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Why the Relaxation Times of Polymers from Brillouin Light Spectroscopy Are Much Shorter than the Primary α - Relaxation Times

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Why the Relaxation Times of Polymers from Brillouin Light Spectroscopy are much shorter than the Primary α -Relaxation Times?

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ABSTRACT

Brillouin light spectroscopy (BLS) of polymers recorded much shorter relaxation times over the same temperature range than those obtained from other spectroscopies, including dielectric relaxation, dynamic light scattering, depolarized Rayleigh scattering, NMR, and molecular dynamics simulations. This is an anomaly because *a priori* BLS is thought to monitor the structural α -relaxation of polymers like all the other techniques. Firstly noted in 1977, the anomaly was repeated confirmed, but it has not been explained, and it remains a puzzling finding in amorphous polymers. In this paper we explain this longstanding anomaly by the Coupling Model (CM), in conjunction with the fact that the α -relaxation of polymers is non-exponential at the relatively high temperatures of BLS measurements. The CM has the primitive relaxation which is part of the Johari-Goldstein (JG) β -relaxation, and the precursor of the structural α -relaxation. The calculated primitive relaxation times match the BLS relaxation times quantitatively. This indicates that the primitive relaxation together with the JG β -relaxation of polymers is responsible for the phonon dispersion at hypersonic (GHz) frequencies, whereas the other spectroscopies probe mainly the α -relaxation. Additional support comes from quasielastic neutron scattering experiment in the same polymer, in which the primitive relaxation/JG β relaxation was directly observed with relaxation times in agreement with the calculated ones as well as the BLS relaxation times. Thus, the longstanding anomaly of polymers observed by BLS now has an explanation.

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1. INTRODUCTION

Brillouin light spectroscopy (BLS) is based on the inelastic scattering of light by the thermally induced hypersonic waves in the material. Energy and momentum conservation leads to the BLS frequency shift $\omega_B(q) = \pm c(q)q$ around the central Rayleigh line at a phonon wave vector, $q = k_s - k_i$, where k_i and k_s are respectively the wave vectors of the incident light with wavelength λ and the scattered light at a scattering angle θ . In a material with refractive index n , phonons having $q = (4\pi n/\lambda)\sin\theta/2$ propagate with the phase velocity $c(q)$. The BLS spectrum of homogeneous material consists therefore of a doublet at $\pm\omega_B$ with a full width at half maximum $\Gamma_B(q)$, and is associated with the longitudinal modulus $M^* = M' + iM''$, with $M' = \rho u^2$ and $M'' = M'\Gamma_B/\omega_B$, and ρ is the mass density of the material. The Brillouin spectrum,^{1,2} is given by $I(q, \omega) \propto 2\Gamma_p \omega_p^2 / \{[\omega_p^2 - \omega^2]^2 + [2\omega\Gamma_p]^2\}$ where, $\omega_p(q)$ and $2\Gamma_p(q)$ approximately correspond to the frequency position $\omega_B(q)$ and the linewidth $\Gamma_B(q)$ of the Brillouin line peaks. BLS has been applied starting from the 1970s to study the dynamics of structural α -relaxation in molecular¹⁻⁸ and polymeric glass-formers^{9,10,11,12,13,14,15,16}. The BLS data were analyzed¹² in terms of $\tan\delta = M''/M' = \Gamma_B/\omega_B$ at a single scattering angle (mostly 90°) or q . The variation of $\tan\delta$ with temperature at constant q attains its maximum at T_{\max} , where the frequency $\omega_B(T_{\max})$ matches the reciprocal of the relaxation time $\tau_{BLS}(T)$, and the relaxation time $\tau_{BLS}(T_{\max})$ is essentially given by $1/\omega_B(T_{\max})$. Since ω_B is in the high frequency range of 5 – 100 GHz, BLS probes relaxation process with relaxation frequency much higher than dielectric relaxation (DR), depolarized light scattering (DLS), photon correlation spectroscopy (PCS) (in the time domain), and ultrasonic attenuation (US).

In this paper we are concerned with the puzzling observation in the dynamics of polymers by BLS ever since the start of using of the technique for this purpose⁹⁻¹³. Operating at GHz

frequencies, BLS probes relaxation of the longitudinal modulus M^* with relaxation times in the range of 10–100 ps. It is supposed to probe the structural α -relaxation, and its relaxation times $\tau_{BLS}(T)$ is expected to be the same as $\tau_{DR}(T)$, $\tau_{DLS}(T)$, $\tau_{NMR}(T)$, and $\tau_{SIM}(T)$ from dielectric relaxation (DR), depolarized Rayleigh scattering (DLS), nuclear magnetic resonance (NMR), and molecular dynamics simulations (SIM). Surprisingly, the relaxation times $\tau_{BLS}(T)$ observed by BLS turn out to be shorter than those from the other spectroscopies by about one and a half orders of magnitude at the same temperatures, irrespective of the procedure used to fit the BLS spectrum¹³. The polymers include 1,4-*cis* polyisoprene (PI)¹³, atactic polypropylene (PP)¹³, and other polymers⁹. This intriguing observation was primarily found by temperature dependent BLS experiments performed at a single wave vector or frequency. More recently it was confirmed by Voudouris et al.¹³ in 1,4-*cis* polyisoprene (PI) by an improved BLS setup that allows the q -variation by almost one decade, and the dispersion measured isothermally by varying the frequency of the propagating density fluctuations from phonons. Moreover, by performing BLS in two samples, PI-1.5 and PI-5 with molecular weights of 1.5 and 5.0 kg/mol respectively, it was found that T_{\max} in PI-5 is higher than in PI-1.5 by 45 K. The difference in T_{\max} is comparable to the difference of 41 K in the T_g of the two samples. From this, it suggests that the frequency dispersion of $M^*(\omega)$ and $\tau_{BLS}(T)$ in PI is somehow associated with the structural α -relaxation and the glass transition. However the puzzling question that remains is why $\tau_{BLS}(T)$ of PI is so much shorter than $\tau_{DR}(T)$, $\tau_{DLS}(T)$, $\tau_{PCS}(T)$, and $\tau_{sim}(T)$ ^{13,17}, all of which are approximately equal and collectively denoted by $\tau_{\alpha}(T)$ from now on. One clue is the significant deviation of the frequency dispersion of $\tan\delta=M''/M'$ from the Debye form, indicative of a non-exponential time dependence. This is suggested also by the BLS study of the molecular glass-former, ortho-terphenyl (OTP).¹³ In contrast to polymers, the $\tau_{BLS}(T)$ of

