Complex Reorientation Dynamics of Sizable Glass-Formers with Polar Rotors Revealed by Dielectric Spectroscopy

Marzena Rams-Baron,* Beibei Yao, Shinian Cheng, Mateusz Dulski, and Marian Paluch

ABSTRACT: We present the results of dielectric measurements for three sizable glass-formers with identical nonpolar cores linked to various dipole-labeled rotors that shed new light on the picture of reorientation of anisotropic systems with significant moment of inertia revealed by broadband dielectric spectroscopy. The dynamics of sizable glass-formers formed by partially rigid molecular cores linked to small polar rotors in many respects differs from that of typical glass-formers. For instance, the extraordinarily large prefactors ($\tau_0 > 10^{-12}$ s) in the Vogel–Fulcher–Tammann equation were found. The rich and highly diverse relaxation pattern was governed by the location of a dipole, its ability to rotate freely, and the degree of coupling to the motion of the entire sizable system.

Molecular dynamics of sizable molecules composed of many atoms arranged in a structure with rigid and flexible subunits represent a fundamental problem with significant technological implications. Broadband dielectric spectroscopy (BDS) can be used to gain insight into the rich dynamics of large molecules. The dielectrically probed fluctuations of molecular dipoles allow the study of molecular motions on many scales, from the internal rotations of side groups to whole molecule reorientations and even supramolecular networks rearrangements. The only necessary condition is the presence of the dipolar group in the material.

Gaining a better understanding of the motion of large systems is undoubtedly one of the most engaging scientific challenges of our time. Macromolecules, biological motors, and artificial machines are the research objects that stimulate the imagination and drive conceptual, experimental, and theoretical efforts in the field. However, basic knowledge about the structure–dynamics relations in the constituent molecules with desired functionality needs to be uncovered as a starting point. Therefore, we have proposed a new concept of sizable glass-forming materials with structural features corresponding to those found in applicable technologies (e.g., in optoelectronics) but at the same time allowing reference to the fundamental issues related to the reorientation dynamics of large, anisotropic, partially planar, and rigid molecular systems.

Sizable molecules cannot be simply regarded as entities containing many atoms (molar masses of approx. 600 g/mol, number of atoms > 80) that match a gap between the low-molecular-weight glass-formers and polymers, both well recognized by the dielectric community in the past. The size criterion, while appropriate, is not the most important. The circumstance that justifies the categorization as a separate class of glass-forming materials is unusual dielectric behavior, distinct from those observed for other groups of glass-formers. For instance, as will be grounded by the results discussed in this Letter, contrary to the most glass-forming liquids, the pre-exponential factor, $\tau_0$, in the Vogel–Fulcher–Tammann (VFT) equation parametrizing the correlation times for a sizable molecule’s reorientations and equated with the inverse attempt frequency for barrier crossing, substantially exceeds the typical phonon-like time-scale of $10^{-14}$ s. Recalling the Bauer’s expression, $\tau_0 \sim (2\pi l/k_B T)^{0.5}$, which takes the moment of inertia, $l$, into account ($k_B$ is a Boltzmann constant, $T$ is temperature), the observed large values of $\tau_0$ imply that the inertia of these partially rigid molecules of considerable sizes determines to some extent their relaxation properties.

The consideration of large systems with significant moments of inertia leads to some questions regarding their rotational dynamics, most of which have not been directly addressed before. Thus, the results presented in this Letter are a wealth of new observations that may revise the scientific understanding of the dielectric response of large and partially rigid glass-formers. We present here dielectric results for three sizable molecules with an identical molecular core containing fluorene and diphenylamine motifs linked to a small polar unit. The partially planar framework of a sizable molecule is charac-
characterized by a certain degree of stiffness conditioned by the presence of many aromatic ring structures functionalized by flexible alkyl chains. From the perspective of dielectric research, it is essential that only one localized dipole contributes to the dielectric response. Considering this, the sizable molecule can be divided into two parts. The large nonpolar framework (assigned as M) is connected via a single C−C bond to the second segment formed by the phenyl ring with the trifluoromethylgroup attached (described as Ph-CF3). The small polar group −CF3 carries the dipole moment, which makes the motions of the whole system detectable by the BDS method. It is variably attached to the phenyl ring (in ortho, meta, or para positions). The corresponding sizable molecules are described as M-Ph-ortho-CF3, M-Ph-meta-CF3, and M-Ph-para-CF3, respectively. They were synthesized on request by TriMen Chemicals (Lodz, Poland) with a purity ≥ 97%. Their chemical structures are shown by the upper panels in Figure 1. Although the value of the dipole moment of the investigated isomers is similar, its orientation differs significantly in individual systems indicated by arrows on the upper panels in Figure 1a–c.

