

Simple-liquid dynamics emerging in the mechanical shear spectra of poly(propylene glycol)

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Abstract The present dielectric investigations of methyl-terminated poly(propylene glycol) (PPG) oligomers reveal that near the glass transition the normal modes and segmental relaxation merge in a single-process susceptibility spectrum, similar to previous observations on OH-terminated species. Moreover, the present shear-mechanical measurements demonstrate that the vanishing of chain modes can be monitored without recourse to dielectric investigations, which are able to access chain dynamics only for the relatively small fraction of type A polymers. As the normal and segmental modes merge, the viscosity displays a crossover from a polymer-like regime governed by the chain dynamics, to a simple-liquid regime governed by the structural relaxation.

Keywords Dielectric spectroscopy · Rheology · Normal modes · Hydrogen bonding

It is well established that sufficiently long polymer chains exhibit entanglements, and these have been studied extensively both experimentally and theoretically [1, 2]. Below the entanglement molecular weight, Rouse-like dynamics dominate the behavior of polymers [3]. Upon further shortening the chains, the sub-Rouse regime is entered [4] until eventually the simple-molecule limit, i.e., the monomer melt state is

reached. This regime in which Rouse dynamics is not (fully) developed has been a matter of stimulating discussion [5–7]. Beyond a chain length of a few monomers, precursors of normal modes emerge which are barely slower than the segmental motion [8]. For the so-called type A polymers, these modes are easily accessible via dielectric spectroscopy. These materials, which are however relatively few in number, feature an electrical dipole moment formed along the backbone contour, so that the chain's end-to-end dynamics is probed via dielectric spectroscopy [9, 10]. Their study revealed that the separation of the (sub-) Rouse mode from the segmental mode depends on temperature T with a tendency for the two processes to approach each other when cooling towards T_g [11–15]. This behavior contradicts the predictions of standard polymer models [2, 3] and was rationalized within theoretical concepts such as the coupling model [16] and the dynamically disordered Rouse model [17], or alternatively ascribed to dynamic heterogeneities [11, 12, 14]. One important still unresolved question is whether these deviations from the classical polymer dynamics picture can be attributed to strong correlations among the chains or among the segments.

Different temperature dependences for the segmental and the normal modes are not only known from dielectric measurements but from rheological studies as well [18, 19], where they are often referred to as “thermorheological complexity” [20, 21]. No mechanical spectroscopy data are available that demonstrate the convergence of the segmental and normal modes to a limit in which the overall response of the polymer chains reduces to a monomodal decay otherwise characteristic for simple (non-associating, non-polymeric) glass forming liquids. The present work uncovers this feature for oligomeric PPG employing shear mechanical experiments. Specifically, a sample with a molecular weight of 770 g/mol corresponding to $N = 13$ repeat units (PPG13–OH) was chosen for which dielectric measurements demonstrated a merging of the two

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relaxations in a conveniently accessible frequency regime [38]. In order to check the extent to which the merging of the two modes is affected by the chemistry of the end groups, we also investigated the dielectric response of $N = 13$ oligomer terminated by methyl groups (PPG13-M). This replacement precludes any inter-chain hydrogen bonding characteristic for “usual” PPG materials.

PPG with different molecular weights (usually above 1000 g/mol) have been intensively studied via dielectric spectroscopy [22–26], Kerr measurements [22, 23], various light scattering methods [24], neutron scattering [27], nuclear magnetic resonance [28], and mechanical spectroscopy [29, 30]. In the present work, the shear-mechanical measurements were performed by combining a modular compact rheometer MCR 502 from Anton-Paar with the piezoelectric modulus gauge described in Ref. [31]. This enabled us to cover frequencies ν ranging from below 10 mHz up to more than 10 kHz. The dielectric spectra of PPG13-M were recorded using the equipment described in Ref. [32].

The real and imaginary parts of the complex shear modulus $G \times (\nu) = G'(\nu) + iG''(\nu)$ measured at temperatures $225 \text{ K} \geq T \geq 200 \text{ K}$ are presented in Fig. 1a, b and demonstrate an excellent agreement between the two data sets in their commonly investigated range. These spectra nicely reveal the failure of frequency-temperature superposition, as the dynamical contrast between the structural relaxation and the terminal chain-mode (best recognized from the deviations of $G' \propto \nu^2$ behavior indicated in Fig. 1a) progressively decreases upon cooling.