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OTP is about the same as $\tau_\alpha(T)$ from the other spectroscopies, with $\tau_{BLS}(T)$ at most a factor 3 shorter than $\tau_\alpha(T)$, while $\tan\delta=M''/M'$ has the Debye form.

The purpose of this paper is to explain the anomalous $\tau_{BLS}(T)$ of polymers theoretically and quantitatively utilizing the Coupling Model¹⁸⁻²⁰ for structural α -relaxation of polymers. This is done by taking into account of the strongly non-exponential time correlation function of the structural α -relaxations of PI and PP obtained by DR, DLS, and molecular dynamics simulations^{13,14}. The fit to these experimental data of the α -relaxation in PI-1.5 by the Kohlrausch stretched exponential function^{13,17},

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

required fractional exponent $\beta_K=0.42\pm 0.02$,^{13,17} significantly less than 1 in the temperature range where $\tau_{BLS}(T)$ are obtained experimentally. We also considered the quasielastic neutron scattering (QENS) data of PI.²¹ The $\tau_{QENS}(T)$ obtained at wave vector $q=1.53 \text{ \AA}^{-1}$ at high temperatures of BLS measurements are in agreement with $\tau_{BLS}(T)$, and this is demonstrated to be another support of the CM explanation for the polymers. The fact found in ortho-terphenyl (OTP) that $\tau_{BLS}(T)$ is about the same as $\tau_\alpha(T)$ is also consistent with the CM explanation because $\tan\delta=M''/M'$ from BLS experiment of OTP has the Debye form, and also the α -relaxation of OTP has nearly exponential time dependence or stretched exponential function with $\beta_K \cong 1$ in the temperature range of BLS experiments.

2. THE COUPLING MODEL

In most studies of glass-forming molecular liquids and polymers, it is the cooperative structural α -relaxation that has attracted most attention in its dynamic and thermodynamic properties. The

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3 involvement of many interacting molecules or repeat units of polymer in the cooperative α -
4 relaxation generates intriguing properties, including dynamic heterogeneity, non-exponentiality,
5 and super Arrhenius temperature dependence. However, the α -relaxation is only the end of a
6 sequence of evolving processes. Chronologically the processes are^{18-20,22,23,24} (1) caged dynamics
7 when all molecules are mutually caged via the intermolecular potential; (2) the decay of cages
8 by the onset of local and independent (primitive) relaxation with relaxation time τ_0 ; (3) increasing
9 number of primitive relaxations with increasing spatial overlap, length-scale, and correlation;
10 and finally (4) the cooperative α -relaxation with the stretched exponential correlation function
11 and relaxation time τ_α , eq.(1), is reached when the length-scale attains the maximum determined
12 by the strength and range of the intermolecular potential. The existence of relations of one process
13 to another, means that the processes are not independent of each other as well as their properties.
14 The existence of this sequence of processes and their relationship were observed directly by
15 molecular dynamics simulations^{25,26}, confocal microscopy of colloidal suspensions²⁷, NMR²⁸,
16 and many other experiments demonstrated in ref.^{18-20,22-24}. The primitive relaxation (process 2)
17 together with its more complex counterpart (process 3) were observed collectively as the Johari-
18 Goldstein (JG) β -relaxation with effective relaxation time τ_β by experiments using various
19 spectroscopic techniques^{18-20,22-24}. The two relaxation times τ_β and τ_0 are approximately equal in
20 order of magnitude, as found in many glass-formers^{18-20,22-24,29}, and this relation was conveyed
21 symbolically by $\tau_\beta \approx \tau_0$. The strong connections of the precursor JG β -relaxation with the α -
22 relaxation (process 4) in properties were found in glass-formers of all kinds^{18-20,22-24,29}. Therefore
23 it is unsurprising to observe the faster JG β -relaxation together with the α -relaxation at
24 temperatures above the glass transition temperature T_g if the experimental time window cover
25 both the time scales of τ_α and τ_β .

