Dynamics of glassy clusters appearing by nonlinear dielectric effect studies

Sylwester J. Rzoska and Jerzy Zioło
Institute of Physics, Silesian University, ulica Uniwersytecka 4, 40-007 Katowice, Poland

(Received 4 August 1998)

Preliminary results of time-resolved nonlinear dielectric effect (NDE) studies in the liquid, glassforming epoxy resin EPON 5 are presented. For all tested temperatures the NDE response of the sample parametrizes the stretched exponential function with exponent $\beta = 0.38 \pm 0.05$. The temperature evolution of relaxation times can be parametrized by means of the Vogel-Fulcher-Tammann function $\tau^{\mathrm{NDE}} = \tau_0^{\mathrm{NDE}} \exp(D_{\mathrm{NDE}} T_0^{\mathrm{NDE}}/T - T_0^{\mathrm{NDE}})$, with $\tau_0^{\mathrm{NDE}} \approx 0.3\,\mathrm{s}$, $D_E \approx 1.2$, and $T_0^{\mathrm{NDE}} \approx 261\,\mathrm{K}$. The latter value is, within the limit of the experimental error, equal to the glass temperature T_g. The relaxation of ''nonlinear'' changes of the dielectric permittivity induced by a strong, steady electric field may be associated with the dynamic equilibrium of glassy clusters and the surrounding fluidlike region. [S1063-651X(99)05302-7]

PACS number(s): 64.70.Pf, 61.20.Lc

The glass transition temperature T_g is one of the characteristic temperatures which can be identified in supercooled glass forming liquids from the analysis of dynamic and thermodynamic properties. It is usually defined as the temperature at which calorimetric quantities show an anomaly [1–3]. In such materials, dynamic properties revealed nonexponential relaxation which may be parametrized by the Kohlrausch-Williams-Watts stretched-exponential relaxation: $R(t) = \exp[-(t/\tau)^{\beta}]$, where $R(T)$ is the normalized response function, t is time, τ is the relaxation time, and β is the stretched exponent [1–4]. This nonexponential relaxation ($\beta < 1$) may be roughly classified into two categories: intrinsic (homogeneous) relaxation, and net relaxation due to spatial heterogeneities. Several studies [2,3] of supercooled liquids near T_g have indicated that heterogeneities occur in length scales from 1 to 5 nm. Nuclear magnetic resonance measurements [4,5] showed that these domains are not static, but their distinct relaxation rates persist long enough to cause the response with broad distribution of relaxation times. Such dynamic heterogeneity, which evolves as the sample responds, was observed by the spectral hole burning method [6,7]. For temperatures above T_g, Fisher in his lecture in [Ref. [8]] postulated the existence of locally closely packed configurations of ''glassy clusters'' in a dynamic equilibrium with ''fluidlike'' regions.

The preliminary results of the time-resolved nonlinear dielectric effect (NDE [9]) presented in this paper seem to point to the appearance of a singularity on approaching the glass transition temperature, which may further be associated with the existence of postulated glassy clusters. In a strong electric field, the dielectric permittivity $\varepsilon^E = \varepsilon + \varepsilon_1 E^2 + O(E^4)$, where ε^E and ε are dielectric perimittivities in strong (E) and weak (measuring) electric fields, respectively. The field-independent magnitude $\mathcal{E}_{\mathrm{NDE}} = \varepsilon_1 = (\varepsilon^E - \varepsilon)/E^2$ is known as the NDE [9]. Studies conducted up to now showed that the NDE is extremely sensitive to inhomogeneities in liquids caused by critical fluctuations [9] or even very weak statistical fluctuations of the polarization [10,11]. Time-resolved NDE studies of near-critical solutions after switching a strong electric field on and off showed that this method can be applied to investigate dynamics of critical fluctuations [11]. In the research reported we applied this method to Epidian 5 [poly(bisphenol *A*-co-epichlorohydrin), glycil end capped] from the epoxy resin family, delivered by Sarzyna Chemical Company, Poland. Its equivalent molecular weight was about 390.

The basic theoretical model for the NDE, based on the Langevin (L) theory of paramagnetism, was given by Debye [12]. It only takes into account the orientation of permanent dipole moment in a strong electric field

$$\mathcal{E}_{\mathrm{NDE}}^{L} \propto \frac{-N\mu^4}{45k^3T^3}, \tag{1}$$

where N is the number of dipolar molecules in a unit volume, k is the Boltzmann constant, and μ is the value of the permanent dipole moment.

