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Study of PVAc/EVA Polymer Series: Influence of the Inter/Intra -molecular Interaction Ratio on the Molecular Mobility at the Glass Transition

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ABSTRACT

In this work, the molecular mobility at the glass transition of poly(vinyl acetate) (PVAc) and poly(ethylene-co-vinyl acetate) (EVA) amorphous sample series was investigated. The temperature and pressure dependences of the intermolecular interactions were studied from time-temperature-pressure superpositions, and from the relaxation time dispersion of the segmental relaxation. The difference in terms of intermolecular interactions due to the lateral group ratio of vinyl acetate (VAc), was then estimated from the activation volume and related to the cooperative behavior. The isobaric fragility and its two contributions (thermal and volumetric) were estimated through high pressure BDS measurements. The volumetric and thermal contributions show different behaviors as a function of the VAc ratio and as a function of the pressure. Thus, the study of PVAc/EVA series has allowed to emphasize that the intramolecular and intermolecular interactions, induced by the dipolar pendant groups, directly influence the thermal and volumetric contributions to the isobaric fragility.

INTRODUCTION

The relaxation process associated with the glass transition in polymers, known as segmental relaxation, has been extensively investigated since the middle of the 20th century.¹⁻⁵ However, the connections between macromolecular chain chemistry, microstructure, and relaxation dynamics remain incompletely understood. A common feature among glass-formers is the viscous slowing down of structural relaxation dynamics observed around the glass transition temperature T_g .⁶⁻⁸ Various models and approaches have been proposed to classify the temperature dependence of the dynamic viscosity and the relaxation time. Angell introduced a classification of glass-forming liquids based on relaxation time variations normalized to T_g .⁹ This classification identifies glass formers as "strong" or "fragile" based on the steepness of their relaxation time temperature dependence near T_g , quantified by the isobaric fragility index m_p with:

$$m_p = \left(\frac{d \log_{10}(\tau)}{d \left(\frac{T_g}{T} \right)} \right) \Bigg|_{P, T=T_g} \quad (1)$$

Classical theories such as the entropic model of Adam and Gibbs¹⁰ and the free volume approach¹¹ attribute the slowing down dynamics near T_g to the growth of the size of dynamically correlated structural units. This leads to the concept of Cooperative Rearranging Regions (CRR) whose size increases with decreasing temperature, leading to vitrification for a CRR volume around 27 nm³ whatever the glass formers.¹²⁻¹⁴ This involves the correlation of molecular rearrangements within local environments.

Among the studies allowing to estimate the CRR size, Donth's approach¹⁵ uses the quantification of temperature fluctuations all over the amorphous medium. The CRR volume V_α and the number of relaxing structural units per CRR N_α , are estimated by using the following relations:

$$V_\alpha = \frac{\left(\frac{1}{C_{p,glass}} - \frac{1}{C_{p,liquid}} \right) k_B T_\alpha^2}{\rho (\delta T)^2} \quad (2)$$

and

$$N_\alpha = \frac{\rho N_A V_\alpha}{M_0} \quad (3)$$

where ρ is the density, N_A is Avogadro's number, M_0 is the molar mass of structural units, C_p is the specific heat capacity at constant pressure, k_B is Boltzmann's constant, T_α is the dynamic glass transition temperature, and δT is the mean square temperature fluctuation associated with the glass transition. In the case of polymers, the structural units are assumed to be the repeating units, i.e. the monomer units.

Supported by much literature, the dynamic nature of the glass transition is associated with dynamic heterogeneities.¹⁶⁻¹⁸ It is characterized by spatial and temporal correlations of molecular motions and a distribution of relaxation times.¹⁹ As noted in the literature, variations in the breadth of the dispersion of α -relaxation under different temperature/pressure conditions can be clearly estimated using the Kohlrausch-Williams-Watts (KWW) function, which is expressed as follows:^{20,21}

$$\Phi(t) = \exp \left[- \left(\frac{t}{\tau_{KWW}} \right)^{\beta_{KWW}} \right] \quad (4)$$

where $\Phi(t)$ represents the relaxation function, classically used for the non-Debye relaxation phenomenon in the time domain, β_{KWW} is the stretching parameter, and τ_{KWW} corresponds to the characteristic relaxation time. The parameter β_{KWW} characterizes the dispersion of the α -

relaxation. A Fourier transform of $\Phi(t)$ allows approximating relaxations measured in the frequency domain.

Despite differences in models using distribution of relaxation times for prediction of dynamic heterogeneities, there is a shared understanding that the dispersion does not fully govern structural relaxation dynamics.²²⁻²⁴ It is often treated independently, whether in time or frequency. The dispersion and the structural relaxation time are predicted separately, with β_{KWW} possibly remaining constant for different temperature and pressure combinations due to compensating effects on molecular mobility. However, the dispersion may vary as it depends on factors like specific volume, configurational entropy, and static structure factor.²³ The heterogeneous dynamics suggest that relaxation processes involve multiple independent relaxations, while the growing heterogeneity length scale is the cause of the drastic relaxation time increase as the system cooling. Therefore, a change in the heterogeneity characteristic length scale would typically alter the spectral shape of relaxation, and independent relaxation modes could deviate from time-temperature-pressure superposition.²⁵

The stretching parameter β_{KWW} is present in approaches to predict the relaxation dynamics. It has been used for explaining the super-Arrhenius behaviors of relaxation time in the coupling model.²⁶ Moreover, β_{KWW} can be used as the contribution of the correlation function in the experimental calculation of the number of dynamically correlated units N_c according to the dynamical heterogeneities.²⁷⁻²⁹ Such method has been applied on different polymers. Comparing N_c and N_α extracted from Donth's approach evidences that the lower the molecular weight of the repeating units M_0 , the closer the values of N_c and N_α . Furthermore, it is noteworthy that an anti-correlation between the stretched parameter and the isobaric fragility m_p [see **Eq. (1)**] has been observed for diverse glass forming liquids, including polymers.³⁰

The molecular mobility at the glass transition is revealed by the isobaric fragility m_p . Its correlation with T_g and cooperativity remains unclear, while these three physical parameters are expected to be related to the rigidity of macromolecules in polymers. Studies employing various techniques have shown no indisputable link between T_g , cooperativity size and m_p for several glass-forming liquids.^{28,31-34} The relationship between T_g , cooperativity and fragility depends on the nature of samples. The effects of structural, chemical, or processing modifications on the segmental dynamics at T_g have been investigated through several works, reporting correlations or anticorrelations between these parameters in complex systems. Some of them focus on geometrically constrained amorphous phase (confinement effect) due to nanoparticles,³⁵⁻³⁷ in intercalated nanocomposites,³⁸ in nanolayers^{39,40} or due to the crystalline phase.⁴¹ The plasticizing effects on this correlation have been also reported.^{42,43} Others worked on the chemical structure by varying backbone stiffness,^{14,44} changing dipole distribution in the polymer chain,⁴⁵ changing the H-bond⁴⁶ or using composite systems.⁴⁷ Various works have also studied the segmental mobility and cooperativity in miscible polymer blends by isolating intermolecular effects,⁴⁸⁻⁵⁰ intramolecular effects^{51,52} or by combining both.⁵³⁻⁵⁶

Among these studies, Puente et al. focused on simple systems, specifically fully amorphous polymers with similar backbone stiffness⁵⁷ for whom only the dipolar side group ratio varies. For this purpose, variations of T_g , m_p and N_α with temperature have been studied in copolymers of poly(ethylene-co-vinyl acetate) (EVA) with different vinyl acetate ratio (VAc), ranging from PVAc (100 wt% VAc) to EVA50 (50 wt% VAc). Keeping the same backbone but varying the ratio of dipolar pendant groups, allows studying the role of different interchain dipolar interactions, which significantly influence the glass transition temperature and the CRR size.⁵⁷ Nevertheless, the isobaric fragility m_p remains unchanged with the wt% VAc. Thus, the constant m_p value and the decrease in cooperativity with decreasing vinyl acetate ratio support the conclusion that a cooperativity/fragility correlation is not a general trend.

One possible explanation of the decorrelation between m_p and cooperativity is the hypothesis of two contributions in the isobaric fragility (thermal and volumetric), according to literature.⁵⁸⁻⁶¹ By using both contributions, Hong et al. provided an expression for m_p that considers the combined effects of temperature and volume variations on the structural relaxation dynamics.⁵⁸ According to this assumption, the isobaric fragility can be expressed as:

$$m_p = m_V + \frac{\Delta V^\#}{\ln 10} \frac{\alpha_T}{k_B \kappa} \quad (5)$$

where $\Delta V^\#$ is the activation volume, k_B is Boltzmann's constant, κ is the compressibility and α_T is the thermal expansion coefficient of the supercooled liquid at T_g . In this equation, the first term represents the thermal contribution (isochoric fragility, m_V), while the second term denotes the volumetric contribution noted ($m_p - m_V$). It solely considers physical parameters related to volume variations, including variations in density that occur during cooling at constant pressure. These two contributions have been identified as explanatory factors for variations in m_p for different chemical structure of polymers.⁶²⁻⁶⁴ An understanding of these effects is provided by the study of glassy liquids under isothermal or isochoric conditions, i.e. with constant thermal or volumetric contributions.⁶⁵

In many studies, broadband dielectric spectroscopy (BDS) serves as a potent tool for investigating molecular dynamics due to its broad frequency range.^{66,67} It is the primary dynamic method for scrutinizing the complex permittivity variations of polymers with temperature and frequency, enabling an understanding of molecular motions and relaxation phenomena as the α -relaxation process, which is intricately linked to segmental motions within the polymer main chains.^{68,69}

The study of the pressure dependence of dielectric relaxation in polymers has received considerable attention in the research community.⁷⁰⁻⁷³ Investigations of the time-temperature-pressure superposition of the α -relaxation provide information on the dispersion of relaxation times with temperature or pressure variations.^{23,74} This overarching principle posits that the broadening of the α -peak, represented by the stretched exponent β_{KWW} , is dependent on the structural relaxation time. It suggests that for a given relaxation time, the shape of the relaxation peak remains invariant regardless of the thermodynamic conditions, such as temperature and pressure combinations.⁷⁵

According to existing literature, β_{KWW} is also associated with the dielectric strength (or polarity of molecules)⁷⁶ and steric constraints on segmental relaxation,⁷⁷ both being related to the cooperative nature of the polymers.

This study extends the work of Puente et al. in depth and aims to understand why the isobaric fragility remains unchanged as a function of wt% VAc, while the glass transition and N_α vary significantly. For this purpose, the pressure was used as a tool to understand this uncorrelation. Segmental relaxation was observed under various conditions, including isothermal, isobaric, and isochronal conditions. Analysis of the segmental relaxation spectra in these configurations provided insight into the dispersion of the characteristic relaxation times, β_{KWW} . The thermal and volumetric contributions of isobaric fragility m_p were investigated experimentally as a function of frequency, temperature and pressure. The activation volumes were compared to the intensity of intermolecular interactions determined by the VAc side group ratio. The volumetric contribution, calculated from ΔV^\ddagger , has reflected the influence of the VAc ratio. Finally, the dependence of the thermal and volumetric contributions on the isobaric fragility was discussed. It allowed to find the structural parameters (intra-intermolecular interactions) that influence the molecular mobility of the systems studied, and therefore their fragility, glass transition and cooperativity.