It is desirable to be able to predict τ_0 quantitatively, and hence τ_β approximately, from τ_α theoretically. As far as we know, the Coupling Model (CM) is the only one capable of doing so by the relation¹⁸

$$\tau_\alpha = [t_c^{-n} \tau_0]^{1/(1-n)}, \quad (2)$$

where $t_c=1$ to 2 ps, τ_α and $(1-n)\equiv\beta_K$ are respectively the relaxation time and stretched exponent of the Kohlrausch correlation function for the α -relaxation in eq.(1). Note that τ_α becomes the same as τ_0 if $\beta_K=1$ or $n=0$. As shown by solutions of simplified models^{18,30}, the stretched exponential correlation function of the α -relaxation originates from classical chaos in molecular systems where the intermolecular potential is anharmonic. However, classical chaos starts only after a time t_c determined by the potential¹⁸. Before t_c the phase space is simple, and molecules relax individually and independently with the primitive relaxation rate $W_0\equiv 1/\tau_0$, and the correlation function is $\varphi(t) = \exp(-t/\tau_0)$. After t_c the relaxation rate assumes the time dependence of $W_0(t/t_c)^{-n}$, where $0\leq n<1$ and its value is determined by the intermolecular potential. The correlation function has the stretched exponential time dependence in eq.(1). The crossover of $\varphi(t)$ from exponential to stretched exponential functions of time was verified by quasielastic neutron scattering experiments, and $t_c=1$ to 2 ps was determined for polymers by quasielastic neutron scattering experiments.^{31-33,18} Continuity of the two correlation functions at t_c leads to the CM equation (3), and the companion approximate relation, $\tau_\alpha \approx [t_c^{-n} \tau_\beta]^{1/(1-n)}$. After giving this background, we are ready to address the anomalous BLS data of polymers.

3. THE NATURE OF THE BLS RELAXATION TIMES OF POLYMERS

In polymers, the structural α -relaxation involves cooperative motion of repeat units dictated by the intermolecular interaction. Its time correlation function is often described by the

Kohlrausch function given by eq.(1), and the corresponding susceptibility is proportional to its Fourier transform, $\varepsilon_K^*(f)$ for DR and $\chi_K(f)$ for DLS. At times shorter than $\tau_\alpha(T)$ or frequencies higher than the corresponding frequency $f_\alpha(T)$, present is the primitive relaxation and the JG β -relaxation.^{18-20,22-26} The primitive relaxation is related to the conformational transition of the polymer chain backbone from one rotational isomeric state to another in a single chain of bulk polymers. The conformational transition is accompanied by distortions of neighboring degrees of freedom in order to localize the motion and not affect the chain ends³⁴. For this reason the primitive correlation function is not an exponential function of time, but adequately described by the Hall-Helfand function,³⁴

$$\varphi_{HH}(t) = \exp(-t/\tau_1)\exp(-t/\tau_2)I_0(t/\tau_1) \quad (3)$$

or other related functions³⁵. The primitive rate is

$$W_0^{HH}(t) \equiv -\varphi_{HH}^{-1}d\varphi_{HH}/dt = \tau_2^{-1} + \tau_1^{-1}[1 - I_1(t/\tau_1)/I_0(t/\tau_1)] \quad (4)$$

where I_1 is the first-order modified Bessel function. The value of τ_1 is shorter than τ_2 by a factor of 3.6 found for polyisoprene in dilute solution³⁶. On applying the CM, the correlation function $\phi_\alpha(t)$ of the α -relaxation in polymers satisfies the equation³⁷,

$$d\phi_\alpha(t)/dt = -W_0^{HH}(t)(t/t_c)^{-n}\phi_\alpha(t). \quad (5)$$

The solution of the differential equation is

$$\phi_\alpha(t) = \exp - \int_0^t dt' W_0^{HH}(t')(t'/t_c)^{-n}, \quad (6)$$

which was obtained before numerically³⁷. The ratio $I_1(t/\tau_1)/I_0(t/\tau_1)$ in eq.(4) initially has zero value but rapidly increases to unity near $t=\tau_1$. Correspondingly, $W_0^{HH}(t)$ decreases from the initial value of $\tau_2^{-1} + \tau_1^{-1}$ and attains the constant value τ_2^{-1} at times $t \gg \tau_1$. From this

property of $W_0^{HH}(t)$, and when $t \gg \tau_1$, it follows that $\phi_\alpha(t)$ of the undiluted polymer becomes the stretched exponential function³⁷,

$$\phi_\alpha(t) = \exp [- (t/\tau_\alpha)^{1-n}], \quad (6)$$

and

$$\tau_\alpha(T) = [t_c^{-n} \tau_2(T)]^{1/(1-n)} \quad (7)$$

These results (6) and (7) are supported by the numerical solution of eq.(5) performed in ref.³⁷.

Eq.(7) enables τ_2 to be calculated from τ_α and the fractional exponent $(1-n) \equiv \beta_K$ in the Kohlrausch correlation (1) of the experimentally observed α -relaxation of the polymer.

Explicitly, τ_2 is given by

$$\tau_2(T) = [\tau_\alpha(T)]^{1-n} (t_c)^n \quad (8)$$

The two relaxation times, τ_1 and τ_2 , are for isolated and independent primitive relaxation occurring at different locations without overlap. The relaxation times of primitive relaxations with spatial overlap and longer length-scales are longer. Together they constitute the JG β -relaxation. To stress that the primitive relaxation is an integral part of it, we denote it by primitive/JG β relaxation from now on. Its most probable relaxation time τ_β is approximately equal to τ_2 in order of magnitude. Symbolized by $\tau_\beta \approx \tau_2$, this was found by experiments in many glass-formers^{18-20,22-24,29}. By rewriting eq.(7) in the form of, $\tau_\alpha/\tau_2 = (\tau_\alpha/t_c)^n$, and since $\tau_\alpha/t_c \gg 1$, it follows that τ_α is longer than $\tau_\beta \approx \tau_2$ if n is larger than zero, as in the case of polymers. On the other hand, τ_α is the same as $\tau_\beta \approx \tau_2$ if $n=0$ as in the case of OTP.

