GLASS TRANSITION AND ENTANGLEMENT IN SEMIFLEXIBLE CONJUGATED POLYMER MELTS

Abigail M. Fenton,[1] Renxuan Xie[1], Daniele Parisi[2], Enrique D. Gomez[1,3] and Ralph H. Colby[2,3]

[1]Department of Chemical Engineering, The Pennsylvania State University, University Park, PA 16802, USA

[2]Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA

[3]The Materials Research Institute, The Pennsylvania State University, University Park, PA 16802, USA

Correspondence to: rhc@plmsc.psu.edu

ABSTRACT

Polymers with conjugated backbones and flexible side chains are semiflexible and exhibit two glass transitions, one for the conjugated backbone and a lower T_g for the side chains. Both glass transitions are broadened, since the side chains are covalently attached to the backbones, and are challenging to detect by standard calorimetry methods (i.e., DSC). By compression molding in a glove box, it is possible to measure the linear viscoelastic response (LVE) of conjugated polymers from the lower T_g up to roughly 300 ºC. The two glass transitions are detected in LVE temperature sweeps at 1 rad/s as local maxima in the loss modulus G" and the width of these transitions is reflected in how much higher in temperature tanδ = G"/G' exhibits a local maximum.[1] A simple model is presented to predict the backbone glass transition from volume fraction of backbone and molecular characteristics of the backbone,[2] enabling molecular design of conjugated polymers for flexible electronics with T_g below ambient.

Many of the conjugated polymers with more rigid backbones exhibit liquid crystalline phases above their melting temperature. The ones with a nematic phase are very easy to detect in the LVE temperature sweeps, as the nematic → isotropic transition is easily seen as a roughly 10 K window where viscosity actually *increases* as temperature is raised[3,4] (which is the biphase) whereas this weakly first order transition is virtually undetectable by DSC. In the isotropic phase at high temperature, the plateau modulus is measured by constructing an LVE master curve and with the molecular weight distribution this is fit to a molecular LVE model based on reptation dynamics, originally developed for more flexible polymers. The Kuhn length is determined either by small-angle neutron scattering in solution or by calculation using the bond angles and lengths via the freely rotating chain model.[4] For semiflexible conjugated polymers, these two methods agree nicely and the plateau modulus G_N^0 is correlated with backbone stiffness, allowing prediction of G_N^0 just by estimating the Kuhn length.[4] That is very powerful, since the plateau modulus (number density of entanglements) is vital for understanding the semicrystalline modulus of conjugated polymers that have T_g below room temperature, needed for flexible electronics.[5]

The liquid crystalline phases, including ones that form in shear flow, can be detected by quantifying the shear rate dependence of birefringence.[6,7] We present some preliminary rheo-optical results using shear-induced polarized light imaging[8] (SIPLI) on an Anton Paar MCR-502 controlled stress rotational rheometer with a transparent bottom plate and a mirror-finish top plate. A polarized white light source comes from below the transparent bottom plate, reflects off the mirror-finish top plate and is collected by a CCD camera below the bottom plate, after passing through a crossed polarizer. This method facilitates identification of the nematic phase (at rest) and the critical shear rate for any flow-induced nematic alignment of polymers that have isotropic phases at rest.

REFERENCES

1. R. Xie, Y. Lee, M. P. Aplan, N. J. Caggiano, C. Müller, R. H. Colby and E. D. Gomez, Glass Transition Temperature of Conjugated Polymers by Oscillatory Shear Rheometry, *Macromolecules* **50**, 5146 (2017).
2. R. Xie, A. R. Weisen, Y. Lee, M. A. Aplan, A. M. Fenton, A. E. Masucci, F. Kempe, M. Sommer, C. W. Pester, R. H. Colby and E. D. Gomez, Glass Transition Temperature from the Chemical Structure of Conjugated Polymers, *Nat. Comm.* **11**, 893 (2020).
3. R. Xie, M. P. Aplan, N. J. Caggiano, A. R. Weisen, T. Su, C. Müller, M. Segad, R. H. Colby and E. D. Gomez, Local Chain Alignment via Nematic Ordering Reduces Chain Entanglement in Conjugated Polymers, *Macromolecules* **51**, 10271 (2018).
4. A. M. Fenton, R. Xie, M. P. Aplan, Y. Lee, M. G. Gill, R. Fair, F. Kempe, M. Sommer, C. R. Snyder, E. D. Gomez and R. H. Colby, Predicting the plateau modulus from molecular parameters of conjugated polymers, *ACS Central Science* **8**, 268 (2022).
5. R. Xie, R. H. Colby and E. D. Gomez, Connecting the Mechanical and Conductive Properties of Conjugated Polymers, *Advanced Electronic Materials*, 1700356 (2017).
6. D. Parisi, J. Seo, B. Nazari, R. P. Schaake, A. M. Rhoades and R. H. Colby, Shear-Induced Isotropic−Nematic Transition in Poly(ether ether ketone) Melts, *ACS Macro. Lett.* **9**, 950 (2020).
7. D. Parisi, J. Seo, R. P. Schaake, A. M. Rhoades and R. H. Colby, Shear-Induced Nematic Phase in Entangled Rod-Like PEEK Melts, *Prog. Polym. Sci.* **112**, 101323 (2021).
8. O. O. Mykhaylyk, N. J. Warren, A. J. Parnell, G. Pfeifer, J. Laeuger, Applications of Shear-Induced Polarized Light Imaging (SIPLI) Technique for Mechano-Optical Rheology of Polymers and Soft Matter Materials, *J. Polym. Sci., Polym. Phys.* **54**, 2151 (2016).