The investigated sizable molecules can be simply illustrated as a rigid unit with a smaller, rapidly rotating element (rotor) bound by a single covalent bond to the rigid part. Such an idealized model perfectly illustrates that, from the dynamics perspective, the sizable systems offer the unique combination of molecular motions on various scales involving whole molecule reorientations (i) and internal rotations (ii). To follow their reorientation dynamics, we measured the complex dielectric permittivity ε*(f) = ε′(f) − iε″(f) of melt-quenched samples using the Novocontrol Alpha analyzer (see Supporting Information for experimental details). The characteristic dynamic parameters are summarized in Table S1. The representative dielectric loss spectra presented in Figure 2 show that the relaxation behaviors of particular isomers vary significantly.

In contrast to M-Ph-para-CF3, the dielectric loss spectra of two other sizable systems reveal a strong secondary β-relaxation being distinguishable above and below the glass transition temperature, Tg, which is assigned to the internal rotation of the polar segment (Ph-CF3). Its properties in terms of relaxation time and dielectric strength in relation to the α-peak are very different. The characteristic relaxation times are shown in Figure 3a–c and were calculated from the fitting parameters obtained by the best fit of the ε″(f) data to the Cole−Cole function, Havriliak−Negami function, or their superposition.3

The reciprocal temperature dependence of the β-relaxation times, τβ, for M-Ph-meta-CF3 and M-Ph-ortho-CF3 shows the Arrhenius dependence below Tg with the activation energies Ea and prefactors τ0 equal to Ea = 50.1 ± 1 kJ/mol and log τ0 = −15.4 for M-Ph-meta-CF3 and Ea = 42.7 ± 2 kJ/mol and log τ0 = −9.3 for M-Ph-ortho-CF3. The substantial overlapping of α- and β-peaks in M-Ph-ortho-CF3 above Tg evidenced that the

Figure 1. (Left axis) Masterplots constructed by horizontal shifting of normalized spectra on the one registered at T = 331 K for M-Ph-para-CF3 (a), 313 K for M-Ph-ortho-CF3 (b), and 315 K for M-Ph-meta-CF3 (c). (Right axis) Representative ε*(f) spectrum and the corresponding dielectric strength Δε. Upper panels show the chemical structures of sizable glass-formers (the arrow approximates the direction of the dipole moment).

Figure 2. Representative dielectric loss spectra of sizable glass-formers with the same large structures differing only in the position of −CF3 group (blue symbols, para isomer; green, ortho; red, meta). For the spectrum recorded at 355 K, the components are disentangled (dashed lines).
VFT pre-exponents $\tau_\alpha$ and the appearance of a robust high temperatures and widens on cooling, revealing the was found for M-Ph-meta-CF$_3$ relative to the manifestation of the individual character of molecular evidences the decreasing degree of cooperativity, which allows Figure 2. The observed splitting of the loss peak at high frequency range up to $f = 10^6$ Hz and confirmed that at high $T$ the main loss peak in M-Ph-meta-CF$_3$ splits into two relaxation processes. The individual contributions to the dielectric response of the meta isomer at $T = 355$ K are unravelled in Figure 3. The characteristic relaxation times ($\tau_\alpha$, $\tau_\beta$, $\tau_\gamma$) plotted versus inverse temperature for para (a), meta (b), and ortho isomers (c) of sizable glass-formers. The solid and dashed lines are fits according to VFT and Arrhenius functions. The values of the VFT pre-exponents $\tau_\alpha$ are given as characteristic parameters describing their reorientation dynamics. Stars are relaxation times determined from TMDSC measurements ($T_{\text{TOPM}}$ is indicated). The insets show simplified block schemes of sizable glass-formers demonstrating the observed types of molecular motion.

