Two crossover regions in the dynamics of glass forming epoxy resins

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Broadband dielectric spectroscopy, heat capacity spectroscopy (3ω method), and viscosimetry have been used to study the dynamic glass transition of two glass-forming epoxy resins, poly [phenyl glycidyl ether]-co-formaldehyde] and diglycidyl ether of bisphenol-A. In spite of their rather simple molecular structure, the dynamics of these systems is characterized by two well-separated crossover regions where the relaxation times of main transition and the two secondary relaxations β and γ approach each other. The main transition has three parts: The α process at high temperature, the α’ process between the two crossover regions, and the α process at low temperatures. Both the γ-crossover region [around a temperature \( T_g(\gamma) \approx (1.4–1.5)T_g \) and a relaxation time \( \tau_g(\gamma) \approx 10^{-10} \text{ s} \)] and the β-crossover region [around \( T_r(\beta) \approx (1.1–1.2)T_g \) and \( \tau_r(\beta) \approx 10^{-6} \text{ s} \)] could be studied within the experimentally accessible frequency–temperature window. Different typical crossover properties are observed in the two regions. The γ-crossover region is characterized by onset of the \((\alpha’, \alpha)\) process, with a relaxation time about one decade greater than that of the quasicontinuous \((\alpha, \gamma)\) trace. The β-crossover region is characterized, besides splitting of main and β relaxation times, by a change in the temperature dependence of the main-relaxation time as reflected by a bend in the Stickel plot of the continuous \((\alpha’, \alpha)\) trace, the separation of individual temperature dependences of different transport properties such as impurity-ions diffusion coefficient and viscosity, and a temperature-dependent main relaxation time that starts to be in accordance (at lower temperatures) with the Adam–Gibbs model. The cooperativity of the main process between the \(\gamma\) and \(\beta\) crossover seems to be small. Below the β crossover, cooperativity increases up to values of order \(N_c–100\) near \(T_g\), and configurational entropy seems to correlate with the main relaxation time. © 2002 American Institute of Physics. [DOI: 10.1063/1.1486214]

I. INTRODUCTION

In condensed matter physics, increasing interest is devoted to the glass transition phenomenon. In this field, some common aspects in the dynamics of different systems suggest that, despite material-specific aspects, some common basic interpretation should be found for the liquid to glass transition. In particular, it is well known that various glasses from small molecules to polymers show a relatively similar relaxation map (i.e., temperature dependence of the characteristic times), with a main dynamic transition (a and α process) whose characteristic time tends to diverge close to the conventional glass transition temperature \(T_g\), and one or more secondary processes (β, γ,...) that persist also below \(T_g\). In the last few years an increasing number of crossover effects along the trace of the main dynamic transition has been reported for several liquids. In these studies, concerned with systems with only one secondary relaxation, the crossover effects usually occur in a narrow frequency–temperature range, a marked region in the Arrhenius diagram above \(T_g\) generally called the crossover region. This region can be characterized (see, e.g., Refs. 1 and 2) by several properties:

(i) Splitting of the high-temperature process (\(a\)) into the cooperative α process and the local secondary process,\(^{3–6}\) as seen from above, or merging of the α and secondary process into the α process, as seen from below.

(ii) Extrapolated onset of the dielectric and calorimetric intensity of the α process \([\text{i.e., } \Delta e_{\alpha} \rightarrow 0, \Delta C_{p,a} \rightarrow 0 \text{ (Refs. 7–9)}]\) for scenario 1 (see below).

(iii) Bend in the trace of the main \((\alpha, \alpha)\) transition, known as Stickel bend,\(^{10–13}\) corresponding to a change, within a small temperature interval, of the Vogel–Fulcher–Tamman parameters for the \(a\) process to different parameters for the \(a\) process. The Vogel temperature \(T_0\) for the \(a\) pro-

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cess is, as a rule (scenario II, see below), smaller than the Vogel temperature for the $a$ process, i.e., $T_g(\alpha) < T_g(\beta)$.

(iv) Separation of the individual temperature dependences of different transport properties such as self-diffusion and viscosity.\textsuperscript{14–16} This is connected with the breakdown of the Stokes–Einstein law of diffusion.\textsuperscript{17}

(v) The plot of the logarithm of the characteristic time for the main transition versus the reciprocal configurational entropy (more precisely, versus $1/TS$), inspired by the Adam–Gibbs relation,\textsuperscript{18} shows a bend.\textsuperscript{19}

By proper extrapolations, characteristic crossover temperatures for the above-mentioned effects are found to range within a temperature interval of about 10 K.\textsuperscript{1,20} For the sake of brevity, we will refer to the crossover temperature as an average temperature value of the crossover region. For fragile glass-formers a typical crossover temperature $T_c$ is about $T_c \approx 1.2 T_g$. The corresponding relaxation time region in the Arrhenius diagram is typically around $\tau \approx 10^{-6}$ s. However, both values ($\tau_c$ and $T_c / T_g$) show a large variance in groups of different substances, as discussed in Refs. 1 and 21. We know also a series of substances where $T_c$ tends systematically to the glass transition temperature, $T_c \rightarrow T_g$, the poly(n-alkyl methacrylate)s, where $T_g$ is reached near the hexyl member.\textsuperscript{22}

As recalled at point (i), crossover effects are often accompanied by the occurrence of a splitting phenomenon, i.e., separation of the relaxation times of dynamic glass transition and a secondary relaxation. In a rough, preliminary classification we can recognize two scenarios of the crossover region\textsuperscript{7,23,24} (see also Refs. 25–27) in connection with the type of splitting region:

Scenarii I. Separate onset of the $\alpha$ process about one to two frequency decades (frequency gap) below the continuous trace of the $a$ and $\beta$ processes. This last trace shows there a more or less pronounced bend in the Arrhenius diagram. The crossover region can be defined by the extrapolation to zero of the $\alpha$ intensity.

Scenarii II. A continuous trace of the main ($a, \alpha$) transition where the crossover region can be defined by the extrapolation from low temperatures of the trace of the $\beta$ process, running into the main process with a large “angle” in the Arrhenius diagram and with a usually small relaxation intensity [e.g., $\Delta \varepsilon_b = (\Delta \varepsilon_{a}, \Delta \varepsilon_{\alpha})$ near $T_g$].

It was speculated\textsuperscript{24} that the molecular cage for the $a$ process is larger for scenario II than for scenario I, inducing for scenario II “more continuity” between the $a$ process and the cooperative $\alpha$ process, with increasing size of the cooperativity regions below the crossover.\textsuperscript{28}

The aim of the present paper is the experimental study of the dynamic glass transition in two epoxy resins: poly[11-phenyl glycidyl ether]-co-formaldehyde (PPGE) and diglycidyl ether of bisphenol-A (DGEBA). The main interest for these systems is that they both show two secondary relaxations that approach the main transition inside the experimentally accessible frequency window. Following the tradition of polymer physics, the secondary relaxation at lower frequencies is called the $\beta$ process, and that at higher frequency is called the $\gamma$ process. We use the term crossover region to indicate a temperature–frequency region where changes take place in the dynamic behavior of the system. From broadband dielectric spectroscopy we have indication of two well-separated crossover regions ($\beta$ crossover and $\gamma$ crossover), with $\tau_{\beta}(\beta) \approx 10^{-6}$ s and $\tau_{\gamma}(\gamma) \approx 10^{-10}$ s. We use additionally viscosity measurements and heat capacity spectroscopy (3o method) to study the following two questions:

(A) Which property (ii)–(v) can be observed in the two different crossover regions ($\beta$ crossover and $\gamma$ crossover)? Especially, can the two crossover regions also be classified within scenario I or scenario II?