It is believed to be the sole molecular mechanism contributing to the negative sign of the NDE [9]. It reflects the fact that in a strong electric field dipoles are less reactive to the action of the weak measuring field. All other molecular processes, including molecular interactions and fluctuations, are expected to give a positive contribution to the total value of the NDE [9]. There are several successful models for stationary NDE behavior as well as its relaxation in simple liquids [9,13–16]. However, their application to complex liquids seems to be very restricted. In this respect studies in critical solutions [17] and in the isotropic phase of liquid crystalline materials [18] are noteworthy. They showed that in both cases the pretransitional effects depend on the appearance of pretransitional fluctuations of the next phase: $\mathcal{E}_{\mathrm{NDE}} \propto \langle \Delta M^2 \rangle_V \chi$, where the first factor denotes the mean square of the order parameter (M) fluctuations, and χ is the susceptibility to an external perturbation. It is worth noting that in nematogens with a permanent dipole moment approximately parallel to the main axis of the molecule, pretransitional effects of the opposite sign were found: $\mathcal{E}_{\mathrm{NDE}} > 0$ for $\omega\tau \ll 1$ and $\mathcal{E}_{\mathrm{NDE}} < 0$ for $\omega\tau \gg 1$, where $f = \omega/2\pi$ is the radio frequency of the measurement field [18].

In this paper we applied the NDE experimental technique, recently developed in our group [19]. It makes use of two electric fields: the weak measuring field ($f = 0.1$–$10\,\mathrm{MHz}$,