MATERIALS & METHODS

MATERIALS. The polymers studied are poly(vinyl acetate) PVAc and copolymers of poly(ethylene-co-vinyl acetate) EVA with different vinyl acetate (VAc) ratio. PVAc was supplied by Aldrich Chemical Company in pellet form. The weight-average molecular weight (Mw) is around 500 kg/mol. EVA pellets containing 80 wt. % of VAc groups (Levapren[®] 800) were obtained from Lanxess Co., with a Mw around 270 kg/mol. EVA pellets with 60 wt. % of VAc groups (Levapren[®] 600) were obtained from Bayer Co. with a Mw around 250 kg/mol. For sake of clarity, EVA80 and EVA60 stand for Levapren[®] 800 and 600, respectively, in the rest of the manuscript. The rate of 60 wt. % and 80 wt. % of VAc in EVA60 and EVA80 respectively are sufficient to keep the systems fully amorphous.⁷⁸⁻⁸⁰ Only EVA containing from 0 up to 50 wt. % of VAc allow samples to crystallize.

The pellets were dried in an oven at 40 °C during 12h. The samples were thermo-molded at 120 °C and 80 °C for PVAc and EVAs, respectively. An average thickness of polymer films was approximately 500 μm .

METHODS. The complex dielectric permittivity was investigated by the broadband dielectric analyzer “Novocontrol Alpha” with Novocontrol Quatro Cryosystem equipped with a two-electrode circuit. Complex dielectric permittivity was measured within the frequency range from

10^{-1} up to 10^6 Hz at atmospheric pressure P_{atm} . Samples were placed between parallel gold-plated electrodes with diameter of 30 mm and thickness of 1,7 mm. The temperature was varied between 123 K up to 311 K in consecutive increasing steps of 10 K, and up to 363 K in consecutive increasing steps of 2 K for PVAc, between 263 K up to 333 K in consecutive increasing steps of 2 K for EVA80, between 123 K up to 233 K in consecutive increasing steps of 10 K, and 234 K up to 298 K in consecutive increasing steps of 1 K for EVA60. The samples were kept in nitrogen atmosphere.

For high-pressure Broadband Dielectric Spectroscopy (BDS) measurements, a high-pressure pump type U111 (from UNIPRESS EQUIPMENT) was additionally employed. The pressure was measured with a Nova Swiss tensiometer with a resolution of ± 0.1 MPa. For these experiments, the sample was measured in a 15 mm diameter by 3.9 mm thick stainless steel parallel plate cell, in the frequency range from 10^{-1} up to 10^6 Hz. The electrodes were put in a Teflon container for the centering, and ensuring good contact with the sample. For improving electrical insulation, the cell was sealed and encased carefully by a Teflon strip. Then, one layer of Polyisoprene was added to separate it from the oil liquid (Julabo Thermal HL80). Infrared measurements were taken before and after the measurements under pressure, and the signals did not indicate that the samples were contaminated with any liquid. The pressure was varied between 20 and 200 MPa in consecutive increasing steps of 20 MPa for PVAc, and of 25 MPa for EVA60 and EVA80. The temperature was controlled using a thermostatic bath, and monitored with a thermocouple with a precision of 0.1 K.

The dielectric relaxation curves obtained were analyzed using the Havriliak-Negami (HN) complex function:⁸¹

$$\varepsilon^*(\omega) = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{[1 + (i\omega\tau_{HN})^{\alpha_{HN}}]^{\beta_{HN}}} \quad (6)$$

where ε^* is the complex permittivity, ω the angular pulsation, ε_{∞} the permittivity value when $\omega \rightarrow \infty$, $\Delta\varepsilon_{HN}$ the dielectric strength, τ_{HN} the relaxation time, and α_{HN} and β_{HN} the symmetric and the asymmetric broadening parameters ($0 < \alpha_{HN}, \beta_{HN} < 1$), respectively. The relaxation time corresponding to the position of maximal loss can be then determined with broadening parameters such as:

$$\tau_{max} = \tau_{HN} \left[\sin \frac{\alpha_{HN}\pi}{2 + 2\beta_{HN}} \right]^{-\frac{1}{\alpha_{HN}}} \left[\sin \frac{\alpha_{HN}\beta_{HN}\pi}{2 + 2\beta_{HN}} \right]^{\frac{1}{\alpha_{HN}}} \quad (7)$$

The contributions of conductivity and a secondary relaxation have been considered on dielectric relaxation curves. The secondary relaxation is taken into account with an HN function with constant the broadening parameters and dielectric strength. Only its the relaxation time is varied. The conductivity is considered in the dielectric loss according to $\varepsilon'' = \sigma_0/\omega\varepsilon_0$ where σ_0 is the ohmic conductivity and is temperature dependent. An example of a dielectric spectrum approximation using the HN fitting function and conductivity is shown in **Figure S1** of

Supplementary Material. The values of HN fitting parameters for the secondary relaxation and the conductivity are given in **Table S1** in the Supplementary Material.

RESULTS AND DISCUSSION

State of the uncorrelation between m_p and V_α

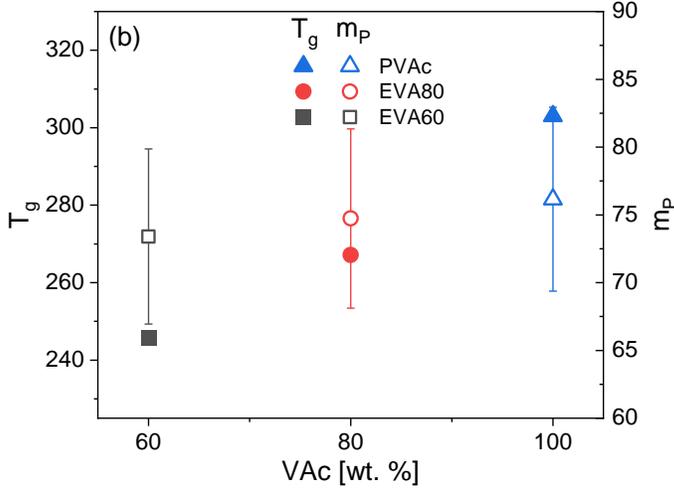
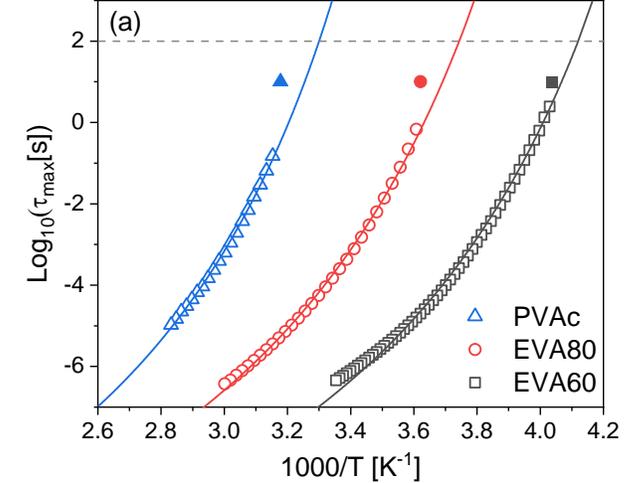
Molecular mobility is primarily analyzed through relaxation time variations with temperature. Thus, the relaxation time of polymer segmental relaxation can be approximated with the Vogel-Fulcher-Tammann law (VFT):⁸²

$$\tau_{max}(T) = \tau_\infty \exp \frac{DT_0}{T - T_0} \quad (8)$$

where τ_0 is the relaxation time at infinite temperatures, D a dimensionless steepness parameter, and T_0 the reference Vogel temperature. The temperature dependence of relaxation time of the samples is shown in **Fig. 1(a)** with the corresponding VFT fits. The glass transition temperature T_g can be obtained by extrapolating the law to a relaxation time of 100 s.⁸³ Both T_g and m_p values are plotted as the function of the VAc ratio in **Fig. 1(b)**. As already observed by Puente et al., the glass transition decreases whereas the isobaric fragility remains quite constant. The invariance of m_p has been attributed to the constant backbone stiffness present in EVA whatever the VAc ratio, while the variation of the glass transition is explained by the role of steric hindrance and polarity of the side group.⁵⁷ Puente et al. even extrapolated fragility as a function of VAc ratio to reach value of a theoretically amorphous polyethylene (PE), i.e. chain with 0 wt. % of VAc groups. In addition, they observed that cooperativity at the glass transition increases with the VAc ratio.

Using an extended Donth's approach proposed by Saiter et al.,³⁸ the number of structural units per CRR N_α and the CRR volume V_α can be determined for any relaxational techniques [see **Eq. (2)** and **Eq. (3)**]. N_α have been obtained by combining Modulated Temperature Differential Scanning Calorimetry (MT-DSC) and BDS analyses. The molar masses M_0 of structural units were calculated by using the molar ratio x of the VAc group, its molar mass ($M_{VAc} = 86 \text{ g. mol}^{-1}$) and the molar mass of the ethylene group ($M_{Eth} = 28 \text{ g. mol}^{-1}$) as follows: $M_{0,EVAx} = M_{VAc}(x) + M_{Eth}(1 - x)$. T_α and δT were determined from BDS analyses (more details about the method can be found in Ref. 84). The specific heat capacities $C_{p,liquid}$ and $C_{p,glass}$ are determined by extrapolating baselines of the liquid and the glass at T_α respectively. These values were obtained by MT-DSC analysis from Ref. 57 with a modulation period of 60 seconds, an amplitude of 1 K and a heating rate of 0.5 K. min⁻¹. For comparison, the T_α determined by MT-DSC analysis is also shown in **Fig. 1(a)**, with $\tau = p/2\pi \approx 10$ s. **Figure 1(c)** shows the variations of N_α as the function of the inverse of temperature normalized at T_g ($\tau = 100$ s). The cooperativity at the glass transition temperature seems to be correlated with the ratio of polar groups in the macromolecular chain, since EVA60 have fewer relaxing units in a CRR than EVA80 and PVAc. Similar results on

cooperativity have been reported when intermolecular interactions are reduced due to temperature increase,^{13,85} pressure decrease⁸⁶ or polymeric structure.⁸⁷



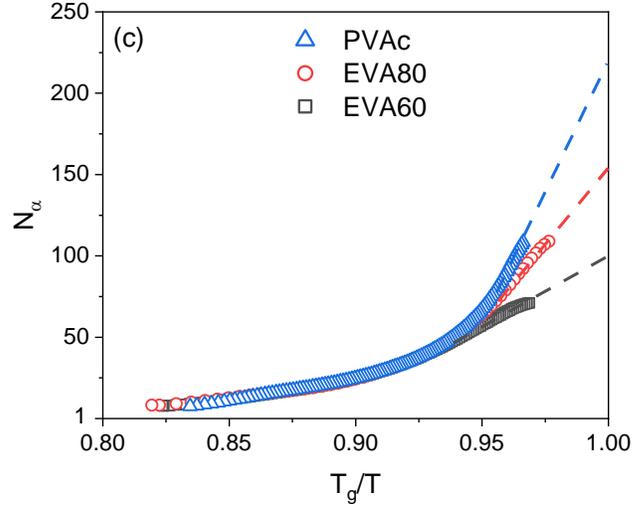


FIG. 1. (a) Temperature dependence of the relaxation time τ for PVAc (blue triangles), EVA80 (red circles) and EVA60 (black squares). The lines represent the VFT fits. The dashed line corresponds to isochrone $\tau = 100$ s, i.e. to the glass transition temperature T_g . The filled symbols are T_α determined by MT-DSC analysis from Ref. 57 with $\tau = p/2\pi \approx 10$ s. (b) T_g and m_p as a function of the VAc ratio at atmospheric pressure. (c) N_α as a function of T_g/T , where $T_g = T(\tau = 100$ s). The dashed lines represent the linear extrapolation of data to visualize N_α at $T = T_g$.