(B) What is the character of the part of the main transition between the two crossovers? Especially, is it more a high-temperature process (similar to the $a$ process, therefore called $a'$), or is it more a cooperative process (similar to the $\alpha$ process, hence the name $\alpha'$)?

The results for our low-molecular-weight epoxy resins will be finally compared with dielectric measurements from literature on other substances with two secondary relaxations.

II. EXPERIMENT

A. Samples

The sample of DGEBA used in this study was purchased from Shell Co. under the trade name of Epon 828 [average molecular weight \~ 380 g/mol, corresponding to $n \sim 0.14$ in the chemical formula reported in Fig. 1(a)]. It is a widely used commercial epoxy resin, and was measured as pur-
to well above the glass transition temperature, in steps of 5 degrees. The results are compared with previously published dielectric data in the frequency range from $10^2$ to $2 \times 10^{10}$ Hz (Ref. 8) and data at lower frequencies down to $10^{-2}$ Hz (Ref. 29). Altogether we present dielectric results for DGEBA covering 12 decades of frequency, obtained in the temperature range from 123.2 to 353.2 K.

The real and imaginary parts of the dielectric constant, $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$, of our samples are displayed in Figs. 1 and 2 at several temperatures. The isothermal data for the dielectric constant were analyzed in terms of linear superposition of relaxation and conductivity contributions (additive ansatz), with each relaxation process described by a Havriliak–Negami (HN) function:

$$\varepsilon^*(\omega) = \varepsilon_\infty - \sum_k \Delta \varepsilon_k [1 + i\omega\tau_{HN,k}]^{-\alpha_k} - \frac{i\sigma}{\omega\varepsilon_0}, \quad (1)$$

In Eq. (1) the index $k$ runs over the relaxation processes and the conductivity effect is taken into account by the term $-i\sigma/\omega\varepsilon_0$ ($\varepsilon_\infty$ is the dielectric permittivity of vacuum). $\varepsilon_\infty$ is the high-frequency limit of $\varepsilon'$ outside the dispersion zone, and $\Delta \varepsilon_k$ is the dielectric strength of each process. The fit with this phenomenological function allows us to extract characteristic parameters for the different relaxation peaks, i.e., the frequency of maximum loss and the peak shape. The frequency of maximum $\varepsilon''$, $f_{max}$, can be analytically calculated from the HN fitting parameters by

$$f_{max} = \left(2\pi\tau_{HN}\right)^{-1} \sin^{1/(1-\alpha)} \left(\frac{\pi(1-\alpha)}{2(1+\beta)}\right) \sin^{-1/(1-\alpha)} \times \left(\frac{\pi(1-\alpha)\beta}{2(1+\beta)}\right). \quad (2)$$

From this quantity a characteristic relaxation time $\tau_{max} = (2\pi f_{max})^{-1}$ can be easily obtained, usually preferred to $\tau_{HN}$ since it is a model-independent parameter. Concerning the shape of the dielectric peak, the HN function gives the asymptotic behavior of $\varepsilon^*(\omega)$ in the low- and high-frequency limits as power laws, $\varepsilon'' \approx \omega^n$ and $\varepsilon' \approx \omega^{-m}$ respectively, whose exponents are simply expressed in terms of the HN shape parameters $\alpha$ and $\beta$ through the relations $m = (1 - \alpha)$ and $n = \beta(1 - \alpha)$.

The real and the imaginary parts of $\varepsilon^*(\omega)$ have been fitted simultaneously by using the nonlinear least-squares Levenberg–Marquardt routine. The uncertainties of the fitting parameters have been estimated by means of a Monte Carlo procedure. In particular, starting from each experimental spectrum 100 “artificial” data sets have been produced by means of the bootstrap Monte Carlo method, replacing a random fraction of original points by duplicated original points. Each data set has been fitted by means of the Levenberg–Marquardt routine, giving a distribution of fitting parameters. An estimate of the error of each parameter has been obtained by the standard deviation of the probability distribution of the fitting parameters. Finally, the errors of the HN fitting parameters have been used to estimate the error of the relaxation time $\tau_{max}$.

B. Measurements

1. Dielectric spectroscopy

Due to the strong permanent dipoles originating from the presence of epoxy groups (~2.1 D per epoxy group), both DGEBA and PPGE are particularly suitable for a dielectric investigation. Measurements of the dielectric constant $\varepsilon^*(\omega,T) = \varepsilon' - i\varepsilon''$ in PPGE were carried out by means of an Alpha Novocontrol dielectric analyzer (Pisa & Mainz) and an impedance analyzer HP4194A (Pisa) in the frequency range from $10^{-2}$ to $10^7$ Hz. A network analyzer HP8753A (Perugia) was used to cover the frequency range from $10^2$ to $3 \times 10^9$ Hz. Isothermal frequency scans were performed in the temperature interval from 357.8 to 133.2 K, during several series of measurements.

The dielectric constant of DGEBA was measured in the frequency range from $10^{-1}$ to $10^5$ Hz by a Novocontrol BDS 4000 based on a Solartron FRA 1260 (Halle). The temperature interval was from 123.2 to 293.2 K, i.e., from far below

chased. PPGE is an epoxy resin with average molecular weight of 345 g/mol. It was obtained from Aldrich Chemicals and was measured as received. The chemical formula of this material is given in Fig. 2(a). The conventional glass transition temperatures are $T_g = 255 \pm 1$ K for DGEBA and $T_g = 258 \pm 1$ K for PPGE. The $T_g$ values were obtained by an equal-area construction from differential scanning calorimetry (DSC) curves, acquired by a Perkin-Elmer DSC 7 apparatus, at a heating rate of $dT/dt = +10$ K/min.

FIG. 2. (a) Real and (b) imaginary part of $\varepsilon^*(\omega)$ for DGEBA (selected data) at several temperatures (353, 343, 333, 323, 313, 303, 298, 293, 288, 283, 278, 273, 268, 263, 259, 256 K) above $T_g$, in the range $10^{-2}$–$2 \times 10^9$ Hz. The solid lines represent a fit with two HN functions. In the inset: dielectric loss at some temperatures below $T_g$, showing the $\gamma$ process at higher frequencies and the $\beta$ process at lower frequencies. The best fit with a symmetrical Cole–Cole function plus a HN function is shown by solid lines.
2. Heat capacity spectroscopy (HCS)

The dynamic effusivity $\rho c_p^* (\omega, T) = \rho c_p \kappa \kappa - i \omega \kappa c_p^*$ (K is the heat conductivity, $\rho$ the density, and $c_p^*$ the dynamic heat capacity) was measured by the 3o method in the frequency range from 0.2 to 2000 Hz. Nickel heaters with a thickness of about 70 nm on poly(ether ether ketone) (PEEK) substrates were used. The temperature coefficient of resistance was about 2000 ppm/K. The nickel heater was placed in a Wheatstone bridge that was equilibrated automatically during the measurements. The remaining difference signal across the bridge was preamplified by a low-noise preamplifier (EG&G 5113). A 12-bit analog to digital converter was used to collect the data. Amplitude and phase of the third harmonic were determined afterwards by a selective Fourier transformation. Further experimental details about our setup are described elsewhere.32,33

Measurements on two different heaters were performed for both epoxy samples: small nickel heaters ($5 \times 6 \text{ mm}^2$) were used for high frequencies ($\geq 1$ Hz), large nickel heaters ($5 \times 10 \text{ mm}^2$) were used for low frequencies (0.2–20 Hz). This ensures the signal amplitude and precision to be large enough at high frequencies (amplitude $\sim \omega^{-1/2}$) and the thermal wavelength to be small compared to the heater dimensions at low frequencies as required by the data evaluation concept. The samples were equilibrated for 30 min before an isothermal frequency sweep was started.