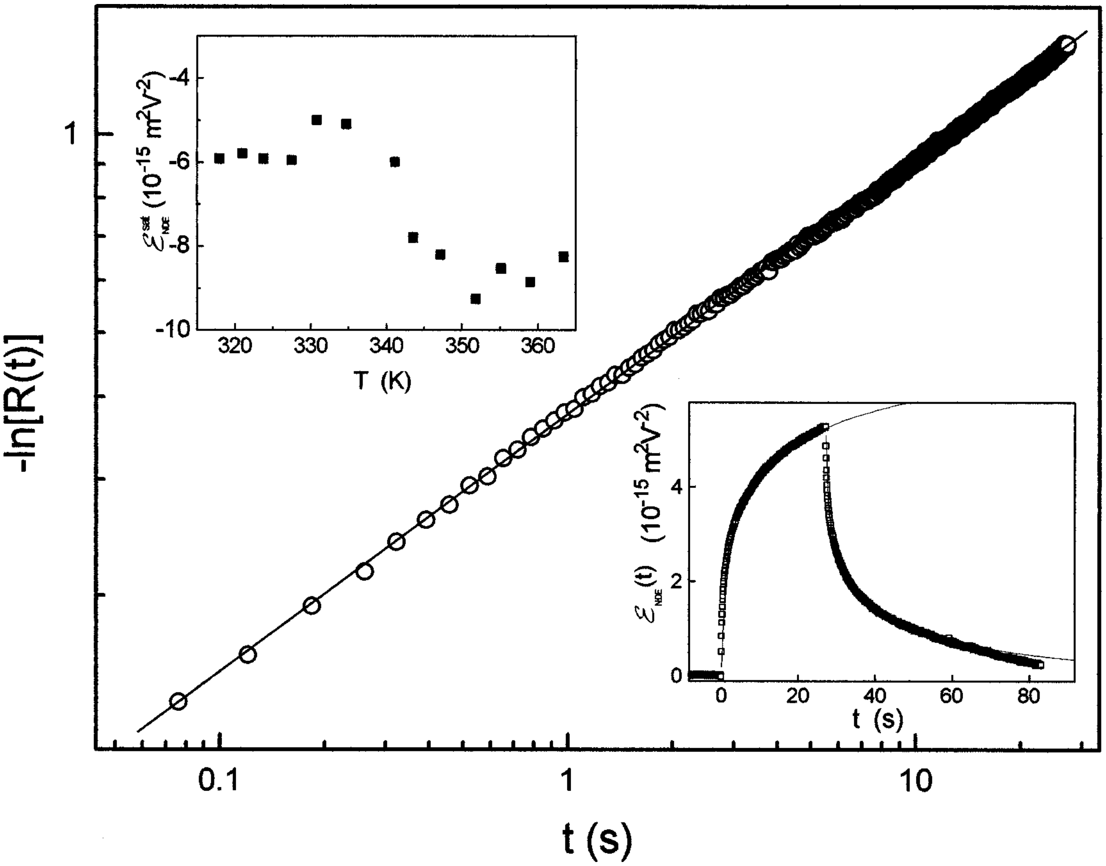

FIG. 1. Stretched-exponential behavior of the response function describing the rise of the NDE signal after switching on the strong electric field ($T=76\,°\mathrm{C}$). The slope of the solid line implies $\beta\approx 0.35$. The bottom inset shows the experimental NDE signal and the SE fit. The upper inset presents the temperature behavior of the ''saturated'' stationary value of the NDE.

$U_{\text{peak-peak}}=1.5\,\mathrm{V}$) and the rectangular ac pulse of a strong electric field; their lengths were $\Delta t=1-64\,\mathrm{s}$ and $U_{\mathrm{ac}}=100-500\,\mathrm{V}$. The sample was placed in a flat parallel capacitor, gap $d=1$ mm and diameter $2r=20$ mm, made from Invar. The temperature was measured by means of a platinum resistor A1 class (DIN 43 260). The temperature was stabilized with a precision of ± 0.02 K/h. In the whole tested temperature range the condition $\Delta\varepsilon^{E}\propto E^{2}$ was always fulfilled [19].

A typical sample response to the rectangular pulse of a strong electric field is shown in the bottom inset in Fig. 1. The deformation of the response is due to the influence of relaxation processes in the sample. The value of Δt was systematically increased upon decreasing the temperature from 90 to 40 °C. However, a limited value of Δt can be applied at each tested temperature. Too large a Δt value caused a shift of the horizontal baseline after the strong electric field was switched off in respect to the initial baseline. This limited the possibility of measurements for $T>40\,°\mathrm{C}$. In the analysis we only used a pulse short enough to avoid the influence of this parasitic factor. Since the ''saturated'' stationary state was never reached, we only have left to analyze the rise of the NDE signal. Its typical form is shown in the bottom inset in Fig. 1. In the tested temperature range the behavior could be described by the stretched exponential response function

$$R(t)=1-\frac{\mathcal{E}_{\text{NDE}}(t)}{\mathcal{E}^{\text{sat}}_{\text{NDE}}}=\exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right], \tag{2}$$

where t is the time from the moment the strong electric field was switched on, and $\mathcal{E}^{\text{sat}}_{\text{NDE}}$ is the extrapolated, saturated, stationary value of the NDE for $t\gg\tau$.

To minimize the error of nonlinear fitting the analysis was conducted using the linear regression: the adjusted value of $\mathcal{E}^{\text{sat}}_{\text{NDE}}$ was changed until the experimental data could be optimally parametrized by a straight line on a log-log scale, as shown in Fig. 1. The parameters of the straight line thus obtained approximated the values of parameters τ and β. The shift of the measurement frequency from $f=100$ kHz to 10 MHz within the limit of the experimental error does not influence on the value of $\mathcal{E}^{\text{sat}}_{\text{NDE}}$. It was always negative, as shown in the upper inset in Fig. 1. The value of $\mathcal{E}^{\text{sat}}_{\text{NDE}}$ was a few orders greater than that observed in simple dipolar liquids [9,10]. Such a large effect was observed only for pretransitional effects in the isotropic phase of nematogenic and smectogenic liquid crystalline compounds [17,18,20].

Figure 2 shows the temperature evolution of relaxation times determined in the analysis presented in Fig. 1. It demonstrates they can be well parametrized by means of the Vogel-Fulcher-Tammann (VFT) function

$$\tau=\tau_0^{\text{NDE}}\exp\left(\frac{D_E T_0^{\text{NDF}}}{T-T_0^{\text{NDE}}}\right). \tag{3}$$

Its validity for representing the primary α relaxation is well known [21], and the dielectric relaxation times in EPON 5 parametrized in such studies are given in the inset in Fig. 2:

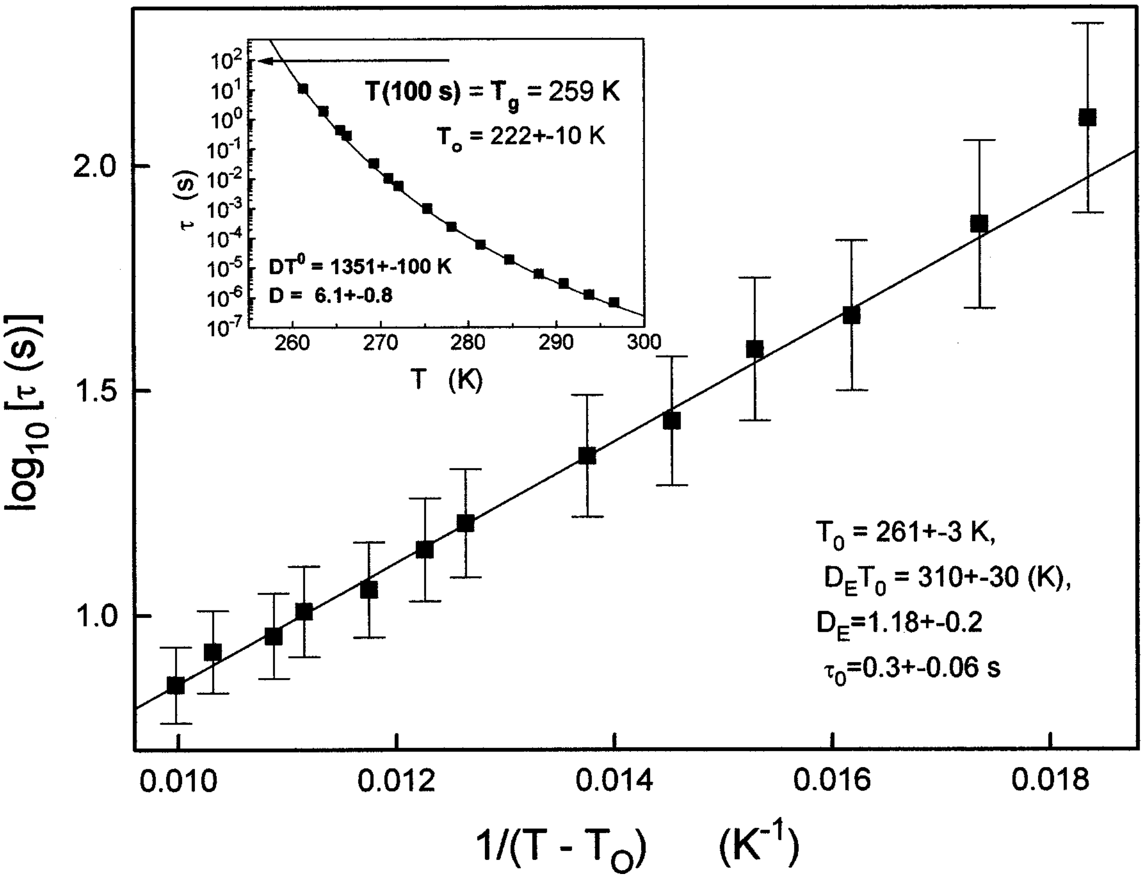

FIG. 2. Temperature evolution of the NDE relaxation times, on a scale displaying the validity of the VFT function. The inset shows the behavior of the primary relaxation times determined from the ''linear'' dielectric relaxation [21].

the analysis gave $\tau_0 \approx 12\,\mu\text{s}$ and $T_0 \approx 222\,\text{K}$. The singular temperature T_0 determined in dielectric relaxation studies is associated with the extrapolated ideal-glass temperature. Examinations of relaxation time of the NDE response gave: $\tau_0^{\text{NDE}} \approx 0.3\,\text{s}$ and $T_0^{\text{NDE}} = 261 \pm 3\,\text{K}$. This temperature conforms well to the glass temperature $T_g \approx 260.6\,\text{K}$ determined in calorimetric studies, and to $T_g = \tau(100\,\text{s}) \approx 259\,\text{K}$ extracted from dielectric relaxation data [21]. When comparing ''linear'' and ''nonlinear'' dielectric relaxation, marked discrepancies in values of both singular temperatures and also prefactors τ_0 and τ_0^{NDE} are clearly visible. The latter can probably be associated with the relatively fast relaxation of a single dipole (dielectric relaxation studies) and slow relaxation of large glassy clusters (NDE studies). Strongly different pretransitional effect for dielectric permittivity and the NDE has already been observed in critical solutions and isotropic phase of nematogens, both in stationary and dynamic properties studies [17,18,20,22]. Noteworthy is the fact that in the isotropic phase of nematogens the negative pretransitional effect appeared when the time scale associated with the strong electric field was much faster than the relaxation time of pretransitional fluctuations [18,22]. This is also the case of presented results: $1/f = 0.16 - 10\,\mu\text{s}$ and $\tau^{\text{NDE}} = 4 - 300\,\text{s}$ in the tested temperature range. The very large, negative, value of the saturated, stationary value of the NDE may probably be explained only if one relates it to the orientation of ''fluctuations'' of the neighboring phase (glassy clusters) in a fluidlike surrounding, as was the case in the aforementioned pretransitional, critical effects.

