

# DETERMINATION OF MOLECULAR WEIGHT DISTRIBUTIONS FROM RHEOLOGICAL DATA: AN APPLICATION TO POLYSTYRENE, POLYMETHYLMETHACRYLATE AND ISOTACTIC POLYPROPYLENE

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## ABSTRACT

Based on a recently introduced generalized mixing rule, which contains the results of the reptation and double reptation model as special cases, it is possible to determine the molecular weight distribution (MWD) from rheological data. By evaluating data from bimodal PS-mixtures Maier et al. (1998) have shown how the MWD can be estimated from the relaxation shear modulus,  $G(t)$ , using an inversion method. Thimm et al. (1999) derived an analytical relation between the relaxation time spectrum and the MWD, which is able to reproduce the result of Maier et al. (1998) with less computational effort. In this article we compare both methods by evaluating data from three different series of polymer mixtures: Polystyrene (PS), Polymethylmethacrylate (PMMA) and isotactic Polypropylene (iPP). We compare the MWD obtained from rheological data with results from size exclusion chromatography (SEC) and discuss differences.

## KURZFASSUNG

Ausgehend von einer kürzlich eingeführten, verallgemeinerten Mischungsregel, die die Ergebnisse des Reptations- und Doppelten Reptationsmodells als Spezialfälle enthält, ist es möglich, die Molekulargewichtsverteilung zu bestimmen. Maier et al. (1998) haben durch Auswertung der Daten von bimodalen PS-Mischungen gezeigt, wie die Molekulargewichtsverteilung mittels eines Rechenverfahrens, das auf Regularisierung beruht, aus dem Relaxationsschermodul  $G(t)$  geschätzt werden kann. Thimm et al. (1999) haben eine analytische Beziehung zwischen dem Relaxationszeitspektrum und der Molekulargewichtsverteilung hergeleitet, die in der Lage ist, die Ergebnisse von Maier et al. (1998) mit weniger Rechenaufwand zu reproduzieren. In diesem Artikel vergleichen wir beide Methoden, indem wir Daten von drei unterschiedlichen Mischungsreihen von Polymermischungen analysieren: Polystyrol, Polymethylmethacrylat und isotaktisches Polypropylen. Wir vergleichen die Molekulargewichtsverteilungen, die aus den rheologischen Daten bestimmt werden, mit Ergebnissen einer SEC-Analyse und diskutieren Unterschiede.

## RÉSUMÉ

A partir d'une loi de mélange généralisée récemment introduite, et qui contient les résultats des modèles de reptation et de reptation double comme cas particulier, il est possible de déterminer, avec des données rhéologiques, la distribution en poids moléculaire (DPM). Maier et al. (1998) ont étudié un mélange bimodal de polystyrène (PS) et ont montré comment la DPM de ce mélange pouvait être calculée à partir de la relaxation du module de cisaillement  $G(t)$  et en utilisant une méthode d'inversion. Thimm et al. (1999) ont développé une relation analytique entre le spectre des temps de relaxation et la DPM qui est capable de reproduire les résultats de Maier et al. (1998) tout en économisant du temps de calcul. Dans cet article, nous comparons ces deux méthodes en les appliquant à l'étude de 3 séries différentes de mélanges de polymères: polystyrène (PS), polyméthylméthacrylate (PMMA) et polypropylène isotactique (iPP). Nous comparons les DPM obtenues à partir des données rhéologiques avec les DPM obtenues au moyen de la chromatographie par exclusion de taille (Size Exclusion Chromatography, SEC) et nous discutons les différences observées.

## KEY-WORDS:

Double reptation, determination of molecular weight distribution, mixing rule, ill-posed inverse problems in rheology

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Figure 6:  
Comparison of SEC (solid)  
with inversion method  
(error bars): Single exponen-  
tial kernel  $\beta=3.2$  (iPP 70:30).