mechanism of these motions is strongly coupled. As shown in Figure 1b, the loss peak in M-Ph-ortho-CF$_3$ is the narrowest at high temperatures and widens on cooling, revealing the appearance of a robust $\beta$-relaxation peak. The distinct behavior was found for M-Ph-meta-CF$_3$. On heating, the asymmetry of the main peak gradually increases, showing apart from the $\beta$-relaxation an additional contribution to the high-frequency flank of the $\alpha$-peak. To explore this further, we extended the frequency range up to $f = 10^6$ Hz and confirmed that at high $T$ the main loss peak in M-Ph-meta-CF$_3$ splits into two relaxation processes. The individual contributions to the dielectric response of the meta isomer at $T = 355$ K are unravelled in Figure 2. The observed splitting of the loss peak at high $T$ evidences the decreasing degree of cooperativity, which allows for the manifestation of the individual character of molecular motion. On approaching $T_g$, the correlation length $\xi$ increases, leading to the stronger coupling of the dynamics of a particular liquid’s subunits. The data in Figure 3b portray how the nature of the motions in M-Ph-meta-CF$_3$ changes on cooling, evolving from a situation where the mobility of each large molecule is independent to a highly intermolecular cooperative behavior. An exceptionally interesting point is a remarkable difference in the character of temperature changes of the relaxation times observed for fast processes, $\tau_\beta$ and $\tau_\gamma$. At the same time, when the $\beta$-process separates from the $\alpha$-peak as the system cools down, the merging of $\alpha$- and $\alpha'$-processes occurs, confirming the principally different origins of both relaxations. Our interpretation of $\alpha$- and $\alpha'$-modes in M-Ph-meta-CF$_3$ takes into account the anisotropic shape of a molecule and is based on two premises: (i) that the movements around the short molecular axis are expected to be slower than those about the long axis and (ii) that the transverse component of the dipole moment is expected to be greater than the longitudinal (this can be deduced from simple trigonometric analysis). Thus, we assigned the slower $\alpha$-process with higher intensity to the fluctuations of the transverse component of the dipole moment. This component may relax through the whole-molecule reorientations around the short axes that have a larger moment of inertia due to stronger coupling with the mass centers. A faster $\alpha'$-process was associated with the relaxation of the longitudinal component of the dipole moment by precession about the long axes. Such relaxation needs to be regarded as a combination of two elementary motions involving a sizable but nonpolar molecular core and a much less volumetric but rapidly spinning polar part. Due to the limited rotational freedom of the polar segment in the M-Ph-ortho-CF$_3$ and its strong coupling with the reorientations of the rest of the sizable molecule, the slowing down of $\alpha'$- and $\beta$-modes compared to M-Ph-meta-CF$_3$ can be expected. Thus, a simpler relaxation pattern found for the ortho isomer can be related to the proximity of the $\alpha$- and $\alpha'$-process time scales, which makes both modes experimentally indistinguishable.

Another interesting observation is the lack of fast relaxation processes in the dielectric loss spectra of the M-Ph-para-CF$_3$. The lack of fingerprints of internal rotations of Ph-CF$_3$ in the para isomer results from the arrangement of the dipole moment in this system. In M-Ph-para-CF$_3$, the dipole moment is directed parallel to the long axis of the sizable molecule (the transverse component of the dipole moment vector is negligible), and it does not change during rotation of the Ph-CF$_3$ fragment. For the same reason, the frequency dispersion of $\alpha$-relaxation in M-Ph-para-CF$_3$ is the narrowest among the investigated sizable systems. As presented in Figure 1a–c, the fits of the $\alpha$-loss peaks by the Fourier transform of the Kohlrausch–Williams–Watts (KWW) equation, $q(t) = \exp\left(-\frac{t}{\tau_{KWW}}\right)$, yields $\beta_{KWW} = 0.52$ at $313$ K for M-Ph-ortho-CF$_3$, $\beta_{KWW} = 0.60$ at $315$ K for M-Ph-meta-CF$_3$, and $\beta_{KWW} = 0.75$ at $331$ K for M-Ph-para-CF$_3$. The substantially smaller frequency dispersion of $\alpha$-relaxation in M-Ph-para-CF$_3$ demonstrated by the highest $\beta_{KWW}$ values is a consequence of the inability of the longitudinally arranged dipole moment in the para isomer to capture all aspects of the molecule’s motions. This remarkable observation is in line with our previous results for other representatives of sizable glass-formers where the dipole moment probing the dynamics is affixed to a very small fragment of the large molecule. Hence, the natural question is how accurately it reproduces the dynamics of the entire system. Our results show that, in the sizable glass-forming molecules, the frequency dispersion of structural relaxation, quantified by $\beta_{KWW}$ values, is strongly related to the arrangement of the dipole moment, impacting the ability to detect all aspects of molecular motion.