The frequency-dependent width of the $\alpha$ peak, $\delta T$, and the dynamic glass transition temperature, $T_{dg}$, were determined by Gaussian fits to the isochronal ($\omega = \text{const}$) data for the imaginary part $\rho c_p \kappa \kappa^*$ of the isothermal HCS signal. The calorimetric $\alpha$ intensity was obtained from a tangent construction to the real part $\rho c_p \kappa \kappa^*(T)$ [see Fig. 3(c)]. To get finally $\Delta (1/c_p)$ values from our 3o method output, the data were adjusted to heat capacities $c_p^*$ from temperature-modulated DSC (TM-DSC) at $\omega = 2\pi/60 \text{s}$. A fixed factor correction was used: all isochrones of one 3o run were divided by a heater-specific mean value of $\rho c_p$. The error caused by this temperature- and frequency-independent mean value $\rho c_p$ correction is found to be small.34

The isochronal HCS sweeps of Fig. 3 are transferred into isothermal $\rho c_p^*$ data versus frequency in Fig. 4.

3. Viscosity measurements

The shear viscosity was measured with a Rheometrics Dynamic Analyzer RDA-II and a Dynamic Stress Rheometer DSR instruments from Rheometrics Scientific in plate-plate geometry. Parallel plates with a diameter of 25 mm were used in the temperature range from 276 to 379 K for PPGE and in the range from 269 to 339 K for DGEBA. The sample thickness was about 1.5 mm. A shear rate sweep over one decade was performed at each temperature to prove the Newtonian behavior of the liquid. The thermal expansion of the tools (about 2.5 $\mu m/K$) and the samples was corrected during the measurements. Some data points at temperatures between 267 and 259 K were added for DGEBA by extending the sample between two 8 mm plates to a hyperboloid with a final length of about 8 mm (for details see Ref. 35). In the temperature range from 332 to 453 K viscosity was measured by an Ubbelohde type viscosimeter ($k = 0.5 \text{ mm}^2/\text{s}^2$). An oil bath was used to control the sample temperature. The viscosity was calculated according to $\eta = {t_1 k p}$ from flow time $t_1$, capillary constant $k$, and temperature-dependent density $\rho$. The density $\rho (T) = \rho_0 (1 - \alpha_v (T - 273))$ for DGEBA was measured by a Guy–Lussac-type picnometer at temperatures between 296 and 318 K and extrapolated to higher temperatures. A thermal...
expansion coefficient $\alpha_v = (6.26 \pm 0.03) \times 10^{-4}$ K$^{-1}$ and a density at 273 K $\rho_0 = 1.1823 \pm 0.0003$ g/cm$^3$ were obtained for DGEBA. The corresponding values for PPGE taken from measurements in the range from 287 to 332 K were $\alpha_v = (6.3 \pm 0.1) \times 10^{-4}$ K$^{-1}$ and $\rho_0 = 1.2266 \pm 0.0003$ g/cm$^3$.

Figure 5 shows the viscosity data for DGEBA and PPGE over the whole temperature range measured. For comparison, the same figure includes some viscosity data for DGEBA from dynamical mechanical measurements, carried out via a Rheometrics RMS 800 in the range from 255 to 374 K and published in a previous article where experimental details were repeated by exploiting the data at lower frequencies and adopting at the highest temperatures ($T > 288$ K) the criterion of keeping invariant the parameter $n_a \sim 0.4$ as found at lower temperature. This criterion was motivated by the time–temperature superposition principle and supported by previous light-scattering results for the shape of the main process in DGEBA over the same temperature interval as the present dielectric investigation. In fact, the mutual consistency of dielectric and depolarized light-scattering shape parameters was observed, although the characteristic times of the process revealed by the two techniques were different. Since in case of light-scattering spectra there is no signature of the secondary peak visible in the dielectric ones, a more reliable determination of the $\alpha$ shape parameters could be made, giving $m_a \sim 0.9$ and $n_a \sim 0.4$. In our dielectric fit procedure the shape parameter $m_a$ was set as free; anyway, its value was found almost constant around 0.9 (see also Table I), thus validating the guess of a shape invariance. The parameters for the $\alpha$ relaxation of PPGE and DGEBA obtained from the HN fit at several temperatures are given in Table I with error estimates.

The isothermal HCS spectra of PPGE and DGEBA reported in Fig. 4 show a well-defined peak in the imaginary part $\rho \varepsilon''(\omega)$, corresponding to the characteristic relaxation step in the real part $\rho \varepsilon'(\omega)$. In the frequency and temperature range investigated here only one relaxation process is observed. In principle, all $\rho \varepsilon''(\omega)$ isotherms could be approximated by a single HN function, giving for each temperature, after reduction by $\rho \varepsilon'$, the frequency of maximum $\varepsilon''$, the calorimetric $\alpha$ intensity $\Delta \varepsilon_a$, and the shape parameters, in a manner similar to Eq. (1). However, several sources of error make the data $\rho \varepsilon''(\omega)$ subject to considerable uncertainty and limit, together with the narrow frequency range accessible, the possibility for determining a reliable set of fit parameters. In the present case, only for a few temperatures can the whole set of HN fit parameters be determined with reasonable accuracy. In particular, the fit of $\rho \varepsilon''(\omega)$ for PPGE at 274 K results in $\Delta \varepsilon_a = (5.96 \pm 0.30) \times 10^{-4}$ F cm$^{-1}$ K$^{-2}$ s$^{-1}$, $\tau_{HN} = (6.7 \pm 1.9) \times 10^{-3}$ s, $m = 0.68 \pm 0.04$, and $n = 0.44 \pm 0.07$, while the fit of $\rho \varepsilon''(\omega)$ for DGEBA at 269.1 K gives $\Delta \varepsilon_a = (5.37 \pm 0.55) \times 10^{-4}$ F cm$^{-1}$ K$^{-2}$ s$^{-1}$, $\tau_{HN} = (1.67 \pm 0.09) \times 10^{-3}$ s, $m = 0.67 \pm 0.06$, and $n = 0.39 \pm 0.11$. The corresponding fitting curves are reported as solid lines in Fig. 4. For each system, the data at all other temperatures were fitted by fixing the shape parameters within the range allowed by these values. The results for $\Delta c_p$ and $\tau_{max}$ are in fair agreement with those obtained in the corresponding temperature range from tangent construction and Gaussian fits to isochronal data. We note that shape parameters obtained by HCS are not far away from those obtained by dielectric spectroscopy. Usually it is found that $c''$ peaks tend to be narrower and more symmetric than the corresponding dielectric loss curves.
However, the significant uncertainty of HCS parameters restrains us from going into a deeper comparison.