3.1 Polyisoprene

The primitive/JG β relaxation contributes to the dielectric susceptibility $\varepsilon_{\beta}^*(f)$ or dynamic light scattering (DLS) susceptibility $\chi_{\beta}(f)$ with relaxation times $\tau_{\beta} \approx \tau_2$. This contribution precedes in time the contribution $\varepsilon_{\alpha}^*(f)$ or $\chi_{\alpha}(f)$ from the α -relaxation with the stretched exponential correlation function (eq.6). The α -relaxation of PI-1.5 were studied, and its relaxation times $\tau_{\alpha}(T)$ and the stretch exponent $\beta_K \equiv (1-n)$ of the Kohlrausch correlation function determined¹⁷ in the same and relatively high temperature range where the relaxation times $\tau_{BLS}(T)$ were determined by BLS.¹³ The α -relaxation is highly non-exponential with β_K significantly less than 1. The same sample PI-1.5 with molecular weight of $M_w=1.5$ kg/mol were studied by DS, DLS, and MD simulations, and the same value $(1-n)=0.42 \pm 0.02$ was deduced, and the values of $\tau_{\alpha}(T)$ determined are practically the same^{13,17}. The experimental relaxation times $\tau_{BLS}(T)$ and $\tau_{\alpha}(T)$ of PI-1.5 shown before in ref.¹³ are replotted against reciprocal temperature in Fig.1. Added in Fig.1 are the two relaxation times²¹, $\tau_{QENS}(q, T)$, from quasi-elastic neutron scattering (QENS) measurements of PI-5 at scattering vector $q=1.53 \text{ \AA}^{-1}$ and $T=300$ and 320 K .²¹ The two $\tau_{QENS}(q, T)$ are located near $\tau_{BLS}(T)$ and also much shorter than $\tau_{\alpha}(T)$. This is not an accident, and the reason for this will be given later. For each datum of $\tau_{\alpha}(T)$, eq.(8) was used to calculate $\tau_2(T)$ with $\beta_K \equiv (1-n)=0.42$ and $t_c=2$ ps determined by QENS experiments for polymers^{18,31-33}. Shown in Fig.1, the calculated $\tau_2(T)$ are much shorter than $\tau_{\alpha}(T)$. More importantly, $\tau_2(T)$ are in approximate agreement with $\tau_{BLS}(T)$. Since $\tau_{\beta}(T) \approx \tau_2(T) = \tau_{BLS}(T)$, it follows that the primitive relaxation/JG β relaxation is the origin of the BLS data, and explains why $\tau_{BLS}(T)$ is about one and a half decades shorter than $\tau_{\alpha}(T)$ determined by DR, DLS and simulations. Moreover, the time dependence of the primitive relaxation given by the H-H function in eq.(3) is non-exponential, and also primitive/JG β relaxation is composed of

the isolated primitive relaxation and overlapping primitive process, it is non-exponential. This explains why $\tan\delta = M''/M'$ of PI-1.5 observed by BLS is broader than the single Debye expression.¹³

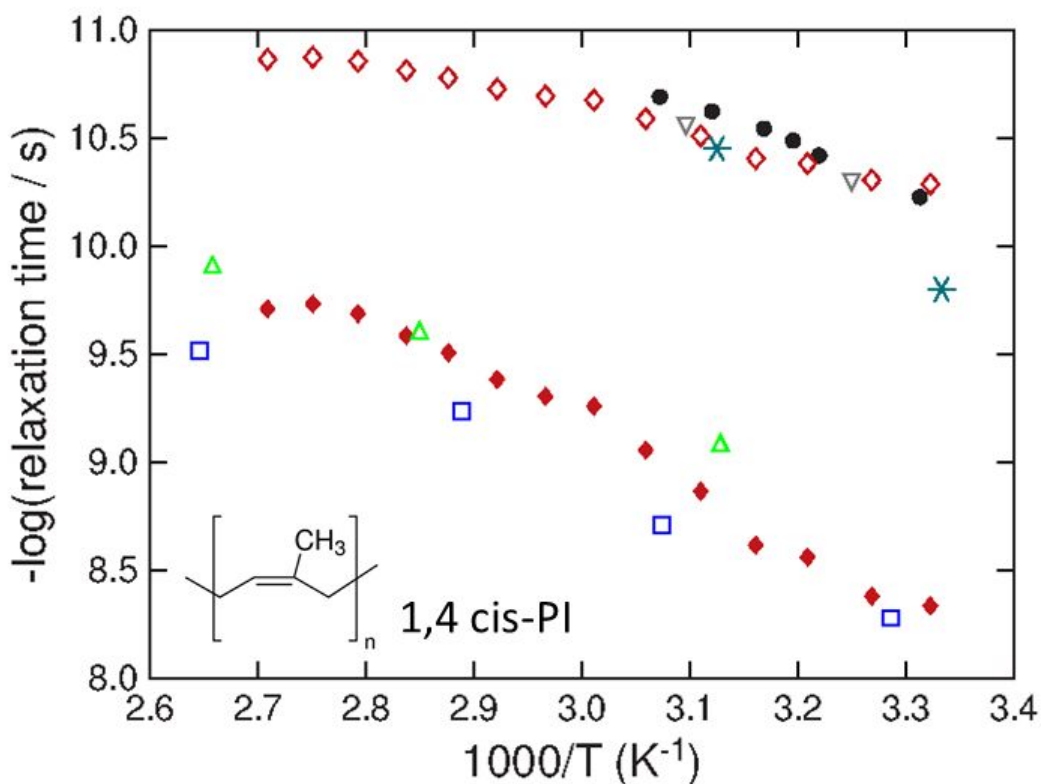


Fig.1 Arrhenius plot of the different α -relaxation times $\tau_\alpha(T)$ of PI-1.5 as probed by different experimental techniques from refs.^{13,17}. DS (closed diamonds), depolarized dynamic light scattering (DLS) (squares) and theoretical predictions from MD simulation of the torsion angle relaxation (open triangles). The BLS relaxation times obtained from the $\tan \delta$ data (\bullet) and from the fit of the generalized hydrodynamic theory to the experimental spectra at a constant wave vector q corresponding to max of $\tan \delta$ for high resolution conditions (open inverted triangles). The open red diamonds represent the calculated $\tau_2(T)$ with $\beta_K \equiv (1-n) = 0.42$ and $t_c = 2$ ps by eq.(8) from $\tau_\alpha(T)$. The two blue stars are $\tau_{QENS}(q, T)$ at $q = 1.53 \text{ \AA}^{-1}$ from neutron scattering²¹.