Fig. 1c presents the dielectric loss spectra of PPG13-M. Its normal modes approach the structural relaxation upon cooling and, as revealed by the spectrum recorded at 186 K, a simple liquid regime is established in the accessible frequency range. Both the shape and the T -evolution of these spectra strongly resemble the ones exhibited by the OH-terminated material [33, 34]. Note that the different temperature ranges covered in the investigations of these two oligomers reveal that the end groups, although not influencing the merging, lead to major differences in the overall dynamics in these materials.

To better visualize the difference in the temperature evolution of the segmental and normal mode dynamics, the current dielectric and shear data are presented on reduced scales in Fig. 2. For reference purposes the dielectric response of the PPG13-OH sample [33, 34] is reproduced in Fig. 2a as permittivity loss ε'' scaled with respect to its maximum values $\varepsilon''_{\text{max}}$ as well as to the loss peak frequency ν_{max} . The same representation was chosen for the present dielectric PPG13-M data in Fig. 2b. In Fig. 2c, the shear spectra for PPG13-OH are scaled vertically by the instantaneous shear moduli $G_{\infty} = G'(\omega \rightarrow \infty)$ accounting for the static characteristics of the spectra, as well as with respect to the mechanical loss peak frequency ν_{max} . The storage (real) part of the modulus turned out to be more useful for the clarity of the T -evolution, as on the low-frequency side of the segmental process excess contributions

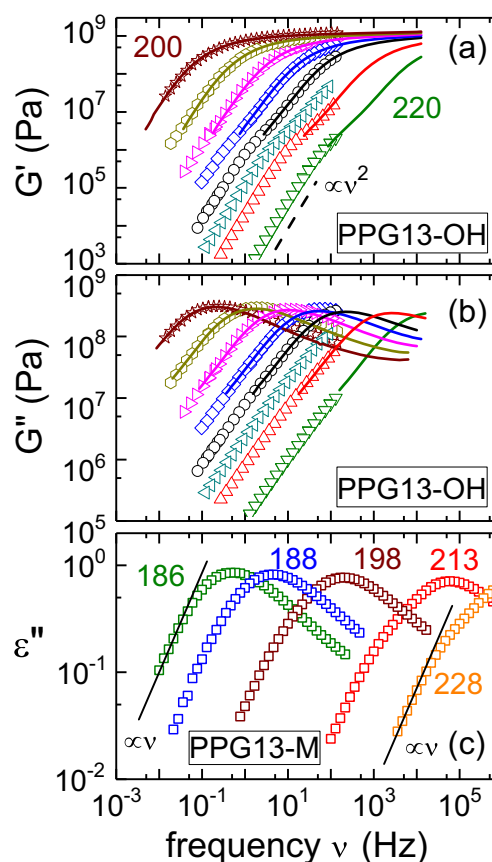


Fig. 1 Frequency dependence of **a** real part and **b** imaginary part of the complex shear modulus for PPG13-OH and of **c** dielectric loss for PPG13-M shown on double-logarithmic scales. In **a** and **b**, the data refer to temperatures (from left to right) of 200, 202.5, 205, 207.5, 210, 212.5, 215, and 220 K. The open symbols and the lines are measurements performed with the Anton-Paar rheometer and with the piezoelectric modulus gauge technique, respectively. In **c**, the numbers indicate the corresponding temperatures in Kelvin. In **a**, the dashed line marks the terminal Maxwell ν -dependence and in **c** the solid lines correspond to the terminal Debye modes

show up most prominently in the stronger frequency-dependent real part $G'(\nu) \propto \nu^2$ with respect to the loss $G''(\nu) \propto \nu^1$ (see Ref. [2]).

The $G'(\nu)$ scaling in Fig. 2 yields an evolution pattern which is similar to that seen in Fig. 2a, b for the dielectric data: Upon lowering the temperature, the time scales of the “sub-Rouse” modes approach those of the segmental relaxation and consequently the slope of the low-frequency contribution successively increases. Finally, near 202.5 K, the two modes merge and the simple liquid (Maxwell) limit [35] is reached for PPG13-OH.