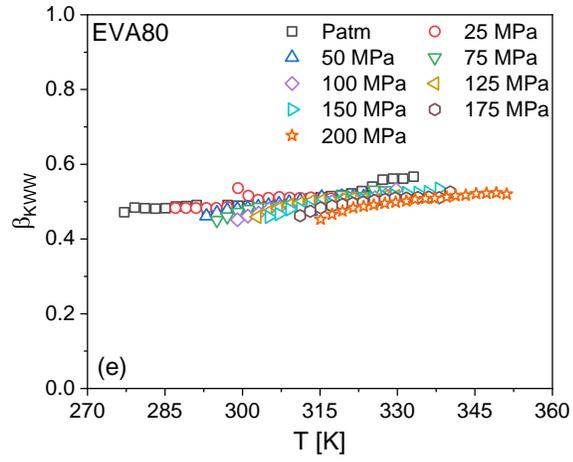
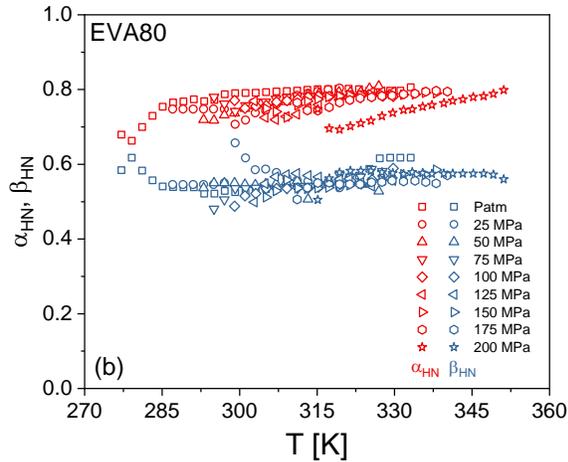
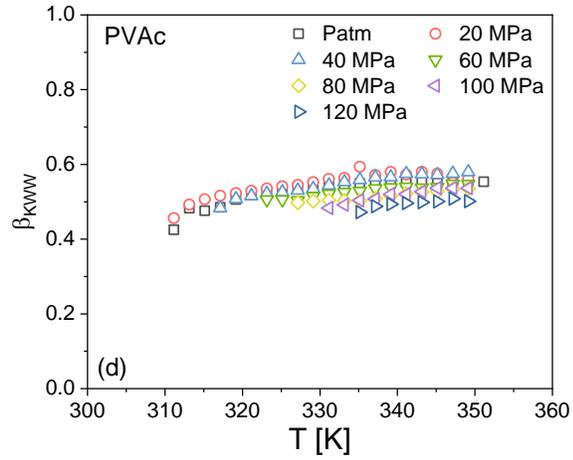
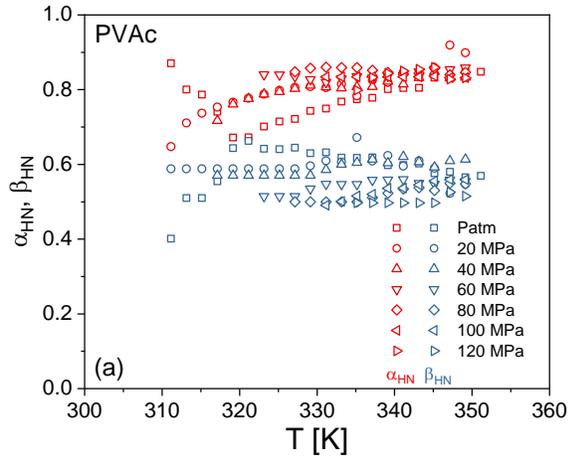
One way to verify the assumptions surrounding the different roles of chemical structure on m_p , T_g and N_α is to use the pressure as a tool to isolate intermolecular interactions, linked to steric hindrance and polarity of the side group, to intramolecular interactions rather connected to the backbone stiffness.

Intermolecular interactions from the dispersion of dielectric relaxation

In the literature, the steric constraints related to rigid or flexible side groups are associated with wide or narrow dispersion of relaxation times.⁷⁷ The dispersion is directly related to the dielectric spectrum shape of the segmental relaxation.⁸⁸ The dielectric spectrum can be analyzed with HN function (**Eq. (6)**). The symmetric α_{HN} and asymmetric β_{HN} broadening parameters are determined from 0.1 MPa up to 200 MPa. The α_{HN} and β_{HN} parameters are plotted in **Fig. 2(a)**, **2(b)** and **2(c)**, for PVAc, EVA80 and EVA60, respectively. The α_{HN} values increase slowly as the temperature increases, and increase strongly with the VAc ratio indicating that the segmental relaxation becomes narrower in both cases. Moreover, the symmetrical broadening parameters appear to remain constant as the dipole ratio increases. Equivalence between broadening parameters with HN function from frequency domain, and dispersion of segmental relaxation of KWW function (**Eq. (4)**) from time domain has been found, leading to the following approximation:^{89,90}

$$\beta_{KWW} = (\alpha_{HN}\beta_{HN})^{0.813} \quad (9)$$

The stretching parameter β_{KWW} , linked to the dispersion of the relaxation times, is reported to be related to intermolecular interactions through dielectric strength and steric hindrance provoked by side groups in polymers.^{76,77} **Figures 2(d), 2(e) and 2(f)** show the variations of β_{KWW} from 0.1 MPa up to 200 MPa as a function of the temperature for PVAc, EVA80 and EVA60, respectively. The stretching parameter β_{KWW} increases with temperature, and the temperature dependence of β_{KWW} seems to be shifted to higher temperature when pressure increases. This reflects the fact that polymer structure needs to be further compressed during heating to keep same dispersion of relaxation times.



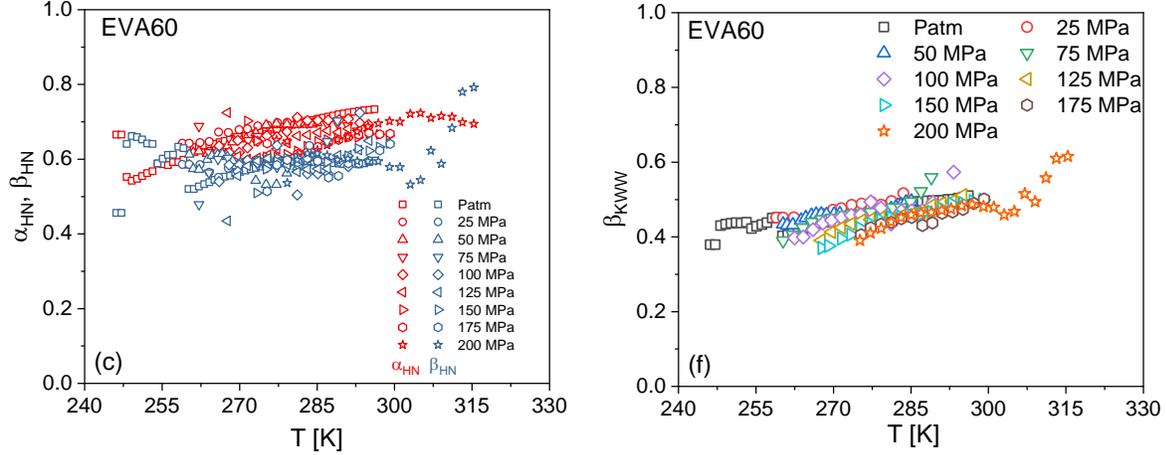


FIG. 2. Isobaric temperature variations of the symmetric α_{HN} (blue symbols) and asymmetric β_{HN} (red symbols) broadening parameters from the segmental relaxation for (a) PVAc, (b) EVA80 and (c) EVA60, and the stretching parameter β_{KWW} for (d) PVAc, (e) EVA80 and (f) EVA60 in the same conditions. Symbols are differently colored for each pressure.

Cooperativity as a function of relaxation time

Studying the role of intermolecular interactions can be biased by multiple contributions due to pressure, temperature or volume. According to the literature^{25,91,92}, dielectric spectrum which have same τ_{max} does not exhibit any dispersion variations with changes in pressure and temperature. It is a common feature of glass forming liquids when any secondary relaxations and excess wings occurred close to the segmental relaxation. As mentioned earlier, a dispersion variation of segmental relaxation is attributed to a change of intermolecular interactions, which are related to cooperativity. Using the extended Donth's approach, cooperativity volume is determined in isobaric conditions from **Eq. (2)** and data from Ref. 93. **Figure 3** shows the evolution of cooperativity volume V_α as a function of the relaxation time for pressure from Patm up to 50 MPa. The relaxation time seems to govern the evolution of the cooperativity for a given chemical structure, varying with pressure and temperature along a master curve. This observation meets the steadiness of β_{KWW} in isochronal conditions, i.e. the dispersion is unchanged at constant relaxation time whatever the temperature and pressure in supercooled liquids for PVAc.²³

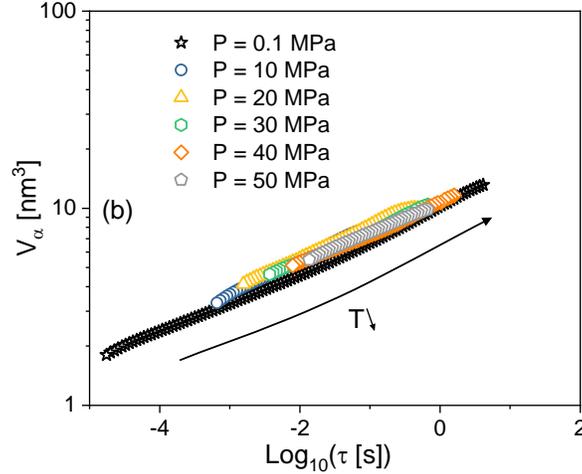


FIG. 3. Cooperativity volume as a function of the logarithm of the relaxation time for isobaric measurements, from P_{atm} up to 50 MPa.

