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Huang, Qian; Mednova, Olga; Rasmussen, Henrik K.; Skov, Anne Ladegaard; Almdal, Kristoffer; Hassager, Ole

Publication date:
2012

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
Huang, Q., Mednova, O., Rasmussen, H. K., Skov, A. L., Almdal, K., & Hassager, O. (2012). *Are Entangled Polymer Melts Different From Solutions?*. Abstract from 16th International Congress on Rheology, Lisbon, Portugal.

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model. In particular, we show the importance of taking into account the monomeric friction coming from the backbone itself in the total drag of the molecule, considering the modification of early time fluctuations and introducing the tube dilation process as a continuous function evolving through time. Then, based on a wide range of experimental data on different comb structures, we explore the limits of the relaxation behavior that comb polymers can show. In particular we have introduced the concepts of “Multiple Fluctuations Modes” (MFM) and the simplified version “Triple Fluctuations Modes” (TFM) to cover the wide dynamic range exhibited by combs depending on their branch length. If the friction from the relaxed side branches is significant, the backbone segments seem to fluctuate with respect to the closest branching point, just like a Cayley-tree molecule. On the other hand if the extra friction is negligible in comparison to the potential barrier of retraction along the backbone, the segments fluctuate with respect to the middle of the molecule, just like a linear chain.

ARE ENTANGLED POLYMER MELTS DIFFERENT FROM SOLUTIONS?

Qian Huang¹; Olga Mednova²; Henrik K. Rasmussen³; Anne L. Skov¹; Kristoffer Almdal²; Ole Hassager¹

¹Department of Chemical and Biochemical Engineering, Technical University of Denmark; ²Department of Micro- and Nanotechnology, Technical University of Denmark; ³Department of Mechanical Engineering, Technical University of Denmark

ABSTRACT

The possible existence of a qualitative difference on extensional steady state viscosity between polymer melts and polymer solutions is still an open question. Recent experiments [1-4] showed the extensional viscosity of both polymer melts and solutions decayed as a function of strain rate with an exponent of -0.5. When the strain rate became higher than the order of inverse Rouse time, the polymer solutions showed an upturn [1, 4]. However, in the same regime for polymer melts, the experiments were contrary: some of the experiments showed an upturn [4, 5], while others did not [2, 3].

In order to further investigate the extensional steady state viscosity of polymer melts, we carefully synthesized two monodisperse polystyrenes with molar masses of 248 and 484 kg/mole. The start-up and steady uniaxial elongational viscosity have been measured for the two melts using a filament stretching rheometer. We then compared the measurements with the bi-disperse polystyrene melts made from the above two polymers. The influence and sensitivity of impurities were studied by adding different percentages of 484k into 248k polystyrene melt. Furthermore a polydisperse polystyrene with weight average molecular weight 230 kg/mole was also measured for comparison. Possible reasons for the differences shown in the previously mentioned experiments are discussed.

PECULIAR RHEOLOGY OF HYPERBRANCHED POLYIONIC LIQUID SOLUTIONS

Simon Bodendorfer¹; Benjamin Kerscher¹; Carina Gillig¹; Natalia Pogodina¹; Christian Friedrich¹

¹Material Research Center (FMF), University of Freiburg, Freiburg, Germany

ABSTRACT

Polyionic liquids (PILs) are a new class of complex fluids with unique and fascinating physical properties, which behavior is not yet understood. We present the studies of novel PILs solutions in the ionic liquids (ILs) in a broad temperature range (from -100°C up to 100°C) by utilizing differential scanning calorimetry (DSC), rheology, X-ray scattering and light microscopy. We synthesized via cationic ring-opening polymerization, functionalization and final anion-exchange-reaction a novel hyperbranched PIL, which contains tetrachloroferrate (FeCl_4^-) anions. The hyperbranched PIL has a degree of branching $\text{DB} = 50\%$ and shows a T_g at 37°C, the corresponding commercial Butylmethylimidazoliumtetrachloroferrate [BMIM] $[\text{FeCl}_4^-]$ IL has a $T_g = -86^\circ\text{C}$. Glassy dynamics in PIL/IL solutions of different concentrations is studied rheologically and discussed. PILs solutions of a certain concentrations reveal a peculiar rheological behavior, which deviates from the one expected for molecular glass-