The results presented so far prove that the complex and diverse relaxation pattern of sizable glass-formers revealed by
dielectric behavior associated with the di- 
formers revealed a surprisingly impressive and notable 
belonging to the latterly constituted class of sizable glass-
particularly, 
properties suitable for many attractive applications. In 
the single dipole moment in a large molecule. Parallel to the 
large and anisotropic glass-forming systems probed by the 
hitherto unexplored aspects of the reorientation motion of 
sizable molecules, being systematized in this Letter, concerns 
e 
an individual subunit 
the onset of inertia, collectivity, and the degree of coupling of 
moment, some basic phenomena were discovered related to 
S2). In sizable molecules, due to the relevance of inertial 
which is 8 times longer for a sizable system compared to low-
liquids where 
τ 

greater than those observed typically for ordinary glass-forming 
materials. This 
weakly depends on the nature of the material (see the 
comparison with propylene carbonate in Figure S1).16 The 
unusually large VFT prefactors (τ0 > 10−12) established for 
reorientation dynamics by dielectric measurements are 
universal for sizable systems tested so far.7,8 Therefore, they 
can be regarded as a characteristic feature distinguishing sizable 
molecules from other classes of glass-forming liquids. This 
unique behavior can be rationalized by the effect of inertia. To 
determine I values, we performed DFT calculations (see 
Supporting Information for more details). For propylene 
carbonate, I = 4.90 × 10−45 kg·m2, while for M-para-CF3, I = 
3.19 × 10−43 kg·m2. These values yielded τ0 = (2πI/kBT)0.5, 
which is 8 times longer for a sizable system compared to low-
molecular-weight glass-former propylene carbonate (Table 
S2). In sizable molecules, due to the relevance of inertial 
effects, we “gain greater resolution” and a unique insight into 
hitherto unexplored aspects of the reorientation motion of 
large and anisotropic glass-forming systems probed by the 
dielectric method.

In summary, our dielectric study of three structural isomers 
belonging to the latterly constituted class of sizable glass-
formers revealed a surprisingly impressive and notable 
dielectric behavior associated with the different positions of 
the single dipole moment in a large molecule. Parallel to the 
spectacular variations in the distribution of structural relaxation 
times among systems “differently labeled” with the dipole 
moment, some basic phenomena were discovered related to 
the onset of inertia, collectivity, and the degree of coupling of 
an individual subunit’s motion. In general terms, the concept of 
sizable molecules, being systematized in this Letter, concerns 
chemical entities being a collection of multiple rigid or 
semirigid frameworks functionalized with floppy elements (like 
alkyl solubilizing groups) and small polar units that have 
properties suitable for many attractive applications. In 
particular, fluorene-based compounds combining different π-
conjugated building blocks are attractive candidates for various 
light-emitting applications, e.g., in organic light-emitting diodes 
(OLEDs),17,18 which could fill the gap of today and future 
demands of flexible electronics. The correlated dynamics of 
several moving parts within a single molecule allow an exciting 
extrapolation to the complex artificial machines and bio-
molecular systems, making sizable systems a platform of 
materials providing an intriguing starting point for these 
intricate objects. The results presented in this Letter and the 
thought-provoking ideas behind them are fascinating due to 
the possibility of introducing the fundamental issues 
untouched so far and directing dielectric research into new, 
hitherto unexplored areas of practical implementation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.1c03088.

Experimental protocols, summary of the dynamic parameters determined from dielectric measurements, rotational constants, and calculated moments of inertia, and comparison of dielectric responses for sizable molecules and propylene carbonate (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Marzena Rams-Baron — August Chelkowski Institute of Physics, University of Silesia, 41-500 Chorzow, Poland; Silesian Center for Education and Interdisciplinary Research, 41-500 Chorzow, Poland; Email: marzena.rams-baron@us.edu.pl

Authors

Beibei Yao — August Chelkowski Institute of Physics, University of Silesia, 41-500 Chorzow, Poland; Silesian Center for Education and Interdisciplinary Research, 41-500 Chorzow, Poland
Shinin Cheng — August Chelkowski Institute of Physics, University of Silesia, 41-500 Chorzow, Poland; Silesian Center for Education and Interdisciplinary Research, 41-500 Chorzow, Poland; orcid.org/0000-0002-5615-8646
Mateusz Dulski — Institute of Materials Engineering, University of Silesia, 41-500 Chorzow, Poland; Silesian Center for Education and Interdisciplinary Research, 41-500 Chorzow, Poland; orcid.org/0000-0001-8686-1853
Marian Paluch — August Chelkowski Institute of Physics, University of Silesia, 41-500 Chorzow, Poland; Silesian Center for Education and Interdisciplinary Research, 41-500 Chorzow, Poland

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpclett.1c03088

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

M.P. is deeply grateful for the financial support by the National Science Centre within the framework of the Maestro10 project (Grant No. UMO-2018/30/A/ST3/00323). We are grateful to Prof. Roman Wrzalik for assistance in rotational constants calculations. The research was supported in part by PL-Grid Infrastructure.