The dielectric relaxation times $\tau_{\text{max}}$ obtained from the fitting procedure, together with the calorimetric characteristic times $\tau_{\text{max}}$ obtained from the location of the peak in the isochronal or isothermal $\rho_{g\kappa}c''$ spectra, are reported in the Arrhenius plot of Figs. 6 and 7 and compared with the viscosity data. The $\alpha$ trace of calorimetry and dielectrics coincide within the experimental uncertainty, and their temperature dependence closely parallels that of $\eta$. Figure 8 shows a convincing check of the relation $\tau_{\text{max}} \propto \eta$ in our samples, up to 332 K in PPGE and 343 K in DGEBA. It displays that a linear fit of log $\tau_{\text{max}}$ vs log $\eta$ has slope $0.99 \pm 0.02$ and $0.98 \pm 0.02$ in PPGE and DGEBA, respectively. According to $\tau_{\text{max}} \propto \eta$, the viscosity data are rescaled up to the highest temperatures measured, and shown as solid lines in the Arrhenius plot of Figs. 6(a) and 7(a). We notice that the proportionality of $\tau_{\text{max}}$ to $\eta$ in supercooled liquids has a physical basis in the $\alpha$-scale universality predicted by the mode coupling theory and verified in different systems (e.g., see Ref. 40), but it is possible that at sufficiently high temperatures a $\tau_{\text{max}} \propto T$ regime ensues, as predicted by the hydrodynamic Debye model and recently observed in low-molecular-weight organic compounds.13 However, the possible differences in Figs. 6 and 7 due to a $\eta \propto \tau_{\text{max}}T$ rescaling of the viscosity data for temperatures higher than those represented in Fig. 8 have no significant effect on the analysis and discussion reported in the following.

Together with the secondary relaxation times, Figs. 6(a) and 7(a) give the complete relaxation map of our samples in the supercooled and glassy state, as revealed by dielectric spectroscopy, HCS, and viscosity measurements. As known, the glass transition phenomenon is commonly described as an ergodic- to nonergodic-state transition and $T_g$ is defined as the temperature at which the ergodicity is broken on the ex-

![Image](https://example.com/image.png)
time approximately exceeds 102 s. The dielectric value in the out-of-equilibrium state occurs when the structural relaxation time scales are reported with diamond and squares, respectively. The dashed line is an Arrhenius fit to the $T_g$ relaxation data [log $\eta$ ($s$) = -14.35 ± 0.13, $E_a$ = 6.6 ± 0.1 kcal/mol]; its extrapolation above $T_g$ is drawn with a dotted line. The dash-dotted line is an Arrhenius fit to the $\beta$ relaxation data [log $\eta$ ($s$) = -14.78 ± 0.09, $E_a$ = 11.38 ± 0.08 kcal/mol]. The $\beta$- and $\gamma$-crossover regions are indicated by arrows. (b) Temperature dependence of the dielectric strengths of DGEBA. The inset shows $\Delta \varepsilon_{\mathrm{PGE}}$ (circles) and $\Delta \varepsilon_{\mathrm{PPGE}}$ (down triangles) above $T_g$, and the calorimetric $\alpha$ intensity $\Delta C_p$ (up triangles, in units J kg$^{-1}$ K$^{-1}$). The solid line is a linear fit to $\Delta \varepsilon_{\mathrm{PGE}}$, extrapolated to the onset temperature $T_{\mathrm{on}}$. The dotted line is drawn as a guide to the eyes. Error bars smaller than the symbol size are omitted.

At lower temperatures the system is in the nonequilibrium glassy state. There, two secondary processes ($\beta$ and $\gamma$ process) coexist, both showing Arrhenius behavior. The corresponding fitting parameters are listed in Table III. The dotted segment in Figs. 6(a) and 7(a) shows that at temperatures higher than $T_g$ the $\gamma$ trace deviates significantly from the extrapolation of the behavior below $T_g$. In particular, it first becomes flatter (i.e., lower apparent activation energy) and then goes on with increasing slope (i.e., increasing apparent activation energy), which becomes comparable to that found below $T_g$. Different approaches for analyzing relaxation functions in the case of the overlap of the two processes are debated in literature, and their repercussions are especially expected in the Arrhenius diagram in the region where the processes tend to merge. Then we cannot completely rule out the possibility of some influence of the analysis method on the higher temperature $\tau_{\mathrm{rel}}$ values. However, such an influence does not affect the data for the $\gamma$ relaxation in the region where the separation from the $\alpha$ process is two decades at least, since under this condition an analysis of the $\alpha\gamma$ separation using the additive ansatz is always justified. In particular, we notice that a deviation from the extrapolated Arrhenius behavior of the $\gamma$ trace occurs just above $T_g$ where the separation of the $\alpha$ and $\gamma$ time scales is nearly ten decades, and this is actually confirmed by deconvoluting the $\alpha$ and $\gamma$ processes according to alternative fitting procedures based on the Williams ansatz. Moreover, the effect of different fitting approaches on the relaxation time values at higher temperatures has been proven not to affect qualitatively the trend of $\tau_{\mathrm{rel}}(T)$, and we have no reason to think also the higher-temperature bending of the $\gamma$ trace to be an artifact of the evaluation method.

Also the dc conductivity, $\sigma$, can be used as an efficient probe of the dynamics of supercooled systems. It should be noted that different samples of the same material might show different absolute $\sigma$ values, since this is proportional to the amount of impurities in the sample (typically chlorine, in epoxy compounds). However, the temperature dependence of the processes
\( \sigma \) is not affected by this problem, and a single curve can be obtained that is representative of the whole temperature behavior. The temperature dependence is expected to be closely related to that of viscosity. In particular, an inverse proportionality of \( \sigma \) to \( \eta \) would be expected in the hydrodynamic regime, though examples of supercooled liquids are not rare where a modified relation such as \( \sigma \eta^m = \text{const} \) holds, with \( 0 < m < 1 \).\(^{50}\) Actually, the inset of Fig. 8(b) shows that a simple proportionality is verified in DGEBA (at least above 306 K, where both conductivity and viscosity data are available for this system). In contrast, a single regime does not describe the data of PPGE [inset of Fig. 8(a)]. In this case the data in a log–log representation can be approximated by two straight lines, corresponding to \( n = 0.77 \) at lower temperature and \( n = 0.94 \) at higher temperature, crossing around 293–298 K.