Variations of dispersion and interactions under pressure with the VAc ratio

The isobaric master curves at 100 MPa for PVAc, EVA80, EVA60 are presented in **Fig. 4(a)**. Only 100 MPa isobar is presented for sake of clarity. The numerical Fourier transforms of the KWW used to fit the master curves are shown as dashed lines for each sample. Deviations from the KWW function are observed at high and low frequency range of the segmental relaxation. The low frequency deviations are due to the ohmic conduction related to the mobile charge carriers. The high frequency deviations arise from the involvement of non-cooperative and localized molecular mobility corresponding to the β -relaxation.⁹⁴ **Figure 4(b)** shows the variations of β_{KWW} at various temperatures for PVAc, EVA80, EVA60 at 100 MPa calculated from **Eq. (9)**. The β_{KWW} value shifts to higher values with temperature and VAc ratio increases, from 0.47 for EVA60 up to 0.54 for PVAc. The difference between these two β_{KWW} values is significant. Indeed, in the case of a polymer whose chemical structure is modified for increasing cooperativity interactions, same β_{KWW} variations have been reported.⁹⁵ Such an increase can be explained by a lower dispersion of the relaxation time due to an increase in the ratio of dipoles.¹⁷ These observations are consistent with those showing that intermolecular interactions, and therefore cooperativity, become more important with increasing VAc content.⁵⁷

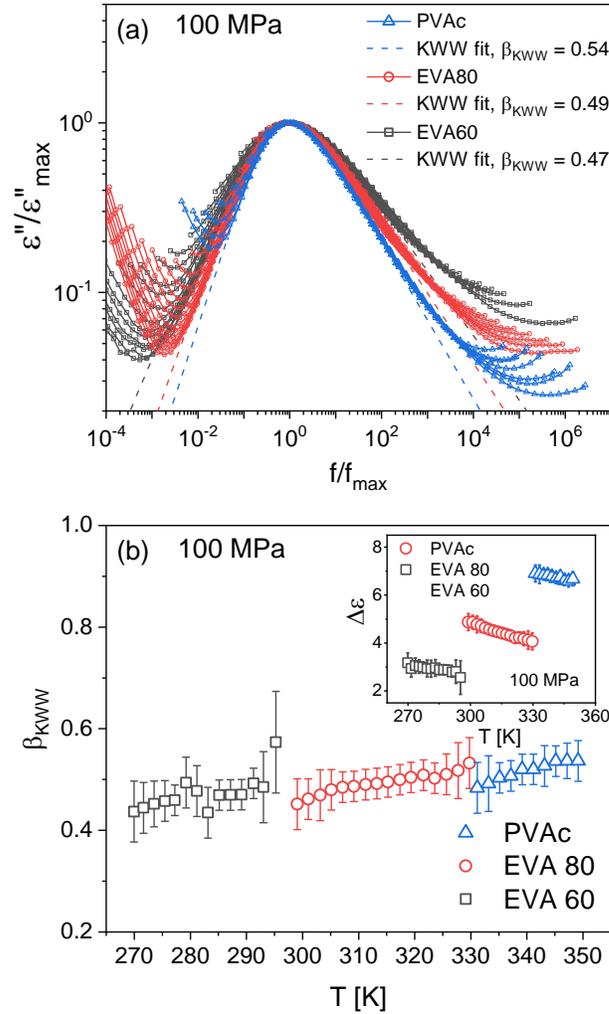


FIG. 4. (a) Log-log plot of the dielectric loss normalized to the peak maximum as a function of the normalized frequency at various temperatures for PVAc, EVA80, EVA60 at 100 MPa. Spectra are interpolation of experimental points. An average β_{KWW} is given for each sample. The list of measured frequencies is given in **Table S1** of Supplementary Material. (b) Variations of the stretching parameter β_{KWW} values as a function of temperature for PVAc, EVA80, EVA60 at 100 MPa. The dielectric strength $\Delta\epsilon$ from the HN fit are plotted in the inset.

Previous studies have noticed coupled effects of intermolecular interactions decrease and dispersion increase. As an example, the addition of plasticizer, which increases the free volume, reduces the interactions, while the β_{KWW} stretching parameters decreases.³⁴ In the case of semi-crystalline polymers, the crystalline phase hinders the amorphous phase, increasing dispersion while cooperativity decreases.^{77,96–98} Nevertheless, some glass forming liquids show opposite

behavior, such as colloidal suspension of soft spherical particles.^{99,100} The dielectric strength $\Delta\epsilon$ is rather an indicator of such interactions according to the Debye theory of dielectric relaxation generalized by Kirkwood and Fröhlich.¹⁰¹ Thus, $\Delta\epsilon$ of the α -relaxation process depends on parameters that influence interactions: the mean dipole moment μ , the dipole density N/V of the process, and the Kirkwood correlation factor g_K . This factor considers short range intermolecular interactions related to the static correlation between the dipoles. Dielectric strength is therefore expressed with the following equation:

$$\Delta\epsilon = \frac{1}{3\epsilon_0} g_K \frac{\mu^2}{k_B T} \frac{N}{V} \quad (10)$$

where ϵ_0 is the dielectric permittivity of vacuum. As expressed in **Eq. (10)** and shown in the inset in **Fig. 4(b)**, the dielectric strength is inversely proportional to the temperature. The $\Delta\epsilon$ variations and the β_{KWW} increase are attributed to the reduction of intermolecular interactions due to the temperature.^{102–104} Schönhals has associated the increase of intermolecular interactions between dipoles with temperature decrease, to the cooperative character of the molecular motion, i.e., the lower the temperature, the stronger the cooperative interactions.¹⁰⁵

However, increase of intermolecular interactions is associated with increase of β_{KWW} values for structural hindrances, as already mentioned. Therefore, variations of the intermolecular interactions due to structural changes have an opposite influence on the stretching parameter than variations due to temperature change. In the case of EVA/PVAc, β_{KWW} increases as a function of VAc ratio, as well as intermolecular interactions. Paluch et al. have shown a correlation between $\Delta\epsilon$ and β_{KWW} for molecular glass formers.⁷⁶ This correlation is attributed to the nature of intermolecular interactions through dipole-dipole interactions. As mentioned by Paluch et al., since these interactions should be more harmonic when $\Delta\epsilon$ is stronger, the dispersion of the relaxation times is narrower.⁷⁶ This observation is in agreement with the effect of intermolecular interactions on the dispersion of relaxation times^{106,107} and cooperativity mentioned in literature.^{108,109}

Determination of interactions through activation volume

Another approach for evaluating the intermolecular interactions is achievable with the determination of the activation volume ΔV^\ddagger .^{110,111} This value is defined from the isothermal relaxation times but can be also obtained from isobaric measurements.¹¹² For all the samples, the temperature dependence of the relaxation time with pressure is plotted in the Arrhenius representation (**Figure 5**). The curves are well fitted by the VFT law [see **Eq. (8)**]. The fit parameters are reported in **Table S2** of Supplementary Material. The temperature decrease and the pressure increase have comparable effects on the molecular mobility, resulting in a relaxation time in increase of both scenarios.

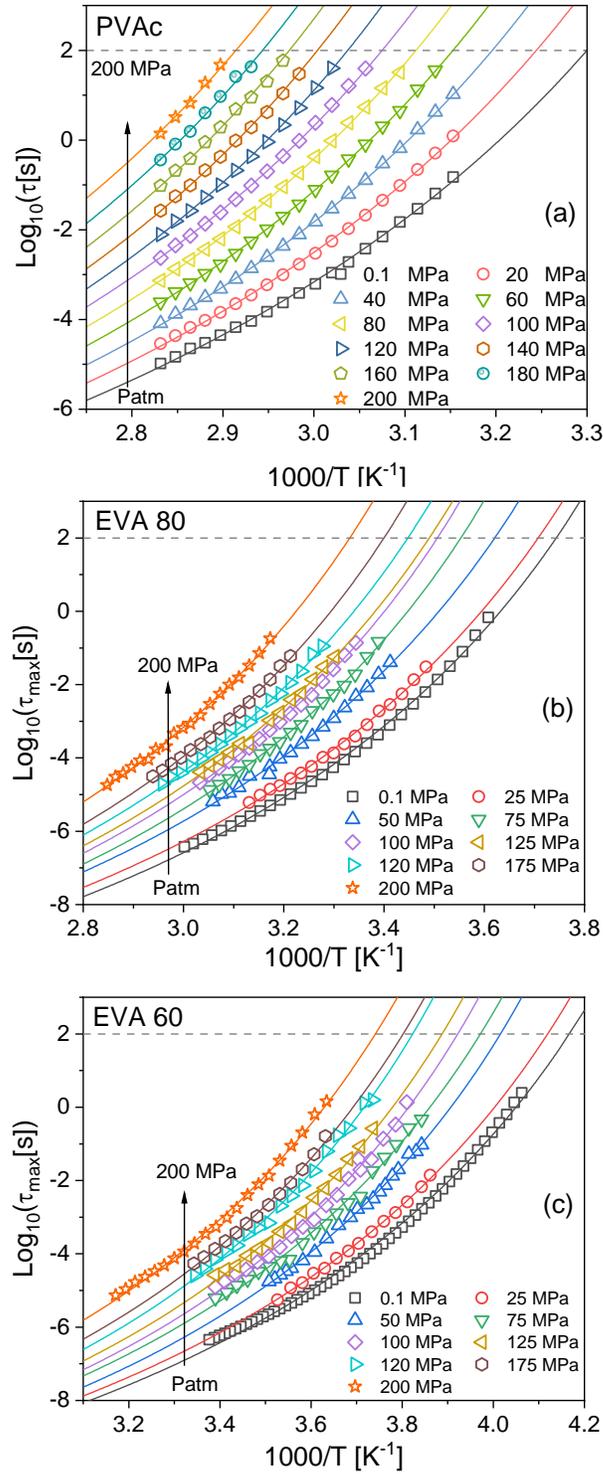


FIG. 5. Logarithm of the dielectric relaxation time (τ_{max}) as a function of the inverse temperature for (a) PVAc, (b) EVA80 and (c) EVA60 under pressure. Solid lines represent

the VFT fits with colors for each pressure. The grey dashed lines correspond to $\tau_{max} = 100$ s, i.e. to the glass transition temperature T_g .

The glass transition temperature T_g was taken at $\tau_{max} = 100$ s. According to the data obtained from VFT fits, the pressure influence on T_g can be analyzed for the PVAc/EVA series as shown in **Fig. S2**. The glass transition temperature increases nonlinearly with the pressure. Thus, the experimental data can be fitted by an Andersson-Andersson model:¹¹³

$$T_g(P) = T_g^0 \left(1 + \frac{P}{\Pi}\right)^{1/b} \quad (11)$$

where T_g^0 is the value of T_g at atmospheric pressure, P , Π and b are fitting parameters. The T_g differences observed in **Fig. 1(b)** and depending on the VAc ratio, are also observed in **Fig. S2** as pressure increase, while the T_g increases with pressure.

From the glass transition and the isobaric fragility variations as a function of the pressure, the activation volume at the glass transition is calculated with the following equation¹¹²:

$$\Delta V^\# = m_P k_B \frac{dT_g}{dP} \ln 10 \quad (12)$$

dT_g/dP being determined from **Eq. (11)**.

Classically, the higher the pressure at constant temperature, the higher the activation volume. $\Delta V^\#(P, T)$ expresses the difference between, an activated volume $V_A(T)$ and a non-activated volume $V_0(P, T)$.¹¹⁴ The activated volume $V_A(T)$ is the volume allowing the relaxation of a structural unit. It decreases with the rise in temperature, and it is pressure independent. V_0 expresses a volume which does not allow relaxation. As the free volume, V_0 should decrease with pressure increase at constant temperature. **Figure 6** presents the evolution of $\Delta V^\#$ at the glass transition temperature as a function of the pressure. PVAc shows the highest value at atmospheric pressure. Whatever the sample, $\Delta V^\#$ decreases with a rise in pressure, a behavior which has been reported in many glass forming liquids.¹¹⁵⁻¹¹⁷ During the pressure increase, V_0 decreases due to free volume compression. In the meantime, $V_A(T_g)$ decreases with pressure due to T_g increase. The fact that $\Delta V^\#$ at T_g diminishes with a rise in pressure indicates that $V_0(P, T_g)$ contraction is weaker than $V_A(T_g)$. Since $\Delta V^\#$ is related to CRR volume V_α ,^{59,93,118} the activation volume $\Delta V^\#$ values are consistent with the intensity of the intermolecular interactions in the PVAc/EVA copolymers.