■ REFERENCES

(1) Ngai, K. L. Relaxation and Diffusion in Complex Systems; Partially Ordered Systems; Springer New York: New York, NY, 2011; Vol. 53; DOI: 10.1007/978-1-4419-7649-9.
(2) Kremer, F.; Lodl, A. The Scaling of Relaxation Processes; Kremer, F., Lodl, A., Eds.; Advances in Dielectrics; Springer International Publishing: Cham, 2018; DOI: 10.1007/978-3-319-72706-6.
(3) Fludas, G.; Paluch, M.; Grzybowski, A.; Ngai, K. L. Molecular Dynamics of Glass-Forming Systems. Effects of Pressure; Kremer, F., Ed.; Springer Science & Business Media: 2010.
(4) Kremer, F.; Schönhals, A. Broadband Dielectric Spectroscopy; Springer-Verlag: Berlin, Heidelberg, 2003.
(5) Kistemaker, J. C. M.; Stacko, P.; Visser, J.; Feringa, B. L. Unidirectional Rotary Motion in Achiral Molecular Motors. Nat. Chem. 2015, 7 (11), 890–896.

(6) Filatov, M. Understanding the Dynamics behind Photo-isomerization of Light-Driven Molecular Rotary Motors. Wiley Interdiscip. Rev. Comput. Mol. Sci. 2013, 3 (5), 427–437.

(7) Jedrzejowska, A.; Matussek, M.; Ngai, K. L.; Grzybowska, K.; Jurkiewicz, K.; Paluch, M. New Paradigm of Dielectric Relaxation of Sizable and Rigid Molecular Glass Formers. Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top. 2020, 101 (1), 010603.

(8) Rams-Baron, M.; Jedrzejowsa, A.; Jurkiewicz, K.; Matussek, M.; Ngai, K. L.; Paluch, M. Broadband Dielectric Study of Sizable Molecular Glass Formers: Relationship between Local Structure and Dynamics. J. Phys. Chem. Lett. 2021, 12 (1), 245–249.

(9) Hill, N. E.; Vaughan, W. E.; Price, A. H.; Davies, M. Dielectric Properties and Molecular Behaviour; Van Nostrand: London, 1969.

(10) Berthier, L.; Biros, G.; Bouchaud, J.-P.; Cipelletti, L.; El Massi, D.; L’Hôte, D.; Ladieu, F.; Pierro, M. Direct Experimental Evidence of a Growing Length Scale Accompanying the Glass Transition. Science 2005, 310 (5755), 1797–1800.

(11) Kohlrausch, R. Theorie Des Elektrischen Rückstandes in Der Leidener Flasche. Ann. Phys. 1854, 167 (2), 179–214.

(12) Williams, G.; Watts, D. C. Non-Symmetrical Dielectric Relaxation Behaviour Arising from a Simple Empirical Decay Function. Trans. Faraday Soc. 1970, 66 (1), 80–85.

(13) Vogel, H. Das Temperaturabhängigkeitsgesetz Der Viskosität von Flüssigkeiten. J. Phys. Z. 1921, 22, 645–646.

(14) Fulcher, G. S. Analysis of Recent Measurements of the Viscosity of Glasses. J. Am. Ceram. Soc. 1925, 8, 339–355.

(15) Tammann, G.; Hesse, W. Die Abhängigkeit Der Viskosität von Der Temperatur Bie Unterkühlten Flüssigkeiten. Z. Anorg. Allg. Chem. 1926, 156, 245–257.

(16) Rault, J. Origin of the Vogel-Fulcher-Tammann Law in Glass-Forming Materials: The β Bifurcation. J. Non-Cryst. Solids 2000, 271 (3), 177–217.

(17) Wong, K. T.; Chien, Y. Y.; Chen, R. T.; Wang, C. F.; Lin, Y. T.; Chiang, H. H.; Hsieh, P. Y.; Wu, C. C.; Chou, C. H.; Su, Y. O.; et al. Ter(9,9-Diarylfluorene)s: Highly Efficient Blue Emitter with Promising Electrochemical and Thermal Stability. J. Am. Chem. Soc. 2002, 124 (39), 11576–11577.