Concluding, in our opinion the results obtained indicate that time-resolved NDE studies in the supercooled liquid may detect the dynamics of glassy clusters. The obtained singularity may result from freezing of the whole system at a transition to the glassy state.

The authors gratefully acknowledge the financial support of the State Committee for Scientific Research (KBN, Poland), Project No. 2 P03B 030 12, and are also grateful to Aleksandra Drozd-Rzoska for stimulating discussions.

---

[1] G. E. Gibson and W. F. Giangue, J. Am. Chem. Soc. **40**, 93 (1923).
[2] E. Donth, J. Non-Cryst. Solids **53**, 325 (1982).
[3] M. T. Cicerone and M. D. Ediger, J. Chem. Phys. **103**, 5684 (1995).
[4] K. Schmidt-Rohr and H. W. Spiess, Phys. Rev. Lett. **66**, 3020 (1991).
[5] A. Heuer, M. Wilhelm, H. Zimmermann, and H. W. Spiess, Phys. Rev. Lett. **75**, 1851 (1995).
[6] R. Boehmer, B. Schiener, J. Hemberger, and R. V. Chamber-

lain, Z. Phys. B **99**, 91 (1995).

[7] B. Schiener, R. Boehmer, A. Loidl, and V. Chamberlain, Science **274**, 752 (1996).

[8] E. W. Fischer, Lecture delivered at the 3rd International Discussion on Relaxation in Complex Systems, Vigo, Spain (unpublished); Physica A **201**, 183 (1993).

[9] A. Chełkowski, *Dielectric Physics* (PWN Elsevier, Warsaw, 1980).

[10] S. Kielich, in *Dielectrics and Related Processes (A Specialist Report)*, edited by M. Davies (The Chemical Society, Burlington House, London, 1972), Vol. 1, Chap. 7.

[11] S. J. Rzoska, M. Górny, and J. Zioło, Phys. Rev. A **43**, 1100 (1991).

[12] P. Debye, *Polare Molekeln* (Verlag von Hirzel, Leipzig, 1929).

[13] W. Alexiewicz, J. Buchert, and S. Kielich, Acta Phys. Pol. A **52**, 445 (1977).

[14] W. Alexiewicz and B. Kasprowicz-Kielich, in *Advances in Chemical Physics*, edited by M. Evans and S. Kielich (Wiley, New York, 1993), Vol. LXXXV.

[15] L. Hellemans and L. de Mayer, J. Chem. Phys. **63**, 3490 (1975).

[16] J. Małecki, J. Mol. Struct. **436-437**, 595 (1997).

[17] S. J. Rzoska, A. Drozd-Rzoska, M. Górny, and J. Zioło, Phys. Rev. E **52**, 6325 (1995).

[18] A. Drozd-Rzoska, S. J. Rzoska, M. Górny, and J. Zioło, Mol. Cryst. Liq. Cryst. **260**, 443 (1995).

[19] M. Górny, J. Zioło, and S. J. Rzoska, Rev. Sci. Instrum. **67**, 4673 (1996).

[20] A. Drozd-Rzoska, S. J. Rzoska, and J. Zioło, Phys. Rev. E **54**, 6452 (1996).

[21] M. Paluch, J. Zioło, and S. J. Rzoska, Phys. Rev. E **56**, 5764 (1997).

[22] A. Drozd-Rzoska, Liq. Cryst. **25**, 835 (1998).