In line with previous ideas [36], the merging of the dielectric normal mode with the segmental or structural dynamics has been interpreted in terms of the coupling model [16]. Following a different line of thought [11, 12, 14], this merging was attributed to an increase in the structural relaxation’s cooperativity length which approaches the scale set by the chain’s end-to-end distance

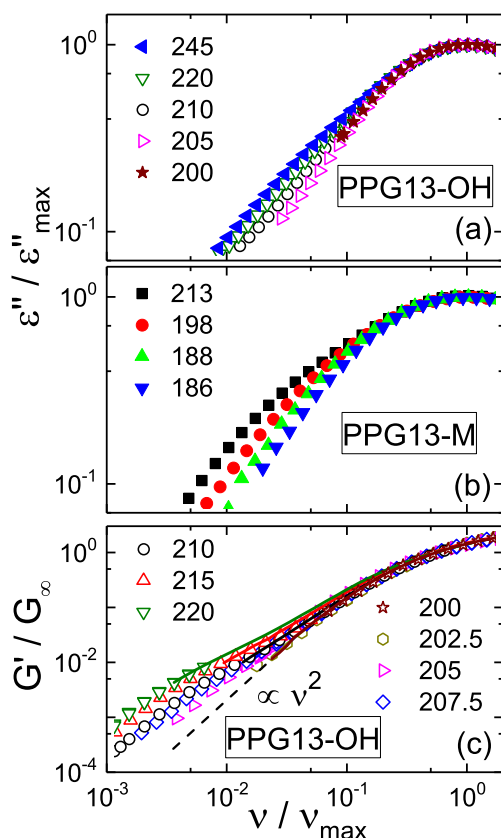


Fig. 2 **a** Doubly-scaled dielectric loss $\varepsilon''(\nu) / \varepsilon''_{\max}$ for PPG13-OH, **b** doubly scaled dielectric loss $\varepsilon''(\nu) / \varepsilon''_{\max}$ for PPG13-M, and **c** doubly scaled shear modulus $G'(\nu) / G'_{\infty}$ for PPG13-OH, all plotted vs. ν / ν_{\max} . In frame **b**, the open symbols and the lines represent data measured with the Anton-Paar rheometer and the piezoelectric modulus gauge technique, respectively. The numbers indicate temperatures in Kelvin. In frame **c**, the dashed line marks $G' \propto \nu^2$. In **a** and **c**, the dielectric as well as the mechanical data, measured at temperatures around 200 K, do no longer exhibit bimodal spectra, signaling that the simple molecule limit is reached

[38]. Thus considering the chains as “molecular rulers”, PPG oligomers of different chain length were exploited to map out the temperature dependence of the cooperativity length scale [38] which semi-quantitatively agreed with other estimates [38, 39]. The elucidation of this merging is an example which demonstrates that its study is beneficial not only from the perspective of polymer dynamics, but for the understanding of the glass transition in general. Yet, most polymer systems lack an along-the-chain dipole moment, while our study demonstrates that elastic normal modes can provide direct access to the same information, but for a much broader range of materials.

The vanishing of the chain dynamics upon cooling is interesting from a rheological perspective in its own right. This is relevant not the least because the merging of the two processes impacts also on the temperature dependence of the shear viscosity η . At high temperatures, η should be governed by the normal modes [40], while below the merging temperature the structural relaxation is expected to prevail. In Fig. 3 for PPG13-OH, we

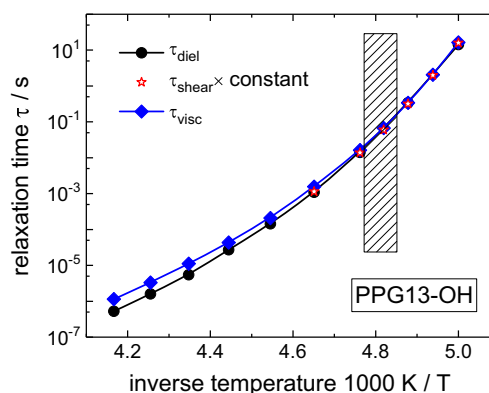


Fig. 3 Arrhenius plot of the time constants from the dielectric susceptibility relaxation peak corresponding to segmental dynamics τ_{diel} (black dots and line) and scaled characteristic time scales obtained from shear modulus $\tau_{\text{shear}} \times \text{constant}$ (red open stars, raw data multiplied with 20) and from viscosity τ_{visc} (blue filled diamonds and line). All characteristic times follow a common temperature dependence in the range $1000\text{K} / T > 4.8 \text{K}^{-1}$, while τ_{visc} separates from τ_{diel} upon heating