We return to discuss the two relaxation times, $\tau_{QENS}(q, T)$, of PI-1.5 from QENS²¹ at $q=1.53 \text{ \AA}^{-1}$ and $T=300$ and 320 K shown in Fig.1. The original data were taken from the relaxation map in ref.²¹ and reproduced in Fig.S1 of Supporting Information (SI), where one can see that the times $\tau_{QENS}(q, T)$ are shorter than $\tau_{DLS}(q, T)$ by about 2 orders of magnitude, and it is like $\tau_{BLS}(q, T)$ in Fig.1. As mentioned before, it can be seen from Fig.1 that $\tau_{QENS}(q, T)$ and $\tau_{BLS}(q, T)$ are comparable. This is no accident because we shall show below that $\tau_{QENS}(q, T)$ at $q=1.53 \text{ \AA}^{-1}$ is one of the q -dependent β -relaxation times, $\tau_{\beta}(q, T)$, of the primitive/JG β relaxation, and should be comparable to $\tau_{\beta}(T) \approx \tau_2(T) = \tau_{BLS}(T)$. By anticipating this result, we conclude the data of $\tau_{QENS}(q, T)$ at $q=1.53 \text{ \AA}^{-1}$ throw additional support of identifying $\tau_{BLS}(T)$ as the primitive/JG β relaxation time, $\tau_{\beta}(T) \approx \tau_2(T)$, of polymers.

The reported q -dependence of the relaxation times $\tau_{QENS}(q, T)$ of PI-1.5 at 300 K ²¹ is reproduced in Fig.S2 of SI. At $q=1.53 \text{ \AA}^{-1}$ or $\log_{10}(q/\text{\AA}^{-1})=0.185$, and $T=300$, $\tau_{QENS}(q, T)$ has the q^2 -dependence as shown by the red broken line in Fig.S2. Such behavior of $\tau_{QENS}(q, T)$ for q larger than q^* at which the static structure factor $S(q)$ shows its first maximum, was found in QENS study of polyisobutylene (PIB) at $T=335, 365, \text{ and } 390 \text{ K}$, and $\tau_{QENS}(q, T)$ in the 10^{-10} s range³⁸, as reproduced in Fig.S3 of SI. From the $\tau_{QENS}(q, T)$ at the 3 temperatures, the Arrhenius activation energy of 0.43 eV or 41.5 kJ/mol for PIB was given, which is close to $24RT_g$ with $T_g=200 \text{ K}$ typical of the activation energy of JG β -relaxation. This is to be compared with $\tau_{BLS}(T)$ of PI-1.5 with $T_g=188 \text{ K}$ having an activation energy of 32 kJ/mol from the fit to the Arrhenius dependence in ref.¹³, and it corresponds to $20.5 RT_g$. Again this is indication of $\tau_{BLS}(T)$ of PI-1.5 corresponds to that of the primitive/JG β relaxation.

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The same properties from QENS of PI-1.5 and PIB was found by molecular dynamics simulations of polyisoprene performed at one temperature 363 K,³⁹ and are reproduced in Fig.S4 of SI. Shown in this figure is the non-Gaussian parameter $\alpha_2(q)$. In the range $q > q^*$ where $\tau_{QENS}(q, T)$ has the q^{-2} -dependence, $\alpha_2(q)$ is large and increases with increasing q to reach a maximum at q slightly larger than 3 \AA^{-1} . Such non-Gaussian character is consistent with the primitive/JG β relaxation, which is a distribution of processes composed of the isolated primitive relaxation at shorter times and those with spatial overlap at longer times. It can be seen from the $S(q)$ of PI given in ref.³⁹ that the wave vector $q=1.53 \text{ \AA}^{-1}$ in the QENS experiment²¹ exceeds q^* . Therefore from the non-Gaussian character, $\tau_{QENS}(q, T)$ of PI-1.5 at $q=1.53 \text{ \AA}^{-1}$ can be identified as one within the distribution of the q -dependent relaxation times $\tau_\beta(q, T)$ of the JG β relaxation. Another support of this conclusion can be drawn from the study of 1,4-*cis-trans* polybutadiene by the nuclear resonance synchrotron X-ray scattering technique covering a wide time range (10^{-9} to 10^{-5} s) and a q range (0.96 to 4.0 \AA^{-1}) by Kanaya et al.⁴⁰ Reproduced in Fig.S5, the results from the experiment show the q -dependence relaxation times $\tau_\beta(q, T)$, and directly prove for $q > q^*$ ($=1.3 \text{ \AA}^{-1}$) that the relaxation probed is within the distribution composing the JG β -relaxation, and not the α -relaxation with τ_α having the distinctly different q^{2/β_K} -dependence at lower values of q ^{38,39}. According to the simulations of PI³⁹, the q^{2/β_K} -dependence of the α -relaxation exists in the q -range, $q < 1 \text{ \AA}^{-1}$, and corresponds to the α -relaxation.