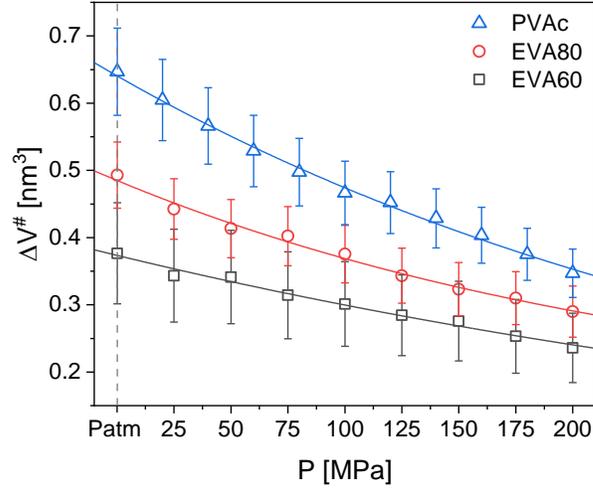
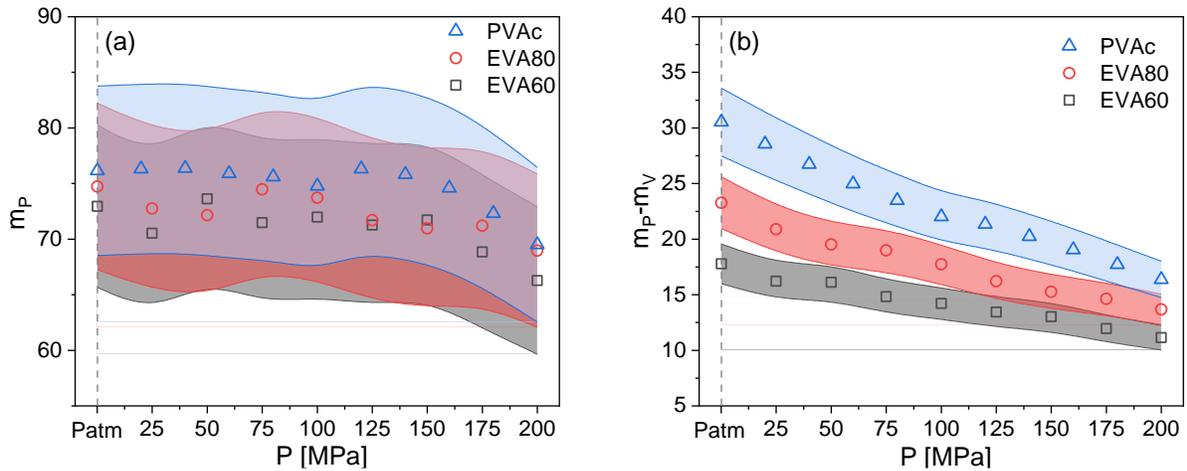


FIG. 6. Activation volume $\Delta V^\#$ at $T_g(P)$ as a function of the pressure. The lines correspond to a one-phase exponential decay function, it serves as a guide for the eyes. The vertical dashed line corresponds to the atmospheric pressure.

Experimental calculation of thermal and volumetric contributions

According to **Eq. (5)**, the volumetric contribution of the isobaric fragility m_p can be deduced from the activation volume. The pressure influence on isobaric fragility m_p , volumetric $m_p - m_V$ and thermal m_V contributions for the PVAc/EVA series are presented at T_g in **Fig. 7**.



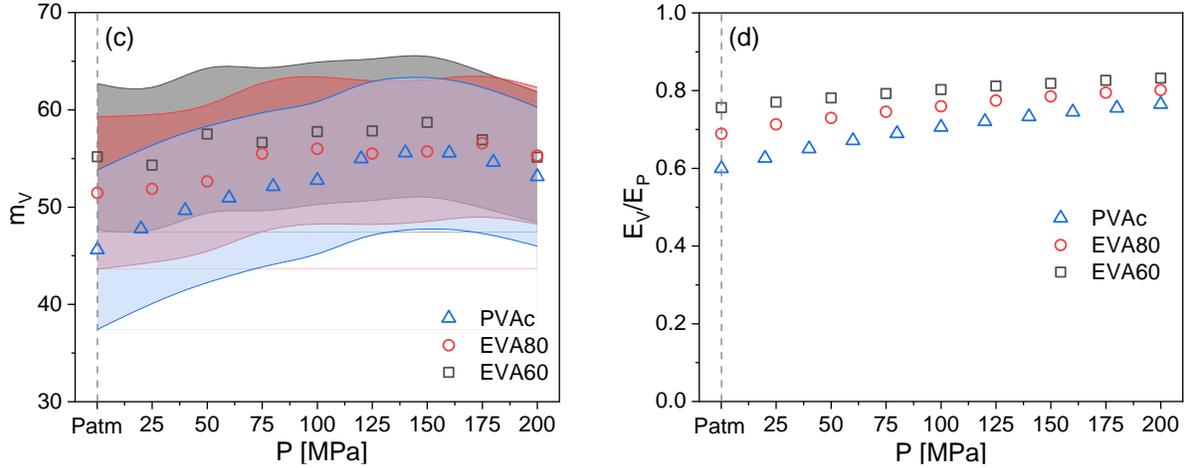


FIG. 7. (a) Isobaric fragility m_p , (b) volumetric contribution ($m_p - m_V$) and (c) thermal contribution m_V as the function of the pressure for PVAc in blue, EVA 80 in red and EVA 60 in grey. The colored areas are the uncertainty zones of the values. (d) Ratio E_V/E_P as a function of pressure. The vertical dashed lines correspond to the atmospheric pressure.

As shown in **Fig. 7(b)**, a decrease in the volumetric contribution is observed with the pressure increase whatever the sample. Supported by preliminary results at atmospheric pressure, the m_p values appear to be weakly sensitive to pressure variations, and to the different ratios of vinyl acetate groups. According to the literature, the volumetric contribution is mainly related to the intermolecular interactions and the free volume ratio in the liquid-like state,⁶³ which may depend on the amount of lateral groups causing the steric hindrance.⁹⁵ The volumetric contribution values in the PVAc/EVA series are consistent with the density of intermolecular interactions due to the VAc ratio. Thus, the reduction of these interactions at the glass transition due to the pressure is in agreement with the reduction of the free volume in the samples. Previous works supported the idea that such increases in intermolecular interactions due to the VAc ratio are correlated with the evolution of the cooperativity volume.⁵⁷ As shown in **Fig. 7(c)**, the thermal contribution shows a slight increase for PVAc values with the pressure, while it remains fairly stable for EVA60. In the literature, m_V is characterized as a purely energetic factor, influenced by the types of intermolecular and intramolecular bonds, as well as the internal degrees of freedom within the molecules.⁵⁹ Thus, some studies have suggested that the thermal contribution may be impacted by the backbone stiffness.^{119,120} Although m_V values are in the uncertainty range, the PVAc/EVA series should not have such a variations, since the main carbon chain remains the same in the whole series. At high pressure, the impact of the pendant group on the thermal contribution m_V is reduced, and therefore, values for PVAc and EVA80 seem to reach the steadiness of EVA60. Such behavior leads to the assumption that the backbone stiffness is not the only feature affecting the thermal contribution. It can be assumed that the side groups have an impact on the thermal contribution, which could be provoked by the packing efficiency. Also called chain packing, it describes the order in which chains are grouped together within the amorphous polymer.¹²¹ It is influenced by the flexibility of

the chain backbone and side groups, as well as by the processing and cooling conditions of polymers.^{119,122} High packing efficiency means that polymer chains are tightly and uniformly arranged. This results in a reduction in free volume and an increase in local density.¹²³ Variations in packing efficiency directly influences the polymer mechanical properties, such as brittleness and fracture resistance.^{124,125} In general, an increase in packing efficiency is associated with an increase in brittleness, whereas a decrease in packing efficiency is associated with higher chain mobility and ductility. For polymer blends of poly(lactic acid) and EVA with VAc ranging from 50 wt. % up to 80 wt. %, the higher the VAc ratio, the more brittle the sample.¹²⁶ Stukalin et al. demonstrated that the packing efficiency of macromolecules can be enhanced when the flexibility of chain side groups is increased.¹²⁷ Studies have shown that a change in packing efficiency could be correlated with a reduction of m_V without changing the polymer chemical structure.^{125,128} They have observed an increase of the thermal contribution m_V due to an increase in the degrees of freedom in the mobile amorphous fraction of semi-crystalline polymers. That degrees of freedom are associated to the packing efficiency of the amorphous chain.¹²⁸

Another approach for comparing the thermal and volumetric contributions is presented in the literature.^{74,129} It consists in calculating the ratio between the constant-volume activation energy E_V and the constant-pressure activation energy E_P at the glass transition. The activation energy E_X of the relaxation process is determined using the relationship, $E_X = k_B(\partial \ln \tau / \partial T^{-1})|_X$, where X is a thermodynamic constant. The ratio E_V/E_P provides insight into the predominance between thermal activation processes ($E_V/E_P \rightarrow 1$) and intermolecular free volume ($E_V/E_P \rightarrow 0$) on molecular dynamics.^{60,130} This ratio at T_g is equal to the ratio between isochoric and isobaric fragilities m_V/m_P .¹³¹ **Figure 7(d)** shows an increase of the ratio E_V/E_P with pressure whatever the sample. Supported by the literature,^{129,132} it indicates that the pressure increases the thermal contribution rate despite the volumetric contribution rate. This observation is consistent with the variations of the volumetric and thermal contributions in **Figures 7(b)** and **7(c)** respectively. Moreover, the lower the VAc ratio, the more the thermal activation process dominates the relaxation process. The value for EVA 60 at Patm ($E_V/E_P \approx 0.75$) is reached for EVA 80 and PVAc at pressures of 100 MPa and 200 MPa, respectively.

The invariance of the isobaric fragility at atmospheric pressure in the PVAc/EVA series can be explained by the thermal and volumetric contributions, which offset each other with the VAc ratio. On the one hand, the volumetric contribution increases with the VAc ratio due to intermolecular interactions, and thus the associated cooperativity also increases. On the other hand, the thermal contribution decreases with VAc ratio. Such variation could be explained by the change in packing efficiency with the density of the dipolar side group in the PVAc/EVA series. The VAc ratio in this series has a combined effect on the isobaric fragility m_P , which keeps its value constant at atmospheric pressure, while the thermal contribution predominates over the volumetric contribution toward high pressure.

CONCLUSIONS

The analysis of the segmental relaxation spectra allows getting an idea of the dispersion of the characteristic relaxation time distributions, and evaluating the intermolecular interactions through the dielectric strength. The activation volume values $\Delta V^\#$ at the glass transition, are consistent with the amount of intermolecular interactions related to the VAc ratio. From the activation volume $\Delta V^\#$, the volumetric ($m_p - m_v$) and thermal (m_v) contributions of the isobaric fragility m_p are deduced. The VAc ratio increase in the chain structure seems clearly correlated with an increase of ($m_p - m_v$), this volumetric contribution diminishing with a rise in pressure, and the thermal one converging towards the same value at high pressure. Thus, only the backbone stiffness seems to influence the thermal contribution at high pressure. Nonetheless, PVAc has the lowest m_v value at atmospheric pressure, such behavior being counter-intuitive since the backbone flexibility is the same than for EVA60 and EVA80. The notion of packing efficiency seems to be another way for explaining such thermal contribution differences. Indeed, the VAc groups seem facilitate the packing efficiency, thereby lowering m_v . Thus, the question of the steadiness of the isobaric fragility whatever the VAc ratio seems to find answer in its volumetric and thermal contributions. The sum of the two contributions justifies why the PVAc/EVA series keeps the same isobaric fragility separately from the rate of dipole in the macromolecular chain.

SUPPLEMENTARY MATERIAL

The following files are available free of charge.

Example of dielectric spectrum approximation (**FIG. S1**); Pressure dependence of T_g (**FIG. S2**); Parameters of HN fits for secondary relaxation and conductivity (**Table S1**); Frequency list of BDS measurements (**Table S2**); Fit parameters of VFT law for isobars (**Table S3**).