plot the relaxation times τ_{diel} and τ_{shear} inferred from the main peak of the dielectric susceptibility and of the shear modulus loss, respectively. Note that a single, temperature independent shift factor leads to a good agreement between the two datasets (in the commonly investigated T range), both characterizing the structural relaxation. In the same figure, we included the time scales obtained from viscosity τ_{visc} which characterizes the long-time, terminal flow. To enable this comparison, the shear data were first transformed to viscosity via $\eta(\omega) = G'(\omega) / (i\omega)$ and the amplitude of the low-frequency plateau of the real part of the complex viscosity $\eta_0 = \eta(\omega \rightarrow 0)$ was used to estimate the corresponding time constants via the Maxwell relation $\tau_{\text{visc}} = K_1 \eta_0 / G_{\infty}$ [35]. The constant K_1 was chosen so that the time scales τ_{diel} and τ_{visc} agree best at the lowest investigated temperatures where a single-peak susceptibility is observed. In the deeply supercooled regime, this agreement is well preserved, but for $T > 210 \text{K}$ ($1000 / T \approx 4.8 \text{K}^{-1}$), the two characteristic times follow slightly different temperature dependences. The area highlighted in Fig. 3 framing this temperature marks the cross-over between two regimes: at lower T than 210 K both the chain (sub-Rouse) modes become absorbed (encroached [16]) by the segmental mode, and this leads to good agreement between segmental dynamics and viscosity. However, at higher T chain modes separate and contribute more towards viscosity, leading to a separation of the two timescales which at high T reaches about a factor of 2, comparable to the shift of the chain mode seen in Fig. 2a, c.

To summarize, the present shear mechanical results for PPG-OH13 demonstrate that below a characteristic merging temperature the separation of the segmental and chain dynamics ceases, corroborating the dielectric results [37]. Whatever is the mechanism at the origin of this complexity, our results demonstrate that the process of merging of segmental and chain dynamics can be investigated irrespective of whether or not a chain carries a dipole

moment along its backbone. A peculiar behavior of the transport coefficients was revealed by the breakdown of frequency-temperature superposition: The oligomer behaves polymer-like at high temperatures and like a simple molecular liquid in its highly viscous state. For PPG, the ability of the end groups to sustain H-bonds does not influence this phenomenology, which thus can be considered to be general for oligomeric chains.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