By the way, the q^{2/β_K} -dependence of τ_α is also a result of the CM via either eq.(2) by inserting the q^{-2} -dependence of τ_0 into eq.(2) or q^{-2} -dependence of τ_2 into eq.(7). Fig.S4 from simulations of PI, the value of the exponent $2/\beta_K=5$ was obtained from slope of the $\log \tau_\alpha$ vs.

log q . Hence, $\beta_K=0.40$, and it compares favorably with $\beta_K=0.42$ from experiments of DS and DLS. The range of τ_α from simulations in Fig.S4 is comparable to that of the experimental τ_α shown in Fig.1. Thus the q^{2/β_K} -dependence of τ_α from simulations provide another support the highly non-exponential time correlation function of the α -relaxation, which is key to understand why $\tau_{BLS}(T)$ is so much faster than $\tau_\alpha(T)$ by the CM eq.(8) with $(1-n)\equiv\beta_K=0.42$.

In the Introduction we have mentioned the BLS measurements in two samples, PI-1.5 and PI-5 with molecular weights of 1.5 and 5.0 kg/mol respectively¹³. The variation of $\tan\delta$ with temperature at constant q attains its maximum at higher T_{\max} in PI-5 by 45 K than in PI-1.5. The difference in T_{\max} is comparable to the difference of 41 K in the T_g of these samples¹³. Notwithstanding, this does not mean $\tau_{BLS}(T)$ of BLS in PI-1.5 has to be identified with the structural α -relaxation. It is true that the temperatures of the α -relaxation times $\tau_\alpha(T)$ from DR, DLS, and molecular dynamics simulations of PI-5 are shifted by amount comparable to the difference of its T_g from that of PI-1.5. Nevertheless, the temperatures of $\tau_2(T)$ calculated from $\tau_\alpha(T)$ by eq.(8) are shifted by the same amount, and hence also $\tau_{BLS}(T)$ because of our explanation that

$$\tau_2(T)\approx\tau_\beta(T)=\tau_{BLS}(T). \quad (9)$$

3.2 Polypropylene

BLS was employed to measure the relaxation times $\tau_{BLS}(T)$ of amorphous polypropylene (PP)¹³. The sample has $M_w=3.5$ kg/mol and $T_g=258$ K. The $\tau_{BLS}(T)$ extracted from the experimental $\tan\delta$ at different q values are shown in Fig. 2 together with the relaxation times $\tau_{DR}(T)$ and $\tau_{PCS}(T)$ obtained from DR and PCS experiments on the same sample and $\tau_{SIM}(T)$

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3 from molecular dynamics simulations (SIM) for an atactic PP melt of similar molecular mass⁴¹.
4 Like PI-1.5, $\tau_{BLS}(T)$ of PP are shorter than $\tau_{DR}(T)$, $\tau_{PCS}(T)$, and $\tau_{SIM}(T)$, interpolated by the
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6 Vogel-Fulcher-Tammann (VFT) law (solid line), by more than an order of magnitude. Included
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8 are the ¹³C NMR relaxation times $\tau_{NMR}(T)$ ⁴², and it was identified before in ref.⁴³ as the
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10 segmental α -relaxation. Deduced from the measured C–H bond vector second-order orientation
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12 autocorrelation function, the time dependence of the α -relaxation was fitted to the Kohlrausch
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14 function in eq.(1) with $\beta_K=0.55$.⁴² This value of β_K is the same as deduced from fit to ¹³C NMR
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16 data of PP by the modified KWW function and shown in Table 2 of ref.⁴⁴. We used this value
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18 of $\beta_K=0.55$ from ref.⁴² and again $t_c=2$ ps in eq.(8) to calculate $\tau_2(T)$ from the VFT dependence
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20 of $\tau_\alpha(T)$. Shown by the blue line in Fig.2, the calculated $\tau_2(T)$ are in approximate agreement
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22 with $\tau_{BLS}(T)$. Since the primitive/JG β relaxation time $\tau_\beta(T)$ is approximately equal to $\tau_2(T)$, it
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24 follows that $\tau_\beta(T)$ is also approximately equal to $\tau_{BLS}(T)$. Thus the primitive relaxation/JG β
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26 relaxation is the origin of the BLS data, and this explains why $\tau_{BLS}(T)$ is about one and a half
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28 decades shorter than $\tau_\alpha(T)$ determined by DR, DLS and simulations.
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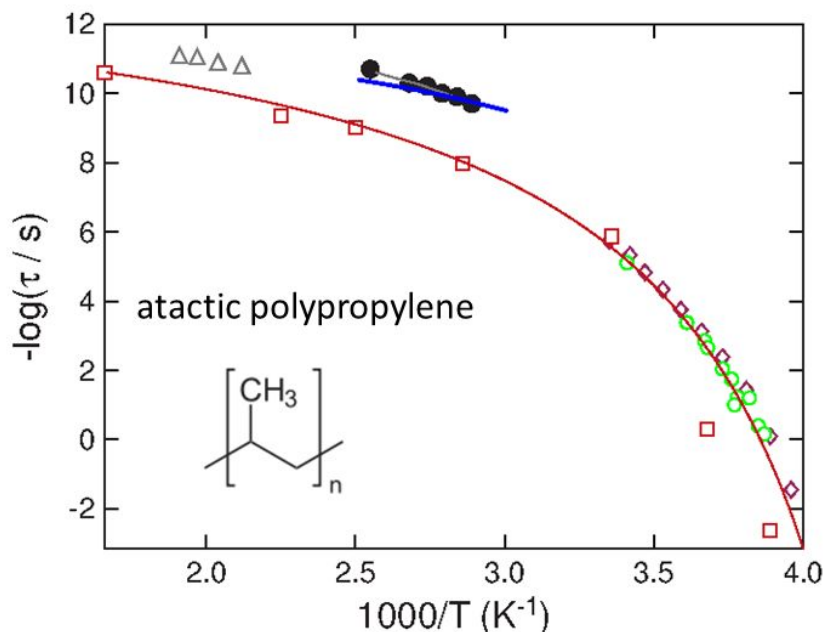