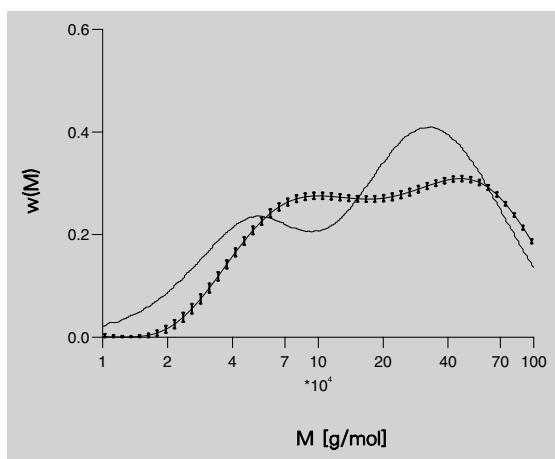


Figure 7:  
Comparison of SEC (solid)  
with inversion method  
(error bars), Single exponen-  
tial kernel ( $\beta=3.2$ ) for  
iPP 10:90.

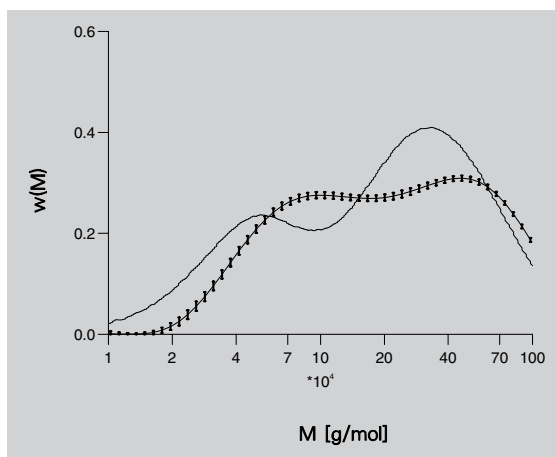


Figure 8:  
Evaluation of PMMA with  
single exponential kernel  
and  $\beta=3.3$ . The results of  
the inversion method are  
indicated by error bars. The  
solid curve represents the  
SEC result (30:70).

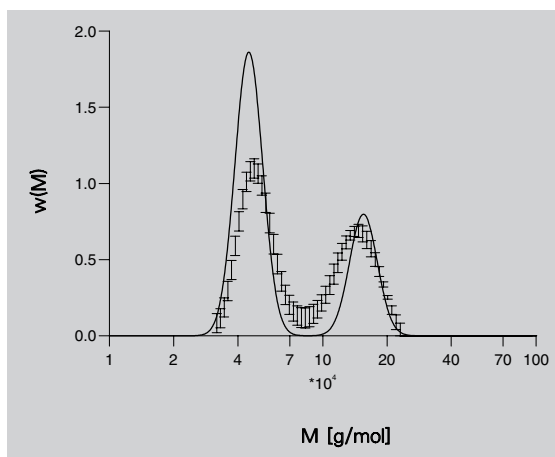
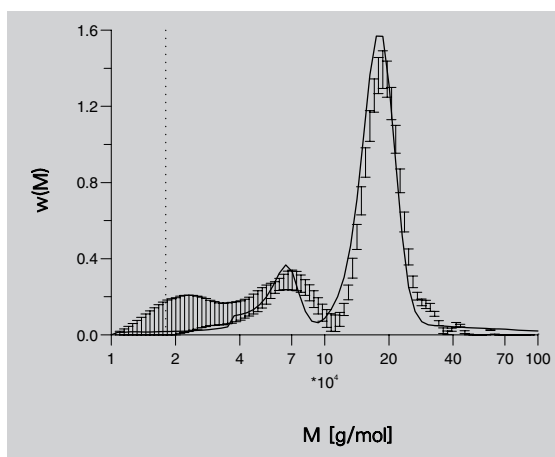


Figure 9:  
Evaluation of PS with single  
exponential kernel and  
 $\beta=3.84$ . The results of the  
inversion method are  
indicated by error bars.  
The solid curve represents  
the SEC result (80:20). The  
entanglement molecular  
weight,  $M_e \approx 18.000$ g/mol,  
is indicated by a dotted line.  
Below  $M_e$  the model is not  
valid and results therefore  
cannot be trusted.



To examine the results obtained by SEC from a statistical point of view is a task for future examinations. Especially the use of a calibration by PS in Toluene for different polymers should be difficult to quantify. We propose to compare the rheological determination and the SEC with experimental methods which are able to determine the molecular weight averages in a different way (e.g. static or dynamic light scattering experiments). We expect that the rheological evaluation should give better results for higher molecular weight. So far, there is no final decision possible, which of the two evaluation methods gives better results from a general point of view.