- Williams G (2009) Chain dynamics in solid polymers and polymerizing systems as revealed by broadband dielectric spectroscopy. *Macromol Symp* 286:1–19
- Doi M, Edwards SF (1986) *The theory of polymer dynamics*. Clarendon, Oxford
- Rouse Jr PE (1953) A theory of the linear viscoelastic properties of dilute solutions of coiling polymers. *J Chem Phys* 21:1272–1280
- Bahar I, Erman B, Monnerie L (1991) Stochastic treatment of conformational transitions of polymer chains in the sub-Rouse regime. *Macromolecules* 24:3618–3626
- Paluch M, Pawlus S, Sokolov AP, Ngai KL (2010) Sub-rouse modes in polymers observed by dielectric spectroscopy. *Macromolecules* 43:3103–3106
- Hintermeyer J, Herrmann A, Kahlau R, Goiceanu C, Rössler EA (2008) Molecular weight dependence of glassy dynamics in linear polymers revisited. *Macromolecules* 41:9335–9344
- Agapov AL, Sokolov AP (2009) Does the molecular weight dependence of T_g correlate to M_e ? *Macromolecules* 42:2877–2878
- Wu X, Liu C, Zhu Z, Ngai KL, Wang L-M (2011) Nature of the sub-rouse modes in the glass–rubber transition zone of amorphous polymers. *Macromolecules* 44:3605–3610
- Baur ME, Stockmayer H (1965) Dielectric relaxation in liquid polypropylene oxides. *J Chem Phys* 43:4319–4325
- Adachi K, Kotaka T (1993) Dielectric normal-mode relaxation. *Prog Polym Sci* 18:585–622
- Schönhals A, Schlosser E (1993) Relationship between segmental and chain dynamics in polymer melts as studied by dielectric spectroscopy. *Physica Scripta* T49:233–236
- Schönhals A, Schlosser E (1993). Relation between main- and normal-mode relaxation. A dielectric study on poly(propyleneoxide). *Prog Coll Polym Sci* 91:158–161
- Mierzwa M, Floudas G, Dorgan J, Knauss D, Wegner J (2002) Local and global dynamics of polylactides: a dielectric spectroscopy study. *J Non-Cryst Solids* 307-310:296–303
- Nicolai T, Floudas G (1998) Dynamics of linear and star poly(oxypropylene) studied by dielectric spectroscopy and rheology. *Macromolecules* 31:2578–2585
- Casalini R, Roland CM (2005) Temperature and density effects on the local segmental and global chain dynamics of poly(oxybutylene). *Macromolecules* 38:1779–1788
- Ngai KL, Schönhals A, Schlosser E (1992) An explanation of anomalous dielectric relaxation properties of polypropylene glycol. *Macromolecules* 25:4915–4919
- Ilan B, Loring RF (1999) Local vitrification model for melt dynamics. *Macromolecules* 32:949–951
- Plazek DJ, O'Rourke VMJ (1971). Viscoelastic behavior of low molecular weight polystyrene. *Polym. Sci., Part A2* 9:209–243
- Plazek DJ, Schlosser E, Schönhals A, Ngai KL (1993) Breakdown of the rouse model for polymers near the glass transition temperature. *J Chem Phys* 98:6488–6491
- Ngai KL, Plazek DJ (1995) Identification of different modes of molecular motion in polymers that cause thermorheological complexity. *Rubber Chem Technol* 68:376–434
- Plazek DJ (1996) Bingham medal address: oh, thermorheological simplicity, wherefore art thou? *J Rheol* 40:987–1014
- Beevers MS, Elliott DA, Williams G (1980) Dynamic Kerr-effect and dielectric relaxation studies of a poly(methylphenyl siloxane). *Polymer* 21:13–20
- Hayakawa T, Adachi K (2001) Dielectric normal mode relaxation of undiluted poly(propylene glycol)s. *Polymer* 42:1725–1732
- Engberg D, Schüller J, Strube B, Sokolov AP, Torell LM (1999) Brillouin scattering and dielectric relaxation in PPG of different chain lengths and end groups. *Polymer* 40:4755–4761
- Mattsson J, Bergman R, Jacobsson P, Börjesson L (2003) Chain-length-dependent relaxation scenarios in an oligomeric glass-forming system: from merged to well-separated α and β loss peaks. *Phys Rev Lett* 90:075702
- Mattsson J, Bergman R, Jacobsson P, Börjesson L (2005) Influence of chain length on the α - β bifurcation in oligomeric glass formers. *Phys Rev Lett* 94:165701
- Swenson J, Köper I, Telling MTF (2002) Dynamics of propylene glycol and its 7-mer by neutron scattering. *J Chem Phys* 116:5073–5079
- Vogel M, Torbrügge T (2007) Nonexponential polymer segmental motion in the presence and absence of ions: ^2H NMR multitime correlation functions for polymer electrolytes poly(propylene glycol)- LiClO_4 . *J Chem Phys* 126:204902
- Cochrane J, Harrison G, Lamb J, Phillips DW (1980) Creep, creep recovery and dynamic mechanical measurements of a poly(propylene glycol) oligomer. *Polymer* 21:837–844
- Saba RG, Sauer JA, Woodward AE (1963) Dynamic shear behavior of poly(γ -benzyl L-glutamate), poly(D,L-propylene oxide), and poly(ethyl vinyl ether). *J Polymer Sci Part A* 1:1483–1490
- Christensen T, Olsen NB (1995) A rheometer for the measurement of a high shear modulus covering more than seven decades of frequency below 50 kHz. *Rev Sci Instrum* 66:5019–5031
- Xing K, Chatterjee S, Saito T, Gainaru C, Sokolov AP (2016) Impact of hydrogen bonding on dynamics of hydroxyl-terminated Polydimethylsiloxane. *Macromolecules* 49:3138–3147
- PPG with this molecular weight were dielectrically studied before, see Park IS, Saruta K, Kojima S (1998) Dielectric Relaxation and Calorimetric Measurements of Glass Transition in the Glass-Forming Dihydroxyl Alcohols. *J Phys Soc Jpn* 67:4131–4138
- Gainaru C, Böhmer R (2009) Oligomer-to-polymer transition of poly-(propylene glycol) revealed by dielectric normal modes. *Macromolecules* 42:7616–7618
- Ferry JD (1970) *Viscoelastic properties of polymers*. Wiley, New York,
- Ngai KL, Rendell RW, Rajagopal AK, Teitler S (1986) Three coupled relations for relaxations in complex systems. *Ann N Y Acad Sci* 484:150–180
- Gainaru C, Hiller W, Böhmer R, Dielectric Study A (2010) Of Oligo- and poly(propylene glycol). *Macromolecules* 43:1907–1914

38. Reinsberg SA, Heuer A, Doliwa B, Zimmermann H, Spiess HW (2002) Length scale of dynamic heterogeneities at the glass transition determined by multidimensional nuclear magnetic resonance. *J Non-Cryst Solids* 307-310:208–214
39. Fragiadakis D, Casalini R, Bogoslovov RB, Robertson CG, Roland CM (2011) Dynamic heterogeneity and density scaling in 1,4-Polyisoprene. *Macromolecules* 44:1149–1155
40. Strobl G (1997) *The physics of polymers*. Springer, Berlin