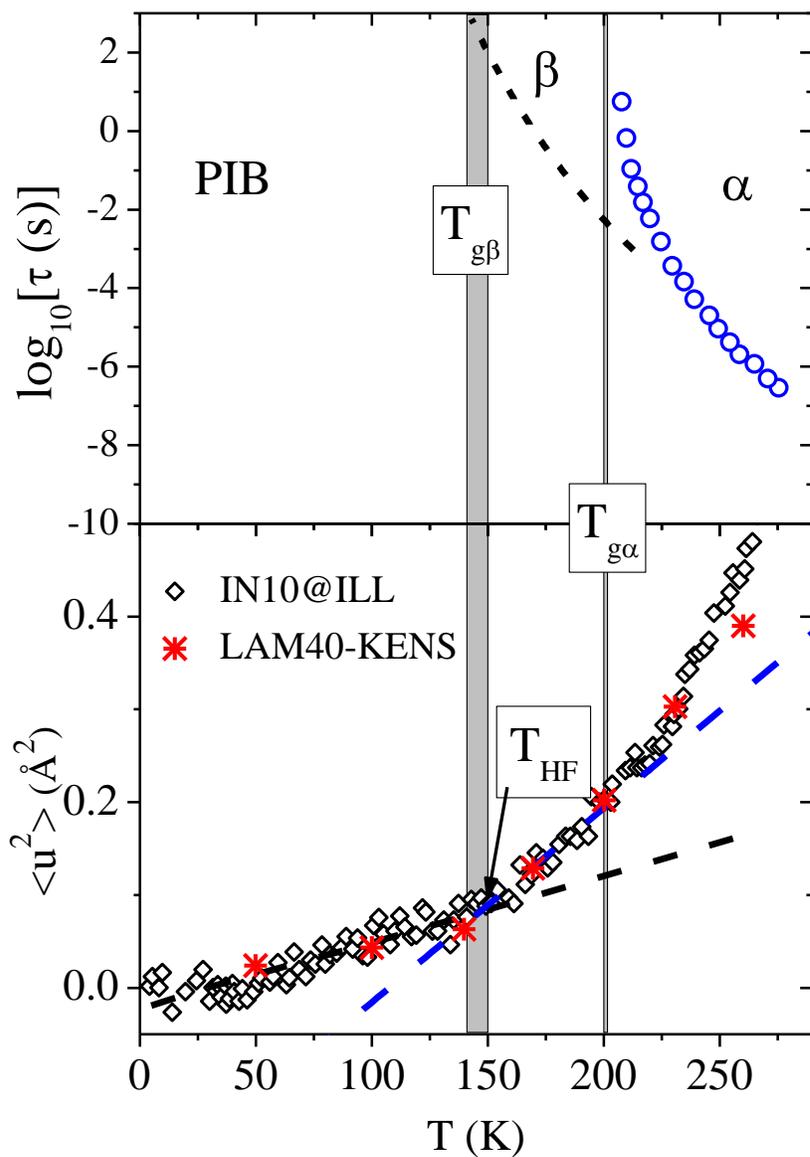


Fig. S2. Upper panel: Logarithm of the JG β -relaxation time^{S2} (black dashed line) and α -relaxation time^{S3} (blue open circles) of PIB plotted as a function of temperature. **Lower panel:** mean square displacement, $\langle u^2 \rangle$, of amorphous PIB as measured at the IN10

spectrometer (open black diamonds)^{S4} and at LAM40-KENS ($\delta E=0.02$ meV) (red asterisks)^{S5} plotted as a function of temperature. In order to have comparable y-range, the LAM40-KENS data have been multiplied by a constant factor ($4.35 = [\langle u^2 \rangle_{\text{IN10}}(T_g)] / [\langle u^2 \rangle_{\text{LAM}}(T_g)]$). The two dashed lines are linear regressions optimized to IN10 data in the low and intermediate temperature region. The arrow indicates the location of T_{HF} as obtained from the crossing of the two linear regressions. The low temperature gray shaded area ranges from the $T_{g\beta}$ value obtained when $\tau(T_{g\beta})=10^3$ s and T_{HF} . The narrow high temperature shaded area marks the value of $T_{g\alpha}$ from ref.[S4].

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