AUTHOR DECLARATIONS

Conflict of Interest

The authors declare no competing financial interest.

Author Contributions

Jules Trubert: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Liubov Matkovska**: Data curation, Formal analysis, Investigation. **Allisson Saiter-Fourcin**: Conceptualization, Funding acquisition, Methodology, Project administration, Supervision, Validation, Writing – review & editing. **Laurent Delbreilh**: Conceptualization, Funding acquisition, Methodology, Project administration, Supervision, Validation, Writing – review & editing.

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DATA AVAILABILITY

The data that supports the findings of this study are available within the article and its Supplementary Material.

REFERENCES

- ¹ M.L. Williams, R.F. Landel, and J.D. Ferry, "The Temperature Dependence of Relaxation Mechanisms in Amorphous Polymers and Other Glass-forming Liquids," *J. Am. Chem. Soc.* **77**(14), 3701–3707 (1955).
- ² B. Schmidtke, M. Hofmann, A. Lichtinger, and E.A. Rössler, "Temperature Dependence of the Segmental Relaxation Time of Polymers Revisited," *Macromolecules* **48**(9), 3005–3013 (2015).
- ³ S. Napolitano, E. Glynos, and N.B. Tito, "Glass transition of polymers in bulk, confined geometries, and near interfaces," *Rep. Prog. Phys.* **80**(3), 036602 (2017).
- ⁴ E.J. Bailey, and K.I. Winey, "Dynamics of polymer segments, polymer chains, and nanoparticles in polymer nanocomposite melts: A review," *Progress in Polymer Science* **105**, 101242 (2020).
- ⁵ D.L. Baker, M. Reynolds, R. Masurel, P.D. Olmsted, and J. Mattsson, "Cooperative Intramolecular Dynamics Control the Chain-Length-Dependent Glass Transition in Polymers," *Phys. Rev. X* **12**(2), 021047 (2022).
- ⁶ M.D. Ediger, C.A. Angell, and S.R. Nagel, "Supercooled Liquids and Glasses," *J. Phys. Chem.* **100**(31), 13200–13212 (1996).
- ⁷ J.C. Dyre, "*Colloquium* : The glass transition and elastic models of glass-forming liquids," *Rev. Mod. Phys.* **78**(3), 953–972 (2006).
- ⁸ T. Hecksher, A.I. Nielsen, N.B. Olsen, and J.C. Dyre, "Little evidence for dynamic divergences in ultraviscous molecular liquids," *Nature Phys* **4**(9), 737–741 (2008).
- ⁹ C.A. Angell, "Spectroscopy simulation and scattering, and the medium range order problem in glass," *Journal of Non-Crystalline Solids* **73**(1–3), 1–17 (1985).
- ¹⁰ G. Adam, and J.H. Gibbs, "On the Temperature Dependence of Cooperative Relaxation Properties in Glass-Forming Liquids," *The Journal of Chemical Physics* **43**(1), 139–146 (1965).
- ¹¹ D. Turnbull, and M.H. Cohen, "Free-Volume Model of the Amorphous Phase: Glass Transition," *The Journal of Chemical Physics* **34**(1), 120–125 (1961).
- ¹² R. Richert, "Geometrical confinement and cooperativity in supercooled liquids studied by solvation dynamics," *Phys. Rev. B* **54**(22), 15762–15766 (1996).

- ¹³ A. Saiter, L. Delbreilh, H. Couderc, K. Arabeche, A. Schönhals, and J.-M. Saiter, “Temperature dependence of the characteristic length scale for glassy dynamics: Combination of dielectric and specific heat spectroscopy,” *Phys. Rev. E* **81**(4), 041805 (2010).
- ¹⁴ B. Rijal, L. Delbreilh, and A. Saiter, “Dynamic Heterogeneity and Cooperative Length Scale at Dynamic Glass Transition in Glass Forming Liquids,” *Macromolecules* **48**(22), 8219–8231 (2015).
- ¹⁵ E. Donth, “The size of cooperatively rearranging regions at the glass transition,” *Journal of Non-Crystalline Solids* **53**(3), 325–330 (1982).
- ¹⁶ M.D. Ediger, “Spatially Heterogeneous Dynamics in Supercooled Liquids,” *Annu. Rev. Phys. Chem.* **51**(1), 99–128 (2000).
- ¹⁷ R. Richert, “Heterogeneous dynamics in liquids: fluctuations in space and time,” *J. Phys.: Condens. Matter* **14**(23), R703–R738 (2002).
- ¹⁸ L. Berthier, “Time and length scales in supercooled liquids,” *Phys. Rev. E* **69**(2), 020201 (2004).
- ¹⁹ S.A. Reinsberg, X.H. Qiu, M. Wilhelm, H.W. Spiess, and M.D. Ediger, “Length scale of dynamic heterogeneity in supercooled glycerol near T_g ,” *The Journal of Chemical Physics* **114**(17), 7299–7302 (2001).
- ²⁰ F. Kohlrausch, “Ueber die elastische Nachwirkung bei der Torsion,” *Ann. Phys. Chem.* **195**(7), 337–368 (1863).
- ²¹ G. Williams, and D.C. Watts, “Non-symmetrical dielectric relaxation behaviour arising from a simple empirical decay function,” *Trans. Faraday Soc.* **66**, 80 (1970).
- ²² C.M. Roland, R. Casalini, and M. Paluch, “Isochronal temperature–pressure superpositioning of the α -relaxation in type-A glass formers,” *Chemical Physics Letters* **367**(3), 259–264 (2003).
- ²³ K.L. Ngai, R. Casalini, S. Capaccioli, M. Paluch, and C.M. Roland, “Do Theories of the Glass Transition, in which the Structural Relaxation Time Does Not Define the Dispersion of the Structural Relaxation, Need Revision?,” *J. Phys. Chem. B* **109**(37), 17356–17360 (2005).
- ²⁴ M. Romanini, M. Barrio, R. Macovez, M.D. Ruiz-Martin, S. Capaccioli, and J.L. Tamarit, “Thermodynamic Scaling of the Dynamics of a Strongly Hydrogen-Bonded Glass-Former,” *Sci Rep* **7**(1), 1346 (2017).
- ²⁵ K. Niss, and T. Hecksher, “Perspective: Searching for simplicity rather than universality in glass-forming liquids,” *The Journal of Chemical Physics* **149**(23), 230901 (2018).
- ²⁶ K.L. Ngai, “Universal properties of relaxation and diffusion in complex materials: Originating from fundamental physics with rich applications,” *Progress in Materials Science* **139**, 101130 (2023).
- ²⁷ L. Berthier, G. Biroli, J.-P. Bouchaud, L. Cipelletti, D.E. Masri, D. L’Hôte, F. Ladieu, and M. Pierno, “Direct Experimental Evidence of a Growing Length Scale Accompanying the Glass Transition,” *Science* **310**(5755), 1797–1800 (2005).
- ²⁸ C. Dalle-Ferrier, C. Thibierge, C. Alba-Simionesco, L. Berthier, G. Biroli, J.-P. Bouchaud, F. Ladieu, D. L’Hôte, and G. Tarjus, “Spatial correlations in the dynamics of glassforming liquids: Experimental determination of their temperature dependence,” *Phys. Rev. E* **76**(4), 041510 (2007).
- ²⁹ S. Capaccioli, G. Ruocco, and F. Zamponi, “Dynamically Correlated Regions and Configurational Entropy in Supercooled Liquids,” *J. Phys. Chem. B* **112**(34), 10652–10658 (2008).
- ³⁰ R. Böhmer, K.L. Ngai, C.A. Angell, and D.J. Plazek, “Nonexponential relaxations in strong and fragile glass formers,” *The Journal of Chemical Physics* **99**(5), 4201–4209 (1993).

- ³¹ X.H. Qiu, and M.D. Ediger, “Length Scale of Dynamic Heterogeneity in Supercooled D - Sorbitol: Comparison to Model Predictions,” *J. Phys. Chem. B* **107**(2), 459–464 (2003).
- ³² C. Crauste-Thibierge, C. Brun, F. Ladieu, D. L’Hôte, G. Biroli, and J.-P. Bouchaud, “Evidence of Growing Spatial Correlations at the Glass Transition from Nonlinear Response Experiments,” *Phys. Rev. Lett.* **104**(16), 165703 (2010).
- ³³ L. Berthier, G. Biroli, J.-P. Bouchaud, W. Kob, K. Miyazaki, and D.R. Reichman, “Spontaneous and induced dynamic correlations in glass formers. II. Model calculations and comparison to numerical simulations,” *The Journal of Chemical Physics* **126**(18), 184504 (2007).
- ³⁴ S. Araujo, N. Delpouve, A. Dhotel, S. Domenek, A. Guinault, L. Delbreilh, and E. Dargent, “Reducing the Gap between the Activation Energy Measured in the Liquid and the Glassy States by Adding a Plasticizer to Polylactide,” *ACS Omega* **3**(12), 17092–17099 (2018).
- ³⁵ F.W. Starr, and J.F. Douglas, “Modifying Fragility and Collective Motion in Polymer Melts with Nanoparticles,” *Phys. Rev. Lett.* **106**(11), 115702 (2011).
- ³⁶ B.A. Pazmiño Betancourt, J.F. Douglas, and F.W. Starr, “Fragility and cooperative motion in a glass-forming polymer–nanoparticle composite,” *Soft Matter* **9**(1), 241–254 (2013).
- ³⁷ C. Zhang, Y. Guo, and R.D. Priestley, “Characteristic Length of the Glass Transition in Isochorically Confined Polymer Glasses,” *ACS Macro Lett.* **3**(6), 501–505 (2014).
- ³⁸ A. Saiter, D. Prevosto, E. Passaglia, H. Couderc, L. Delbreilh, and J.M. Saiter, “Cooperativity length scale in nanocomposites: Interfacial and confinement effects,” *Phys. Rev. E* **88**(4), 042605 (2013).
- ³⁹ S.F. Nassar, S. Domenek, A. Guinault, G. Stoclet, N. Delpouve, and C. Sollogoub, “Structural and Dynamic Heterogeneity in the Amorphous Phase of Poly(L , L -lactide) Confined at the Nanoscale by the Coextrusion Process,” *Macromolecules* **51**(1), 128–136 (2018).
- ⁴⁰ B. Rijal, L. Delbreilh, C. Sollogoub, E. Baer, and A. Saiter-Fourcin, “Multiscale Analysis of Segmental Relaxation in PC/PETg Multilayers: Evidence of Immiscible Nanodroplets,” *Macromolecules* **55**(15), 6562–6572 (2022).
- ⁴¹ C. Schick, and E. Donth, “Characteristic length of glass transition: experimental evidence,” *Phys. Scr.* **43**(4), 423–429 (1991).
- ⁴² X. Monnier, N. Delpouve, N. Basson, A. Guinault, S. Domenek, A. Saiter, P.E. Mallon, and E. Dargent, “Molecular dynamics in electrospun amorphous plasticized polylactide fibers,” *Polymer* **73**, 68–78 (2015).
- ⁴³ S. Araujo, N. Delpouve, S. Domenek, A. Guinault, R. Golovchak, R. Szatanik, A. Ingram, C. Fauchard, L. Delbreilh, and E. Dargent, “Cooperativity Scaling and Free Volume in Plasticized Polylactide,” *Macromolecules* **52**(16), 6107–6115 (2019).
- ⁴⁴ D. Huang, D.M. Colucci, and G.B. McKenna, “Dynamic fragility in polymers: A comparison in isobaric and isochoric conditions,” *The Journal of Chemical Physics* **116**(9), 3925–3934 (2002).
- ⁴⁵ C.V. Grigoras, and A.G. Grigoras, “Nanoscale cooperativity on a series of statistical methacrylates copolymers with electron donor–acceptor pendant groups,” *J Therm Anal Calorim* **103**(2), 661–668 (2011).
- ⁴⁶ M. Nakanishi, and R. Nozaki, “Model of the cooperative rearranging region for polyhydric alcohols,” *Phys. Rev. E* **84**(1), 011503 (2011).