The most traditional way of plotting relaxation times and viscosity and conductivity data as a function of temperature is the Arrhenius diagram, which magnifies the deviation from thermal activated behavior. On the other hand, a representation that goes into details of the temperature dependence and magnifies deviations from Vogel–Fulcher–Tamman (VFT) behavior at the same time is given by plotting the quantity \( \log_{10} \omega \) vs \( T \), the so-called *Stickel plot*,\(^1\) where \( x \) is the physical quantity usually reported in the Arrhenius diagram. In the Stickel plot a VFT behavior translates into a linear behavior. Figure 9 shows that a VFT regime extending over a wide temperature range can be certainly identified in both systems at higher temperature. At the same time it demonstrates a clear deviation of the lower-temperature data that could at first be approximated by a VFT equation with a different set of parameters. Since there is not a sharp but a continuous change in the trace of the data in the Stickel plot, a crossover temperature \( T_B \) can be identified with some difficulty: we located \( T_B \) where a bend starts in the higher temperature data, with a typical uncertainty of about \( \pm 10 \) K (see Table II). It should be noticed that intrinsic limits affect the Stickel procedure—it operates a shrinkage of several decades of dynamical data to a linear scale proportional to the temperature range, resulting in a smaller sensitivity for the low-temperature side, where a huge slowing down of the dynamics occurs in few tens of degrees—and different analytical strategies\(^{30,51,52}\) can be adopted for testing the applicability of the VFT equation and for identifying changes in the temperature dependence of relaxation data.\(^{53}\) It is found that the results for the lower-temperature range are mainly affected, where the validity itself of the VFT equation is questionable. Anyway, other procedures confirm the higher-temperature VFT regime in our data (the fitting curves for \( T > T_B \) are reported in Fig. 9 as straight lines), but indicate a large variability in the set of VFT parameters describing the lower-temperature data (depending on the data range fitted) and a possible underestimation of \( T_B \). The best VFT parameters obtained for \( \tau_{\text{max}} \) and \( \eta \) in the high- and low-temperature regions separated by \( T_B \) are listed in Table III. We observe that the set of parameters in Table III fitting the data for \( T < T_B \) also fit the data up to \( -T_B + 10 \) K comparably well.

It must be noticed that in a previous investigation of DGEBA (see Fig. 5 of Ref. 50) we interpreted the small deviation of conductivity data from the linear behavior in the Stickel plot in a narrow temperature region (365–380 K) as the presence of a further deviation from a single VFT behavior. The possibility given here [Fig. 9(b)] of accessing much higher temperatures with viscosity data leads us to exclude the existence of such deviation and, within the experimental error, to identify a single VFT regime from \( T_B \) up to the highest temperatures.

A further source of information about crossover effects along the trace of the dynamic glass transition are the relaxation strengths. The fitting procedure of the dielectric spectra gives the strengths \( \Delta \) of main and secondary relaxations as a function of temperature for PPGE and DGEBA, as reported in Figs. 6(b) and 7(b), respectively. They show very similar trends and comparable absolute values. Below the glass transition temperature, the \( \beta \)-relaxation strength \( \Delta \varepsilon_\beta \) shows a very small value, systematically decreasing by increasing the temperature (by a factor of 3 over \( \sim 100 \) K). In contrast, the \( \gamma \)-relaxation strength \( \Delta \varepsilon_\gamma \) gets much higher, accompanied by a rapid decrease of the \( \alpha \)-relaxation strength \( \Delta \varepsilon_\alpha \). Figure 7(b) shows that in DGEBA \( \Delta \varepsilon_\alpha \) really becomes very small and linearly extrapolates to zero at a finite onset temperature \( \Delta \varepsilon_\alpha \rightarrow 0 \) for \( T \rightarrow T_{\text{on}} \). In the case of PPGE the data do not give direct access to the \( \alpha \) onset region, and a larger extrapolation of the linear fit [solid line in Fig. 6(b)] is needed to locate \( T_{\text{on}} \).

We end this section by introducing an additional indicator of dynamic crossovers that we have considered in the present study, the cooperativity \( N_a \), which is the number of particles per cooperatively rearranging region\(^{18,24}\) (CRR). Calorimetric parameters from HCS are used to calculate \( N_a \) as the ratio between the volume of a CRR, \( V_a = \frac{\cal{V} \Delta \varepsilon_\alpha}{c_p} \), and the mean volume of one molecule, according to a Nyquist-type fluctuation formula\(^{54–56}\) derived in the von Laue approach to thermodynamics:

\[
N_a = RT^2 \Delta (1/c_p)/M_0 \delta T^2 \approx RT^2 \Delta (1/c_p)/M_0 \delta T^2.
\]
TABLE III. Parameters of Arrhenius fit, \( t = T_{\text{max}} \) (from dielectric spectroscopy) and viscosity (\( \eta \)).

<table>
<thead>
<tr>
<th>Material</th>
<th>Main relaxation</th>
<th>Secondary relaxations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \gamma ) relax. (( T &gt; T_b ) or ( T &gt; T_g ))</td>
<td>( \beta ) relax. (( T &gt; T_b ) or ( T &gt; T_g ))</td>
</tr>
<tr>
<td></td>
<td>( E_a ) (kcal mol(^{-1}))</td>
<td>( E_b ) (kcal mol(^{-1}))</td>
</tr>
<tr>
<td>PPGE</td>
<td>6.67 ± 0.15</td>
<td>14.7 ± 0.2</td>
</tr>
<tr>
<td>DGEBA</td>
<td>6.60 ± 0.01</td>
<td>14.3 ± 0.13</td>
</tr>
</tbody>
</table>

FIG. 9. Stickel plot (i.e., \( [d \log (1/v) / dT]^{-1/2} \) vs \( T \)) for (a) PPGE and (b) DGEBA, obtained from \( x = x_{\text{max}} \cdot \eta \), and \( \alpha \). The symbols are explained in the legend. The straight line is a VFT fit to the high-temperature data. Arrows indicate the temperature of bending, \( T_b \), and the temperature, \( T_m \), where the dielectric \( \alpha \) strength tends to zero.

In this formula, the isochoric specific heat \( c_v \) is approximated by the isobaric specific heat \( c_p \), and \( \Delta (1/c_p) \) is calculated as \( \Delta (1/c_p) = 1/c_p\)glass \(- 1/c_p\)liquid with \( c_p\)glass and \( c_p\)liquid being the specific heat values for the glass and the liquid at the dynamic glass temperature \( T_m \) from a tangent construction [Fig. 3(c)]. The average temperature fluctuation of a CRR, \( \delta T \), is determined as the Gaussian dispersion of \( c_p(T) \). \( M_0 \) is the molecular weight and \( R \) the molar gas constant. The temperature dependence of cooperativity as obtained from Eq. (3) is presented in Fig. 10. It should be noted that other approaches produce different expressions and yield significantly different estimates for the size of the CRR.

IV. DISCUSSION

The above-reported results show that our epoxy resins have a rich relaxation map characterized by, at least, the main \((a, \alpha)\) transition and two secondary processes labeled \( \beta \) and \( \gamma \). In this section two crossover regions will be recognized, somehow related to the \( \beta \) and \( \gamma \) processes and called \( \beta \)- and \( \gamma \)-crossover regions. The following discussion will also try to give an answer to the two questions (A) and (B) asked at the end of the Introduction, i.e., which of the crossover properties (ii)–(v) listed in the Introduction can be observed in the \( \beta \)- and \( \gamma \)-crossover region, and what is the character of that part of the main transition between the two crossovers. We will start with PPGE. The comparison with DGEBA and other systems with two secondary relaxations will be delegated to the last two subsections (E and F).
A. γ-crossover region