## 7 CONCLUSIONS

We have shown in this article that rheological data evaluation is a tool, which can be used to determine the molecular weight distributions in an accurate way. Especially for polymers which are not solvable, this method should prove helpful. Since the real, microscopical MWD for such materials cannot be checked in different ways, we propose to use a rheological evaluation as described above as standard for MWD determination of such materials.

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We thank A. Eckstein and K. Fuchs for measuring the rheological data on which this evaluation is based. W.B. Thimm gratefully acknowledges the support of the Deutsche Forschungsgemeinschaft by the "Graduiertenkolleg für Strukturbildung in makromolekularen Systemen".

## BIOGRAPHY

Wolfgang Thimm was born 1972 in Bonn, achieved his diploma in physics at the University of Karlsruhe (T.H.) with a mean in theoretical solid state physics, before changing for his PhD thesis in the field of rheology to the group of Prof. Dr. Honerkamp at the Materials Research Center (FMF).  
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Dr. Dieter Maier born 1965 in Freiburg was awarded the prize of the German Rheological Society in 1999. He achieved his PhD in physics in the group of Prof. Dr. Honerkamp at the FMF in 1996. He was from 1996-1998 head of the group of scientific data processing of the FMF. Since 1998 he researches in a company dealing with image processing.

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Prof. Dr. Josef Honerkamp was born 1941 in Laer/Osnabrück (PhD 1967 Hamburg, hab. 1972 Bonn, H3-Prof. 72-74 Bonn, oProf. 1974 Freiburg). He was one of the founders of the FMF. He has become well-known in the field of rheology for the statistical methods to solve ill-posed inverse problems, he developed with his collaborators.

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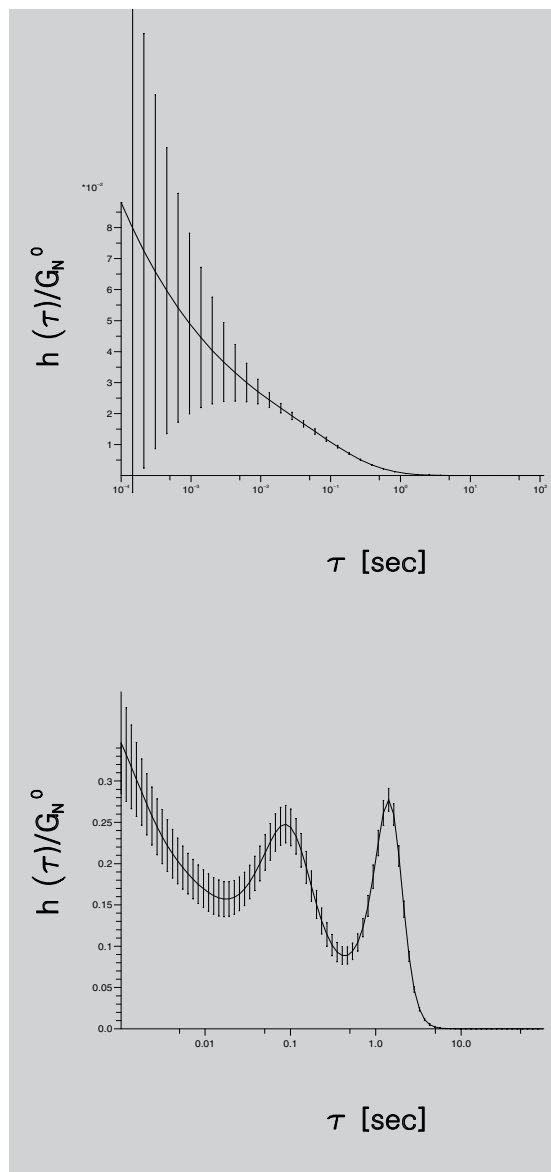


Figure 10:  
The terminal relaxation peak in the relaxation time spectrum is smoothed out for iPP. The spectrum for 70:30 is shown (upper picture). There is a sharp terminal relaxation peak in the spectrum of Polystyrene 80:20 (lower picture).