- ⁴⁷ M. Sharma, G. Madras, and S. Bose, “Unusual Fragility and Cooperativity in Glass-Forming and Crystalline PVDF/PMMA Blends in the Presence of Multiwall Carbon Nanotubes,” *Macromolecules* **48**(8), 2740–2750 (2015).
- ⁴⁸ A. Zetsche, and E.W. Fischer, “Dielectric studies of the α -relaxation in miscible polymer blends and its relation to concentration fluctuations,” *Acta Polymerica* **45**(3), 168–175 (1994).
- ⁴⁹ N. Shafqat, A. Alegría, A. Arbe, N. Malicki, S. Dronet, L. Porcar, and J. Colmenero, “Disentangling the Calorimetric Glass-Transition Trace in Polymer/Oligomer Mixtures from the Modeling of Dielectric Relaxation and the Input of Small-Angle Neutron Scattering,” *Macromolecules* **55**(17), 7614–7625 (2022).
- ⁵⁰ N. Shafqat, A. Alegría, N. Malicki, S. Dronet, F. Natali, L. Mangin-Thro, L. Porcar, A. Arbe, and J. Colmenero, “Microscopic versus Macroscopic Glass Transitions and Relevant Length Scales in Mixtures of Industrial Interest,” *Macromolecules* **56**(5), 2149–2163 (2023).
- ⁵¹ T.P. Lodge, and T.C.B. McLeish, “Self-Concentrations and Effective Glass Transition Temperatures in Polymer Blends,” *Macromolecules* **33**(14), 5278–5284 (2000).
- ⁵² K.L. Ngai, S. Valenti, and S. Capaccioli, “Molecular dynamic in binary mixtures and polymer blends with large difference in glass transition temperatures of the two components: A critical review,” *Journal of Non-Crystalline Solids* **558**, 119573 (2021).
- ⁵³ R.H. Colby, and J.E.G. Lipson, “Modeling the Segmental Relaxation Time Distribution of Miscible Polymer Blends: Polyisoprene/Poly(vinylethylene),” *Macromolecules* **38**(11), 4919–4928 (2005).
- ⁵⁴ D. Cangialosi, A. Alegría, and J. Colmenero, “Predicting the Time Scale of the Component Dynamics of Miscible Polymer Blends: The Polyisoprene/Poly(vinylethylene) Case,” *Macromolecules* **39**(20), 7149–7156 (2006).
- ⁵⁵ A. Arbe, J.A. Pomposo, I. Asenjo-Sanz, D. Bhowmik, O. Ivanova, J. Kohlbrecher, and J. Colmenero, “Single Chain Dynamic Structure Factor of Linear Polymers in an All-Polymer Nano-Composite,” *Macromolecules* **49**(6), 2354–2364 (2016).
- ⁵⁶ C.-C. Huang, M.-X. Du, B.-Q. Zhang, and C.-Y. Liu, “Glass Transition Temperatures of Copolymers: Molecular Origins of Deviation from the Linear Relation,” *Macromolecules* **55**(8), 3189–3200 (2022).
- ⁵⁷ J.A.S. Puente, B. Rijal, L. Delbreilh, K. Fatyeyeva, A. Saiter, and E. Dargent, “Segmental mobility and glass transition of poly(ethylene-vinyl acetate) copolymers: Is there a continuum in the dynamic glass transitions from PVAc to PE?,” *Polymer* **76**, 213–219 (2015).
- ⁵⁸ L. Hong, P.D. Gujrati, V.N. Novikov, and A.P. Sokolov, “Molecular cooperativity in the dynamics of glass-forming systems: A new insight,” *J. Chem. Phys.* **131**(19), 194511 (2009).
- ⁵⁹ L. Hong, V.N. Novikov, and A.P. Sokolov, “Is there a connection between fragility of glass forming systems and dynamic heterogeneity/cooperativity?,” *Journal of Non-Crystalline Solids* **357**(2), 351–356 (2011).
- ⁶⁰ G. Floudas, M. Paluch, A. Grzybowski, and K. Ngai, *Molecular Dynamics of Glass-Forming Systems* (Springer Berlin Heidelberg, Berlin, Heidelberg, 2011).
- ⁶¹ S. Napolitano, editor, *Non-Equilibrium Phenomena in Confined Soft Matter: Irreversible Adsorption, Physical Aging and Glass Transition at the Nanoscale* (Springer International Publishing, Cham, 2015).

- ⁶² C.M. Roland, and R. Casalini, “Effect of chemical structure on the isobaric and isochoric fragility in polychlorinated biphenyls,” *The Journal of Chemical Physics* **122**(13), 134505 (2005).
- ⁶³ S. Araujo, F. Batteux, W. Li, L. Butterfield, N. Delpouve, A. Esposito, L. Tan, J.-M. Saiter, and M. Negahban, “A Structural Interpretation of the Two Components Governing the Kinetic Fragility from the Example of Interpenetrated Polymer Networks,” *J. Polym. Sci. Part B: Polym. Phys.* **56**(20), 1393–1403 (2018).
- ⁶⁴ W.-S. Xu, J.F. Douglas, W. Xia, and X. Xu, “Understanding Activation Volume in Glass-Forming Polymer Melts via Generalized Entropy Theory,” *Macromolecules* **53**(17), 7239–7252 (2020).
- ⁶⁵ K. Niss, and C. Alba-Simionesco, “Effects of density and temperature on correlations between fragility and glassy properties,” *Phys. Rev. B* **74**(2), 024205 (2006).
- ⁶⁶ F. Kremer, and A. Schönhal, editors, *Broadband Dielectric Spectroscopy* (Springer Berlin Heidelberg, Berlin, Heidelberg, 2003).
- ⁶⁷ F. Kremer, editor, *Dynamics in Geometrical Confinement* (Springer, Cham, 2014).
- ⁶⁸ S. Hensel-Bielowka, J. Ziolo, M. Paluch, and C.M. Roland, “The effect of pressure on the structural and secondary relaxations in 1,1'-bis (p-methoxyphenyl) cyclohexane,” *The Journal of Chemical Physics* **117**(5), 2317–2323 (2002).
- ⁶⁹ A.C. Santos, A.F. Santos, H.P. Diogo, S.P. Alves, J.P.S. Farinha, N.T. Correia, M. Dionísio, and M.T. Viciosa, “Bulk dynamics of the thermoresponsive random copolymer of di (ethylene glycol) methyl ether methacrylate (MEO2MA) and oligo (ethylene glycol) methyl ether methacrylate (OEGMA),” *Polymer* **148**, 339–350 (2018).
- ⁷⁰ K. Mpoukouvalas, and G. Floudas, “Effect of Pressure on the Dynamic Heterogeneity in Miscible Blends of Poly(methyl methacrylate) with Poly(ethylene oxide),” *Macromolecules* **41**(4), 1552–1559 (2008).
- ⁷¹ A. Gitsas, G. Floudas, H.-J. Butt, T. Pakula, and K. Matyjaszewski, “Effects of Nanoscale Confinement and Pressure on the Dynamics of pODMA-*b*-p*t*BA-*b*-pODMA Triblock Copolymers,” *Macromolecules* **43**(5), 2453–2462 (2010).
- ⁷² M. Tarnacka, T. Flak, M. Dulski, S. Pawlus, K. Adrjanowicz, A. Swinarew, K. Kaminski, and M. Paluch, “High pressure polymerization of glycidol. Kinetics studies,” *Polymer* **55**(8), 1984–1990 (2014).
- ⁷³ V. Speranza, R. Salomone, and R. Pantani, “Effects of Pressure and Cooling Rates on Crystallization Behavior and Morphology of Isotactic Polypropylene,” *Crystals* **13**(6), 922 (2023).
- ⁷⁴ C.M. Roland, S. Hensel-Bielowka, M. Paluch, and R. Casalini, “Supercooled dynamics of glass-forming liquids and polymers under hydrostatic pressure,” *Rep. Prog. Phys.* **68**(6), 1405–1478 (2005).
- ⁷⁵ D. Heczko, J. Grelska, K. Jurkiewicz, P. Szychalska, A. Kasprzycka, K. Kamiński, M. Paluch, and E. Kamińska, “Anomalous narrowing of the shape of the structural process in derivatives of trehalose at high pressure. The role of the internal structure,” *Journal of Molecular Liquids* **336**, 116321 (2021).
- ⁷⁶ M. Paluch, J. Knapik, Z. Wojnarowska, A. Grzybowski, and K.L. Ngai, “Universal Behavior of Dielectric Responses of Glass Formers: Role of Dipole-Dipole Interactions,” *Phys. Rev. Lett.* **116**(2), 025702 (2016).

- ⁷⁷ K.L. Ngai, and C.M. Roland, "Intermolecular cooperativity and the temperature dependence of segmental relaxation in semicrystalline polymers," *Macromolecules* **26**(11), 2688–2690 (1993).
- ⁷⁸ A. Arsac, C. Carrot, and J. Guillet, "Determination of Primary Relaxation Temperatures and Melting Points of Ethylene Vinyl Acetate Copolymers," *Journal of Thermal Analysis and Calorimetry* **61**(3), 681–685 (2000).
- ⁷⁹ A. Saiter, E. Bureau, C. Cabot, and J.M. Saiter, "Fragility – Density of state and relaxation processes in polymeric materials," *Journal of Non-Crystalline Solids* **352**(42–49), 5067–5071 (2006).
- ⁸⁰ M.M. Kummali, A. Alegría, L.A. Miccio, and J. Colmenero, "Study of the Dynamic Heterogeneity in Poly(ethylene-*ran* -vinyl acetate) Copolymer by Using Broadband Dielectric Spectroscopy and Electrostatic Force Microscopy," *Macromolecules* **46**(18), 7502–7512 (2013).
- ⁸¹ S. Havriliak, and S. Negami, "A complex plane representation of dielectric and mechanical relaxation processes in some polymers," *Polymer* **8**, 161–210 (1967).
- ⁸² G. Tammann, and W. Hesse, "Die Abhängigkeit der Viskosität von der Temperatur bei unterkühlten Flüssigkeiten," *Z. Anorg. Allg. Chem.* **156**(1), 245–257 (1926).
- ⁸³ L. Delbreilh, M. Negahban, M. Benzohra, C. Lacabanne, and J.M. Saiter, "Glass transition investigated by a combined protocol using thermostimulated depolarization currents and differential scanning calorimetry," *J Therm Anal Calorim* **96**(3), 865–871 (2009).
- ⁸⁴ B. Rijal, J.A. Soto Puente, B. Atawa, L. Delbreilh, K. Fatyeyeva, A. Saiter, and E. Dargent, "Correlated and cooperative motions in segmental relaxation: Influence of constitutive unit weight and intermolecular interactions," *Phys. Rev. E* **94**(6), 062502 (2016).
- ⁸⁵ J. Korus, E. Hempel, M. Beiner, S. Kahle, and E. Donth, "Temperature dependence of *a* glass transition cooperativity," *Acta Polymerica* **48**(9), 369–378 (1997).
- ⁸⁶ G. Floudas, C. Gravalides, T. Reisinger, and G. Wegner, "Effect of pressure on the segmental and chain dynamics of polyisoprene. Molecular weight dependence," *The Journal of Chemical Physics* **111**(21), 9847–9852 (1999).
- ⁸⁷ C. Liu, Z. Liu, X. Yin, and G. Wu, "Tuning the Dynamic Fragility of Acrylic Polymers by Small Molecules: The Interplay of Hydrogen Bonding Strength," *Macromolecules* **48**(12), 4196–4206 (2015).
- ⁸⁸ K.L. Ngai, "Dynamic and thermodynamic properties of glass-forming substances," *Journal of Non-Crystalline Solids* **275**(1–2), 7–51 (2000).
- ⁸⁹ F. Alvarez, A. Alegra, and J. Colmenero, "Relationship between the time-domain Kohlrausch-Williams-Watts and frequency-domain Havriliak-Negami relaxation functions," *Phys. Rev. B* **44**(14), 7306–7312 (1991).
- ⁹⁰ A. Alegria, E. Guerrica-Echevarria, L. Goitiandia, I. Telleria, and J. Colmenero, "alpha.-Relaxation in the Glass Transition Range of Amorphous Polymers. 1. Temperature Behavior across the Glass transition," *Macromolecules* **28**(5), 1516–1527 (1995).
- ⁹¹ A. Tölle, H. Schober, J. Wuttke, O.G. Randl, and F. Fujara, "Fast Relaxation in a Fragile Liquid under Pressure," *Phys. Rev. Lett.* **80**(11), 2374–2377 (1998).
- ⁹² S. Hensel-Bielowka, S. Pawlus, C.M. Roland, J. Ziolo, and M. Paluch, "Effect of large hydrostatic pressure on the dielectric loss spectrum of type-*A* glass formers," *Phys. Rev. E* **69**(5), 050501 (2004).