Fig. 2 Arrhenius plot of the different relaxation times associated with the glass transition process in PP as probed by different experimental techniques PCS (circles), DS (rombi), BLS (filled circles), NMR (open triangles) and MD simulations (squares).¹³ The solid line denotes the VFT fit of the PCS, DS, and MD α -relaxation times. The blue line near the BLS data $\tau_{BLS}(T)$ is $\log \tau_2$ calculated by eq.(8) with $\beta_k=0.55$ determined by simulations and ¹³C NMR in refs.42 and 44 respectively. The straight grey line is drawn to indicate temperature dependence of $\tau_{BLS}(T)$ is close to Arrhenius.

3.3 Ortho-terphenyl (OTP)

In the previous two subsections we have explained the finding of $\tau_{BLS}(T)$ being much shorter than $\tau_\alpha(T)$ in polymers by identifying $\tau_{BLS}(T)$ with the primitive/JG β relaxation times $\tau_2(T) \approx \tau_\beta(T)$. The crux of the explanation is the non-exponential time correlation function of the α -relaxation, or $\beta_k \equiv (1-n)$ significantly less than 1, making it possible for $\tau_2(T)$ calculated by eq.(8) to match $\tau_{BLS}(T)$. Hypothetically, if there is a polymer having the time correlation function of the

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α -relaxation being exponential or $\beta_K \equiv (1-n) = 1$, then τ_2 becomes the same as τ_α . Our CM explanation would not be consistent unless for this hypothetical polymer that $\tau_{BLS}(T)$ becomes the same as $\tau_\alpha(T)$ from DR and DLS. So far no polymer studied by BLS satisfy the condition of $\beta_K \equiv (1-n) = 1$ to test consistency of our explanation. However, the molecular glass-former ortho-terphenyl (OTP) offers an opportunity for such test. This is because at temperatures high above $T_g = 243$ K, and in the range of BLS measurements of $\tau_{BLS}(T)$ for OTP, a single Lorentzian line describes well the DLS spectra,¹³ indicating the correlation function of the α -relaxation is an exponential function of time, or $\beta_K \equiv (1-n) = 1$ in the Kohlrausch function in eq.(1). The exponential behavior of the α -relaxation far above T_g is consistent with the $\tan\delta = M''/M'$ from BLS of OTP conforming to the Debye function.

BLS spectra were also measured for OTP at different temperatures and at different q .¹³ The BLS relaxation times $\tau_{BLS}(T)$ obtained in the same manner as PI-1.5 and PP were plotted in Fig. 7 of ref.¹³ together with the α -relaxation times $\tau_\alpha(T)$ from depolarized DLS^{13,45-49}, PCS⁴⁵ and dielectric relaxation⁵⁰, and acoustic⁵¹ (impulsive stimulated thermal scattering) measurements in the sub-gigahertz region. The collection of the data are reproduced in Fig.S6 in SI. Based on these extensive experimental data of $\tau_\alpha(T)$ from several DLS studies⁴⁵⁻⁴⁹ put together to compare with $\tau_{BLS}(T)$, it was shown in ref.¹³ that $\tau_{BLS}(T)$ and $\tau_\alpha(T)$ are practically the same and the disparity is no more than a factor of 3 with BLS being faster. Therefore the anomaly of BLS found in the polymers is no longer present in OTP, and this finding verifies consistency of the CM explanation for polymers.

4. DISCUSSION AND CONCLUSION

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The main objective of this paper is to provide a theoretical explanation of the anomaly found in the study by Brillouin light spectroscopy (BLS) of the structural α -relaxation in amorphous polymers. It is generally found that the BLS relaxation times $\tau_{BLS}(T)$ are shorter by more than one order of magnitude than the structural α -relaxation times $\tau_{\alpha}(T)$ identified with either $\tau_{DR}(T)$, $\tau_{DLS}(T)$, or $\tau_{SIM}(T)$ obtained respectively from dielectric relaxation, dynamic light scattering, and molecular dynamics simulations. The anomaly was noticed first by Patterson⁹ in 1977 and later by others¹⁰⁻¹² based on a single wave vector (frequency). Finally the anomaly was firmly established by Voudouris et al.¹³ using a new q -dependent BLS spectrometer at gigahertz frequencies in polyisoprene (PI) and atactic polypropylene (PP) in 2010. Despite the experimental advance, the anomaly remained unexplained on a theoretical basis since then.