Referring to the Arrhenius diagram and to the dielectric intensity $\Delta \varepsilon_{\alpha}$ for PPGE (Fig. 6), we find in the region where the relaxation times of main transition and $\gamma$ relaxation approach each other, two properties that are typical of scenario I described in the Introduction, namely the onset of the $\alpha$ process with linearly increasing dielectric intensity [property (ii) of the Introduction] and the presence of a frequency gap in the Arrhenius plot between the extrapolated trace of the $\alpha$ process and the continuous trace of the $\alpha$ and $\gamma$ processes. We refer to the region where the $\alpha$ intensity extrapolates to zero and the $\gamma$ process continues into the $\alpha$ process of the main transition as the $\gamma$-crossover region. The onset extrapolation for $\Delta \varepsilon_{\alpha}$ is rather long, about 50 K, but the linear trend is well documented in a large temperature interval below 330 K. The onset of the $\alpha$ process is estimated at $(T_\text{on} = 391 \text{ K}, \log_{10}(\omega_\alpha^0(\text{rad/s})) \approx 10)$, see Table II, and the frequency gap to the extrapolated $\gamma$ process at $T_\text{on}$ is about $\Delta \log_{10}(\omega) \approx 1$ decade, with a large uncertainty. The extrapolation of the $\gamma$ trace in the Arrhenius diagram (Fig. 11) above the glass transition temperature is complicated by two things: a significant curvature and a declining of the $\gamma$ trace below the linear extrapolation from temperatures lower than $T_g$. We recall that both effects of the $\gamma$ trace are not an artifact from the data evaluation since $\Delta \varepsilon_{\gamma}$ is large and the trace of the main transition in the Arrhenius diagram is two or more frequency decades below the measured $\gamma$ trace.

Concerning $\Delta \varepsilon_\gamma(T)$ data from HCS, given in inset of Figs. 6(b) and 7(b) for comparison with dielectric data, they indicate a behavior similar to $\Delta \varepsilon_{\alpha}(T)$. Actually, we have no physical arguments for a linear extrapolation of $\Delta c_p$ and, if any, such a large extrapolation does not give a reliable value for the temperature where $\Delta c_p = 0$. Here we limit ourselves to note that the temperature behavior of $\Delta c_p$ is consistent with going linearly to zero around the temperature $T_\text{on}$ determined from dielectric data.

Unexpectedly, dielectric relaxation times and viscosity do not show any evidence of a Stickel bend [property (iii) of the Introduction] at the $\gamma$ crossover (Fig. 9), i.e., the temperature dependence of dielectric relaxation time and viscosity does not reflect the change from the $\alpha$ trace to the $\alpha$ trace occurring with a one decade gap at $T_\text{on}$. No evidence is also given for a separation of the individual temperature dependences of different transport properties, such as electric conductivity and viscosity, and for an Adam–Gibbs bend [properties (iv) and (v) of the Introduction].

B. β-crossover region

Referring again to the Arrhenius diagram and to the dielectric intensities in Fig. 6, we find now in the region where the relaxation times of main transition and $\beta$ relaxation approach each other, two properties of scenario II: the continuous trace of the main transition and, second, the weak $\beta$ relaxation, which runs into the main transition with a considerable “angle” in the Arrhenius diagram. We call this region the $\beta$-crossover region. The definition of a temperature where the separation of time scales between main and secondary relaxation occurs is not an unambiguous operation, since reflects the mentioned difficulty, in theory and practice, of analyzing the spectra in regions of strong overlap of the relaxation peaks. We refer to the $\alpha\beta$ splitting temperature $T_\beta$ as the temperature where the linearly extrapolated Arrhenius behavior of $\tau_\beta$ intersects the $\alpha$ trace. In the extrapolation we obtain $T_\beta = 298 \text{ K}$ and $\log \omega_\beta(\text{rad/s}) = 6.2$ (Table II). Both the dielectric and the shear measurements of the main transition show a significant Stickel bend at the $\beta$ crossover [property (iii), Fig. 9]. The Vogel temperatures are $T_0(T>T_\beta) = 240 \text{ K}$ and $T_0(T<T_\beta) = 214 \text{ K}$, higher for the highest-temperature regime, in coincidence with the rule mentioned in the Introduction. There is an indication for start of separation of the individual temperature dependences of viscosity.

FIG. 10. Temperature-dependent cooperativity for PPGE and DGEBA. The lines are fits to the data using Eq. (4). The Vogel temperature ($\text{PPGE}: T_v = 214 \text{ K}$; $\text{DGEBA}: T_v = 209 \text{ K}$) was fixed and the $A$ value was varied systematically to find the optimal fit (bold line) and the corresponding crossover temperature (PPGE: $A = 5.3$, $T_v = 327 \text{ K}$; $T_v = 309 \text{ K}$; DGEBA: $A = 5.5$, $T_v = 325 \text{ K}$. The thin lines are shown to give an impression of adjustments with different $A$ values and their compatibility with data. Corresponding $T_v$ are given in the legend. The straight lines are linear fits to the data (PPGE: $T_v = 296 \text{ K}$; DGEBA: $T_v = 291 \text{ K}$). Typical errors are indicated.

FIG. 11. Schematic sketch of the Arrhenius diagram near the $\gamma$-crossover region.
and electric conductivity in the β-crossover region [property (iv), Fig. 8]. Calorimetric data published elsewhere$^{60}$ indicate a weak Adam–Gibbs bend in the same region [property (v)]; in Table II, $T_{\text{AG}}$ is the temperature above which the deviation from the Adam–Gibbs relation, log $\tau^{-2}(S,T)^{-1}$, becomes appreciable]. The discussion of Secs. IV A and IV B is summarized in Table IV.

<table>
<thead>
<tr>
<th>Property*</th>
<th>γ-crossover</th>
<th>β-crossover</th>
</tr>
</thead>
<tbody>
<tr>
<td>Onset ($\Delta T_{\text{on}}=0$) of the low-temperature process (ii)</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Frequency gap</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Scenario</td>
<td>I</td>
<td>II</td>
</tr>
<tr>
<td>Stickel bend (iii)</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Decoupling of $\eta$ and $\sigma$ (iv)</td>
<td>?</td>
<td>Yes</td>
</tr>
<tr>
<td>Adam–Gibbs bend (v)</td>
<td>?</td>
<td>Yes (Ref. 60)</td>
</tr>
</tbody>
</table>

*The roman numerals in parentheses are related to the properties (ii)–(v) of the Introduction.

and electric conductivity in the β-crossover region [property (iv), Fig. 8]. Calorimetric data published elsewhere$^{60}$ indicate a weak Adam–Gibbs bend in the same region [property (v)]; in Table II, $T_{\text{AG}}$ is the temperature above which the deviation from the Adam–Gibbs relation, log $\tau^{-2}(S,T)^{-1}$, becomes appreciable]. The discussion of Secs. IV A and IV B is summarized in Table IV.