- ⁹³ J. Trubert, L. Matkowska, A. Saiter-Fourcin, and L. Delbreilh, “Highlighting the interdependence between volumetric contribution of fragility and cooperativity for polymeric segmental relaxation,” *The Journal of Chemical Physics* **160**(4), 044909 (2024).
- ⁹⁴ K.L. Ngai, and M. Paluch, “Classification of secondary relaxation in glass-formers based on dynamic properties,” *The Journal of Chemical Physics* **120**(2), 857–873 (2004).
- ⁹⁵ K.L. Ngai, and C.M. Roland, “Chemical structure and intermolecular cooperativity: dielectric relaxation results,” *Macromolecules* **26**(25), 6824–6830 (1993).
- ⁹⁶ N. Delpouve, A. Saiter, and E. Dargent, “Cooperativity length evolution during crystallization of poly (lactic acid),” *European Polymer Journal* **47**(12), 2414–2423 (2011).
- ⁹⁷ F. Hamonic, D. Prevosto, E. Dargent, and A. Saiter, “Contribution of chain alignment and crystallization in the evolution of cooperativity in drawn polymers,” *Polymer* **55**(12), 2882–2889 (2014).
- ⁹⁸ A. Esposito, N. Delpouve, V. Causin, A. Dhotel, L. Delbreilh, and E. Dargent, “From a Three-Phase Model to a Continuous Description of Molecular Mobility in Semicrystalline Poly(hydroxybutyrate- *co* -hydroxyvalerate),” *Macromolecules* **49**(13), 4850–4861 (2016).
- ⁹⁹ J. Mattsson, H.M. Wyss, A. Fernandez-Nieves, K. Miyazaki, Z. Hu, D.R. Reichman, and D.A. Weitz, “Soft colloids make strong glasses,” *Nature* **462**(7269), 83–86 (2009).
- ¹⁰⁰ K.L. Ngai, *Relaxation and Diffusion in Complex Systems* (Springer New York, New York, NY, 2011).
- ¹⁰¹ J.G. Kirkwood, “THE LOCAL FIELD IN DIELECTRICS,” *Annals of the New York Academy of Sciences* **40**(5), 315–320 (1940).
- ¹⁰² R. Nozaki, and S. Mashimo, “Dielectric relaxation measurements of poly(vinyl acetate) in glassy state in the frequency range 10^{-6} – 10^6 Hz,” *The Journal of Chemical Physics* **87**(4), 2271–2277 (1987).
- ¹⁰³ H. Yin, S. Napolitano, and A. Schönhals, “Molecular Mobility and Glass Transition of Thin Films of Poly(bisphenol A carbonate),” *Macromolecules* **45**(3), 1652–1662 (2012).
- ¹⁰⁴ P.-M. Déjardin, F. Pabst, Y. Cornaton, A. Helbling, and T. Blochowicz, “Temperature dependence of the Kirkwood correlation factor and linear dielectric constant of simple isotropic polar fluids,” *Phys. Rev. E* **105**(2), 024108 (2022).
- ¹⁰⁵ A. Schönhals, “Evidence for a universal crossover behaviour of the dynamic glass transition,” *Europhys. Lett.* **56**(6), 815–821 (2001).
- ¹⁰⁶ S.A. Reinsberg, A. Heuer, B. Doliwa, H. Zimmermann, and H.W. Spiess, “Comparative study of the NMR length scale of dynamic heterogeneities of three different glass formers,” *Journal of Non-Crystalline Solids* **307–310**, 208–214 (2002).
- ¹⁰⁷ K.L. Ngai, “Why the glass transition problem remains unsolved?,” *Journal of Non-Crystalline Solids* **353**(8–10), 709–718 (2007).
- ¹⁰⁸ E. Hempel, G. Hempel, A. Hensel, C. Schick, and E. Donth, “Characteristic Length of Dynamic Glass Transition near T_g for a Wide Assortment of Glass-Forming Substances,” *J. Phys. Chem. B* **104**(11), 2460–2466 (2000).
- ¹⁰⁹ Th. Bauer, P. Lunkenheimer, and A. Loidl, “Cooperativity and the Freezing of Molecular Motion at the Glass Transition,” *Phys. Rev. Lett.* **111**(22), 225702 (2013).
- ¹¹⁰ A. Drozd-Rzoska, “Activation volume in superpressed glass-formers,” *Sci Rep* **9**(1), 13787 (2019).

- ¹¹¹ A. Grzybowski, S. Urban, S. Mroz, and M. Paluch, “Activation volume of selected liquid crystals in the density scaling regime,” *Sci Rep* **7**(1), 42174 (2017).
- ¹¹² M. Paluch, J. Gapinski, A. Patkowski, and E.W. Fischer, “Does fragility depend on pressure? A dynamic light scattering study of a fragile glass-former,” *The Journal of Chemical Physics* **114**(18), 8048–8055 (2001).
- ¹¹³ S.P. Andersson, and O. Andersson, “Relaxation Studies of Poly(propylene glycol) under High Pressure,” *Macromolecules* **31**(9), 2999–3006 (1998).
- ¹¹⁴ G. Floudas, “Effects of pressure on systems with intrinsic orientational order,” *Progress in Polymer Science* **29**(11), 1143–1171 (2004).
- ¹¹⁵ M. Paluch, C.M. Roland, and S. Pawlus, “Temperature and pressure dependence of the α -relaxation in polymethylphenylsiloxane,” *The Journal of Chemical Physics* **116**(24), 10932–10937 (2002).
- ¹¹⁶ R. Casalini, M. Paluch, and C.M. Roland, “Influence of molecular structure on the dynamics of supercooled van der Waals liquids,” *Phys. Rev. E* **67**(3), 031505 (2003).
- ¹¹⁷ K. Mpoukouvalas, G. Floudas, and G. Williams, “Origin of the α , β , ($\beta\alpha$), and ‘Slow’ Dielectric Processes in Poly(ethyl methacrylate),” *Macromolecules* **42**(13), 4690–4700 (2009).
- ¹¹⁸ A. Błażytko, M. Rams-Baron, and M. Paluch, “The influence of molecular shape on reorientation dynamics of sizable glass-forming isomers at ambient and elevated pressure,” *Sci Rep* **14**(1), 887 (2024).
- ¹¹⁹ K. Kunal, C.G. Robertson, S. Pawlus, S.F. Hahn, and A.P. Sokolov, “Role of Chemical Structure in Fragility of Polymers: A Qualitative Picture,” *Macromolecules* **41**(19), 7232–7238 (2008).
- ¹²⁰ J. Dudowicz, K.F. Freed, and J.F. Douglas, “The Glass Transition Temperature of Polymer Melts,” *J. Phys. Chem. B* **109**(45), 21285–21292 (2005).
- ¹²¹ J. Dudowicz, K.F. Freed, and J.F. Douglas, “Fragility of Glass-Forming Polymer Liquids,” *J. Phys. Chem. B* **109**(45), 21350–21356 (2005).
- ¹²² E.U. Mapesa, D.P. Street, M.F. Heres, S.M.I. Kilbey, and J. Sangoro, “Wetting and Chain Packing across Interfacial Zones Affect Distribution of Relaxations in Polymer and Polymer-Grafted Nanocomposites,” *Macromolecules* **53**(13), 5315–5325 (2020).
- ¹²³ P. Pan, B. Zhu, and Y. Inoue, “Enthalpy Relaxation and Embrittlement of Poly(L-lactide) during Physical Aging,” *Macromolecules* **40**(26), 9664–9671 (2007).
- ¹²⁴ T. Huang, M. Miura, S. Nobukawa, and M. Yamaguchi, “Chain Packing and Its Anomalous Effect on Mechanical Toughness for Poly(lactic acid),” *Biomacromolecules* **16**(5), 1660–1666 (2015).
- ¹²⁵ J. Zhang, D.-Z. Jia, G.-Q. Ma, H. Lin, H.-D. Huang, G.-J. Zhong, and Z.-M. Li, “Mechanically rejuvenated glassy polylactide with spatial heterogeneity and packing efficiency: Time dependence of deformation behavior,” *Polymer* **298**, 126876 (2024).
- ¹²⁶ P. Ma, D.G. Hristova-Bogaerds, J.G.P. Goossens, A.B. Spoelstra, Y. Zhang, and P.J. Lemstra, “Toughening of poly(lactic acid) by ethylene-*co*-vinyl acetate copolymer with different vinyl acetate contents,” *European Polymer Journal* **48**(1), 146–154 (2012).
- ¹²⁷ E.B. Stukalin, J.F. Douglas, and K.F. Freed, “Application of the entropy theory of glass formation to poly(α -olefins),” *The Journal of Chemical Physics* **131**(11), 114905 (2009).

¹²⁸ N. Delpouve, L. Delbreilh, G. Stoclet, A. Saiter, and E. Dargent, “Structural Dependence of the Molecular Mobility in the Amorphous Fractions of Polylactide,” *Macromolecules* **47**(15), 5186–5197 (2014).

¹²⁹ G. Floudas, K. Mpoukouvalas, and P. Papadopoulos, “The role of temperature and density on the glass-transition dynamics of glass formers,” *The Journal of Chemical Physics* **124**(7), 074905 (2006).

¹³⁰ Motosuke. Naoki, Hideki. Endou, and Katsuhiko. Matsumoto, “Pressure effects on dielectric relaxation of supercooled ortho-terphenyl,” *J. Phys. Chem.* **91**(15), 4169–4174 (1987).

¹³¹ R. Casalini, and C.M. Roland, “Thermodynamical scaling of the glass transition dynamics,” *Phys. Rev. E* **69**(6), 062501 (2004).

¹³² M. Rams-Baron, A. Blazytko, R. Casalini, and M. Paluch, “Insight into properties of sizable glass former from volumetric measurements,” (2024).