We applied the Coupling Model (CM) to explain the BLS anomaly. The CM predicts the presence of the independent primitive relaxation and overlapping primitive relaxations with larger length-scales at longer times. Altogether these processes are combined into the primitive/JG β relaxation having a distribution of relaxation times, and is the indispensable precursor of the cooperative α -relaxation. The primitive relaxation time and the JG β -relaxation time are comparable, and can be obtained by the CM eq.(8) quantitatively from the relaxation time τ_{α} and the fractional exponent $\beta_K \equiv (1-n)$ of the Kohlrausch correlation function of the α -relaxation. The latter for polymers at temperatures where the BLS relaxation times $\tau_{BLS}(T)$ were measured, and β_K typically falls within the range $0.45 < \beta_K < 0.60$, and the α -relaxation time $\tau_{\alpha}(T)$ are longer than about 1 ns. Under this condition, the calculated primitive relaxation times and hence the JG β -relaxation time $\tau_{\beta}(T)$ are in quantitative agreement with the experimentally observed BLS relaxation times $\tau_{BLS}(T)$. Thus it is the primitive relaxation/JG β relaxation that is picked up by BLS at higher frequencies, while the slower α -relaxation is observed by DR and

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DLS at lower frequencies. This is a quantitative explanation of the anomalous Brillouin light scattering data of polymers. Additional support of the explanation comes from quasielastic neutron scattering (QENS) experiment of polymers²¹. The experiment found $\tau_{QENS}(q, T)$ of PI-1.5 at $q=1.53 \text{ \AA}^{-1}$ is much shorter than $\tau_{\alpha}(T)$, and from its q^2 -dependence that it can be identified as one in the distribution of relaxation times of the primitive/JG β -relaxation. Moreover, $\tau_{QENS}(q, T)$ at $q=1.53 \text{ \AA}^{-1}$ is approximately the same as $\tau_2(T)$ calculated from the CM and $\tau_{BLS}(T)$ from the BLS experiment.

It is worthwhile to point out that the independent primitive relaxation time $\tau_2(T)$ calculated by eq.(8) is much shorter than $\tau_{\alpha}(T)$ for all temperatures considered in Figs.1 and 2. This is because $n \equiv (1 - \beta_K)$ is non-zero (0.58 for PI and 0.45 for PP), and $t_c = 1$ to 2 ps, and eq.(8) ensures that. Thus the primitive relaxation and the shorter time processes in the JG β relaxation observed in BLS experiment have not merged with the α -relaxation in these polymers over the temperature range where $\tau_{BLS}(T)$ and $\tau_{QENS}(q, T)$ at $q=1.53 \text{ \AA}^{-1}$ shown in Fig.1.

Had the correlation function of the α -relaxation been exponential or close to exponential function of time, i.e., $\beta_K=1$, the CM eq.(8) would predict no difference between $\tau_{\alpha}(T)$ and $\tau_{BLS}(T)$ because $\tau_2(T)$ or $\tau_0(T) = \tau_{\beta}(T) = \tau_{\alpha}(T)$. In other words, BLS also detects the same α -relaxation as DR and DLS, and the anomaly is no longer present. This scenario is realized in the molecular glass-former ortho-terphenyl, as demonstrated by Voudouris et al.¹³ We add another example of this behavior from the molten salt $2\text{Ca}(\text{NO}_3)_2 \cdot 3\text{KNO}_3$. The data are shown in Fig.S6 of SI.

Supporting Information

Quasielastic neutron scattering of PI, q^2 -dependence of relaxation times of PI and PIB, static structure factor and non-Gaussian parameter of PI, q -dependence of JG β -relaxation of

polybutadiene by the nuclear resonance synchrotron X-ray scattering technique, various relaxation times of OTP and CKN including those from BLS.

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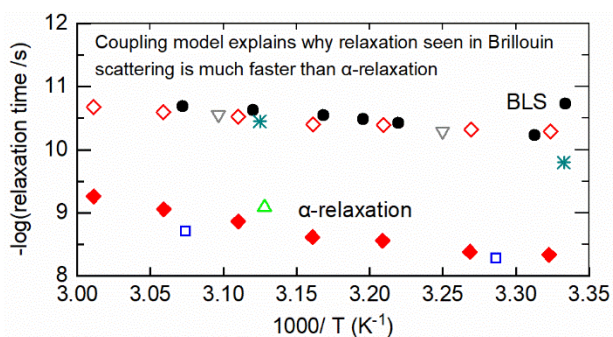
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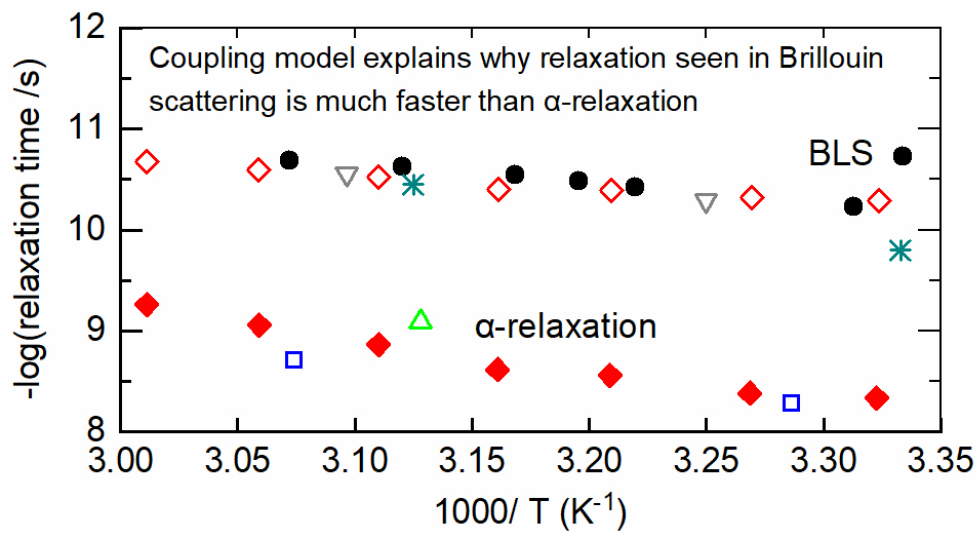
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