C. α process below the β crossover

For the discussion of the α process below the β crossover we use the experimental cooperativity $N_\alpha(T)$ obtained from the 3o-method calorimetry (Fig. 10). A fair representation of its temperature dependence is usually$^{28,34,61}$

$$N_{\alpha}^{1/2} = A(1-x)/x,$$

with $x$ a reduced temperature between Vogel temperature ($x=0$) and a formal cooperativity-onset temperature ($x \to 1, N_{\alpha}^{1/2} \to 0$),

$$x = (T-T_0)/(T_{\text{on}}^{\alpha} - T_0),$$

where $A$ is a constant typically between 2 and 15,$^{61} T_0$ the Vogel temperature, and $T_{\text{on}}^{\alpha}$ the cooperativity-onset temperature. For PPGE, Fig. 10 contains $N_\alpha$ data for temperatures between $T=264$ K and 283 K, and the β-crossover region is located around $T=298$ K. In extrapolating Eq. (4) to find the cooperativity-onset temperature we take the Vogel temperature $T_0$ from the VFT parameters for the low-temperature part of the α trace (Table II), $T_0 = 214$ K. Using Eq. (4), we obtain the best fit of the data of Fig. 10 for $A = 5.3$ and $T_{\text{on}}^{\alpha} = 327$ K. This gives a more realistic onset temperature corresponding to $N_\alpha = 1, T(N_\alpha = 1) = T_{\text{on}}^{(1)} \approx 309$ K (Fig. 10). Considering the large uncertainty affecting $N_\alpha(\sim 30\%)$, a good fit of the data is still obtained with $A = 7.5$, which gives $T_{\text{on}}^{(1)} \approx 299$ K. This value is not far from that which can be obtained from a linear extrapolation of the same data, giving $T_{\text{on}}^{(1)} \approx 296$ K. These temperature values indicate that the cooperativity-onset temperature $T_{\text{on}}^{(1)}$ for PPGE as defined by $N_\alpha = 1$ is inside, or slightly above, the β-crossover region.$^{62}$

D. Of which type is the main process between β and γ crossovers, a’ or a’’?

We come now to the question (B) asked at the end of the Introduction: What is the character of that part of the main transition between the two crossover regions? In general, for liquids of moderate molecular and structural complexity characterized by a single crossover region$^{24,28}$ the main transition can be characterized as follows.

Above the crossover region we have the α process with the higher Vogel temperature when fitted by a VFT equation. In the molecular picture discussed in Ref. 24, the corresponding diffusion can be described as escaping of the particle from a cage$^{40}$ formed by the nearest neighbors. The cooperativity is of order $N_\alpha \sim 1$ when determined by Eq. (3) and decreases with higher temperatures. Such small cooperativities are unexpected and may be explained by an extraordinary concentration of free volume as generated by the Lévy distribution describing the escaping process. We may think about a “cage door” of size of about one particle temporarily opened by this concentration of free volume.$^{24}$

Below the crossover region we have the α process with the lower Vogel temperature. The spatial aspect of its dynamic heterogeneity may be described$^{24}$ by an island of high mobility$^{63}$ assisted by a cooperativity shell of low mobility. The particle diffusion may be considered as generated by a diffusion of this island (Glarum defect diffusion$^{64}$). This island of mobility may also be explained by an extraordinary concentration of free volume from a Lévy distribution. The spatial scale, however, is larger than that for the high-temperature α process and may generate sufficient free space for a secondary process at the island. In this molecular picture, the CRR as a representative subsystem for the main transition consists of two parts: the island of mobility and the cooperativity shell; the mobility contrast between these parts is responsible for the dynamic heterogeneity of the α process. The cooperativity is then the number of particles per CRR; it increases sharply with low temperatures and reaches values of order $N_\alpha \sim 100$ some 50 K below the crossover region.

Since we have two crossover regions in PPGE, the question arises whether the main process between the two crossovers is more an α process (in which case it will be called the a’ process), because it is above the β crossover, or it is more an α process (in which case it will be called the a’’ process), because it is below the γ crossover. Reflecting the discussion in the previous subsections, Table IV, and the above criteria, we obtain the following indications.

In favor of an α’ process, we have the small cooperativity $N_\alpha \sim 1$ obtained from the extrapolation at temperatures higher than the β crossover. This result is deduced upon the condition that there is no $N_\alpha$ increase with increasing temperature as observed for 19 systems studied so far by heat capacity spectroscopy$^{28}$ (apart from the indication of a weak $N_\alpha(T)$ irregularity in the β-crossover region of ortho-cresyl glycidyl ether$^{65}$). Other arguments for an a’ process are the location above a Stickel bend, above the start of a η-σ decoupling, and above a bend in the Adam–Gibbs plot.

In favor of an α’’ process, we have the occurrence at higher temperature of a dielectric onset with frequency gap, i.e., the location below a crossover region of the type described as scenario I.

Summarizing this subsection, we find more arguments suggesting that the main process between the β and γ crossovers is an α process (hence, a’’ process). Accordingly, we
should properly call the dielectric onset observed in the
$\gamma$-crossover region the ($a',\alpha$) onset. However, the intensity
onset and frequency gap in the $\gamma$-crossover region indicate
that there is, in PPGE, a qualitative difference between the
$\alpha'$ process and the high-temperature $\alpha$ process, i.e., below
and above the $\gamma$ crossover. In particular, the presence of a
frequency gap between the extrapolated $\alpha'$ and $\alpha$ processes
at the $\gamma$ crossover could be interpreted, following general
scaling principles, as an indication of a length scale for the
$\alpha'$ mode that is larger than that of the $\alpha$ modes emerging
from the $\gamma$ process.

E. Comparison between PPGE and DGEBA

The overall behavior of both epoxy resins is the same
(Figs. 6, 7, 9, and 10): We find two crossover regions sepa-
rated by a frequency difference of about four decades. The $\gamma$
crossover seems to conform to scenario I (onset), the $\beta$
crossover belongs to scenario II. The characteristic tempera-
tures of crossover effects in DGEBA are compiled in Table II
with those for PPGE. Unlike PPGE, in DGEBA low-temperature
conductivity data for assessing the presence of a $\sigma-\eta$ bend (indicating the start of different temperature
dependences for the different transport activities) are not
available, and the weak bend of the dielectric $\gamma$-process in-
tensity $\Delta\varepsilon_{\gamma}(T)$ at the $\beta$-crossover temperature is hardly
perceived. From Fig. 10, the cooperativity of the $\alpha$ process,
extrapolated to the $\beta$-crossover temperature, is about $N_{\alpha}$
$\sim 5$ for DGEBA, i.e., a bit larger than that for PPGE. The
extrapolation of $N_{\alpha}^{1/2}$ gives $N_{\alpha} = 1$ at $T_{on}^{(1)} \sim 291$ K for
the linear fit, and $T_{on}^{(1)} \sim 306$ K for the best adjustment of Eq. (4)
with $T_0 = 209$ K ($A = 5.5$ and $T_{on}^{\infty} = 325$ K). The cooperativity
$N_{\alpha}$ at the glass transition temperature, independently
determined from DSC measurements is $N_{\alpha}(T_g) = 75 \pm 20$
for PPGE and $N_{\alpha}(T_g) = 110 \pm 30$ for DGEBA. 66 These values are
consistent within the experimental errors with those ex-
trapolated according to Eq. (4), and give comparable values
for the cooperativity length $\xi_{\alpha}$ at the glass transition ther-
ton for both PPGE and DGEBA [$\xi_{\alpha}(T_g) \approx 3.3 \pm 0.3$
and $3.8 \pm 0.4$ nm, respectively].

As recalled in Sec. III, the determination of $T_0$ as the
temperature where the $\alpha$ trace tends to diverge is not unam-
biguous (in fact, it ranges from the values reported in Table
III to values more than 10 K lower). It is worth noting that
despite this large uncertainty the best adjustments of Eq. (4)
with different values of $T_0$ do not entail changes in the ex-
trapolated values of $T_{on}^{(1)}$ and $N_{\alpha}(T_g)$ that are significant
within the experimental errors.

