Influence of the Molar Mass Distribution on the Elongational Behaviour of Polymer Solutions in Capillary Breakup

J. P. Plog, W.-M. Kulicke*, C. Clasen

Institute for Technical and Macromoleculare Chemistry,
University of Hamburg, Bundesstr. 45, 20146 Hamburg, Germany

*Email: kulicke@chemie.uni-hamburg.de

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Abstract:
Commercially available, blended methylhydroxyethyl celluloses with similar weight-average molar masses but varying molar mass distributions were characterized by different techniques like steady shear flow and uniaxial elongation in capillary breakup experiments. The determined relaxation times τ were then correlated with the absolute molar mass distribution acquired via SEC/MALLS/DRI (combined methods of size-exclusion-chromatography, multi angle laser light scattering and differential refractometer). In order to describe the longest relaxation time of the polymers in uniaxial elongation via integral mean values of the molar mass distribution, defined blends of polystyrene standards with varying molar mass distributions were characterized. The obtained data was scaled via different moments of the molecular weight distribution and could be correlated with the results obtained for the methylhydroxyethyl celluloses.

Zusammenfassung:
Kommerziell erhältliche Methylhydroxyethylzelluloseblends mit ähnlichem gewichtsgemittelten Molekulargewicht aber unterschiedlicher Molekulargewichtsverteilung wurden mittels verschiedener Methoden wie stationäres Scherfliessen und uniaxialer Dehnung in Kapillaraufbruchexperimenten charakterisiert. Die ermittelte Relaxationszeit t wurde dann mit der absoluten Molekulargewichtsverteilung in Beziehung gesetzt, die durch SEC/MALLS/DRI (Kombination von Grössenausschluss-Chromatographie, Vielwinkellaserlichtstreuung und differentielle Refraktometrie) gemessen wurde. Um die längste Relaxationszeit der Polymere in uniaxialer Dehnung durch integrale Mittelwerte der Molekulargewichtsverteilung zu bestimmen, wurden defnierte Polystyrolblendstandards mit unterschiedlicher Molekulargewichtsverteilung charakterisiert. Die erhaltenen Daten wurden mit verschiedenen Momenten der Molekulargewichtsverteilung skaliert und konnten in Beziehung gesetzt werden mit den Ergebnissen für Methylhydroxyethylzellulose.

Résumé:
Nous avons caractérisé des mélanges commerciaux de méthyle-hydroxyéthyle de cellulose possédant des poids moléculaires moyens identiques, mais dont les distributions en poids sont différentes, au moyen de différentes techniques comme l'écoulement en cisaillement constant et l'extension uniaxe obtenue à l'aide d'un capillaire à rupture de filament. Les temps de relaxation mesurés ont été corrélés avec les distributions en masses molaires obtenues par SEC/MALLS/DRI (méthodes combinées de chromatographie à exclusion de tailles, diffusion de lumière à angles multiples et réfractomètre différentiel). Dans le but de décrire les temps de relaxation les plus longs des polymères en élongation uniaxe à partir des valeurs moyennes intégrales de la distribution en poids molaires, des mélanges définis de polystyrènes standards possédant des distributions en poids molaires variées ont été caractérisés. Les données obtenues ont été quantifiées au moyen des différents moments de la distribution en poids moléculaires, et ont pu être corrélés avec les résultats obtenus pour les méthyle-hydroxyéthyles de cellulose.

Key words: Elongational rheology, polystyrene blends, MHEC, MWD

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sion that correlates directly with specific moments of the molecular weight distribution. This determined scaling law (see Eq. 7) can be directly assigned to blends of commercially available, blended celluloseethers to obtain information on the MWD of these polymers. In comparison to small amplitude oscillatory shear this method is faster and more sensitive.

The results could then be correlated with the absolute molar mass distributions obtained via means of SEC/ MALLS/ DRI (see Fig. 8). It could be shown in this paper that uniaxial elongation in CaBER like experiments is a more sensitive method for the detection of the molecular weight distribution then steady shear flow for samples with similar weight-average molar mass and therefore similar flow properties in steady shear flow experiments (see Figs. 1 and 3). Uniaxial elongation in CaBER like experiments also allows for a sensitive detection of non molecularly dispersed fractions of the investigated native cellulose derivative (see Figs. 2 and 9) and can thus predict the processability of these polymers in elongational flows.

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