Note that the frequency–temperature position of $\beta$ and $\gamma$
relaxations in PPGE and DGEBA are nearly identical (Table
III). This indicates that the molecular mechanism of the sec-
ondary relaxations in both substances is similar. This aspect
and the fact that there are two pronounced secondary pro-
cesses in cross-linked DGEBA systems 67,68 may be the start-
ing point of further studies on this topic.

F. Comparison with other substances

There are several substances with two secondary relax-
ations investigated in the literature. 39–75 However, only in a
very few of these samples do both secondary relaxations ap-
proach the main transition inside the experimentally acces-
sible frequency window below 10 GHz and is information
about dielectric strengths available. We will discuss below a
few previously investigated samples and compare their be-
havior with our epoxy resins.

Schematic Arrhenius diagrams for poly($e$-caprolactone)
from Fig. 9 of Ref. 73 and for our epoxy resins (Figs. 6 and
7) show significant differences (Fig. 12). For poly($e$-capro-
lactone) the dielectric $\alpha$ onset coincides with the $\alpha\beta$
merging, and the frequency gap to the continuous $\gamma$ process
is about two decades. We may imagine, purely phenomeno-
logically, that the poly($e$-caprolactone) scenario would
emerge from our epoxy resin situation when the $\gamma$-process
frequency near the onset is about two frequency decades
lower. Then the two crossover regions of the epoxy resins
would coincide and the $\alpha'$ process between the two cross-
overs would disappear. For poly($e$-caprolactone) the $\gamma$
process deviates less from the linear extrapolation, but a small
sigmoidal shape of the $\gamma$ trace in the Arrhenius diagram
seems also to occur. As a whole, it seems that the difference
between the two diagrams in Fig. 12 is caused by the differ-
ence in the crossover frequency.

A comparison of our data for PPGE and DGEBA with
those for another epoxy resin with two secondary relax-
ations, ortho-cresyl glycidyl ether 65 also indicates differ-
ences. There is no dielectric $\alpha$ onset in the $\gamma$-crossover
region, but the $\beta$ as well as $\gamma$ crossover is accompanied by a
Stickel bend, i.e., a change in the temperature dependence of
the main relaxation time. In contrast, the data for triphenyl-
lolmethane triglycidyl ether 24 indicate, as far as data are
available in the temperature range below 1.22 $T_g$, many simi-
larities with the features of PPGE and DGEBA.

Another class of substances with two secondary relax-
atations are the poly($n$-alkyl methacrylate). Due to the high
frequency of the $\gamma$ relaxation in samples with high molecular
weight, less is known about the details of a possible $\gamma$
crossover. However, for short poly($n$-butyl methacrylate) oligo-
mers the $\gamma$-relaxation intensity increases with decreasing
chain length. 75 This is also reflected by an increase of the
calorimetric $\alpha$ intensity and the cooperativity near $T_g$, indi-
cating relations between local $\gamma$ dynamics and main transi-
tion besides those in the well-investigated $\beta$-crossover
region. 7,22,43
V. CONCLUSIONS

The dynamic glass transition of PPGE and DGEBA has been studied by means of broadband dielectric spectroscopy, heat capacity spectroscopy ($3\omega$ method), and viscosimetry. Two well-separated crossover regions ($\beta$ crossover and $\gamma$ crossover) have been identified, around $T_c(\beta) \sim (1.1 - 1.2)T_g$, $\tau_c(\beta) \sim 10^{-6}$ s, and $T_c(\gamma) \sim (1.4 - 1.5)T_g$, $\tau_c(\gamma) \sim 10^{-10}$ s, respectively.

The $\gamma$ crossover is characterized by the onset of the $(\alpha', \alpha)$ transition, with a relaxation time about one decade greater than that of the continuous trace of the $(\alpha, \gamma)$ processes, the $\alpha$ process being the high-temperature part of the main dynamic transition. In the intermediate-temperature region, between the $\gamma$ and $\beta$ crossover, the main transition seems to be characterized by a low cooperativity $N_a \sim 1$, and it has been labeled $\alpha'$ for analogies with the high-temperature $\alpha$ process. At lower temperatures, the $\beta$ crossover is characterized by a continuous trace of the main $(\alpha', \alpha)$ transition where the crossover region is identified by the extrapolation from lower temperatures of the $\beta$ relaxation time to the main relaxation time; a Stickel bend in the trace of the $(\alpha', \alpha)$ transition with a Vogel temperature $T_0$ for the $\alpha$ process which is smaller than that for the $\alpha'$ process; and the separation of the individual temperature dependences of different transport properties such as impurity-ion diffusion coefficient and viscosity (breakdown of the Stokes–Einstein law).

The comparison of dielectric relaxation times with configurational entropy data from calorimetry shows the validity of the Adam–Gibbs relation for the temperature dependence of the $\alpha$ relaxation time at temperatures below the $\beta$-crossover region.60 There, cooperativity starts to increase significantly.

Also the secondary relaxations show changes across the glass transitions. A significant curvature and a lowering of the $\gamma$ trace below the linear extrapolation from temperatures lower than $T_g$ can be clearly observed in the Arrhenius plots of both PPGE and DGEBA. These effects are not an artifact of the data evaluation since $\Delta e_\gamma$ is large enough and the trace of the main transition in the Arrhenius plot is two or more frequency decades below the measured $\gamma$ trace. Another interesting feature shown by secondary processes is the influence of freezing-in on the amplitude of the $\gamma$ relaxation $\Delta e_\gamma(T)$, which shows a significant bend at $T_g$. This suggests the existence of some intrinsic relation between the dynamic glass transition and secondary relaxations. Temperature effects on secondary relaxations promise to be important for a deeper understanding of the glass transition phenomenon and are currently the subject of further theoretical and experimental effort.

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We thank P. A. Rolla and M. Lucchesi for helpful discussions, and acknowledge financial support from MIUR-PRIN2000, the Deutsche Forschungsgemeinschaft DFG (in particular, S.C. acknowledges the SFB 418 supporting her stay in Halle) and the Fonds Chemische Industrie FCI.
In that work we called $\beta$ relaxation what is labeled here $\gamma$ relaxation.


This finding is consistent with the change of Vogel temperatures in the $\beta$-crossover region, mentioned above. Interpreting $k_B T_0$ as a measure of the roughness for the relevant energy landscape (Refs. 21 and 51), we see that the landscape for the $\alpha$ process has a lower roughness than those of the $\alpha'$ or $\alpha''$ process. (see Sec. IV D) above the $\beta$-crossover region. Increasing the cooperativity permits the phase-space point of representative subsystems to find its way through the landscape with low “saddles” accessible also at low temperature. Above the $\beta$ crossover, at higher temperatures, the system can do with higher landscape saddles and does not need the cooperativity with rare low saddles.

62. This finding is consistent with the change of Vogel temperatures in the $\beta$-crossover region, mentioned above. Interpreting $k_B T_0$ as a measure of the roughness for the relevant energy landscape (Refs. 21 and 51), we see that the landscape for the $\alpha$ process has a lower roughness than those of the $\alpha'$ or $\alpha''$ process. (see Sec. IV D) above the $\beta$-crossover region. Increasing the cooperativity permits the phase-space point of representative subsystems to find its way through the landscape with low “saddles” accessible also at low temperature. Above the $\beta$ crossover, at higher temperatures, the system can do with higher landscape saddles and does not need the cooperativity with rare low saddles.