

Prediction of Molecular Weight Distribution of Cellulose by Using the Rheological Method

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ABSTRACT: In this article, a rheological method that can predict the molecular weight distribution (MWD) of polymer was introduced. Using this method, the MWDs of four cellulose samples were compared from rheological data of the cellulose / *N*-methyl morpholine *N*-oxide (NMMO) / H₂O solutions. The MWDs of cellulose also were determined by gel permeation chromatography (GPC) calibrated with narrow distribution polystyrene standards, using 0.5% lithium chloride (LiCl) in *N,N*-dimethylacetamide (DMAc) as the eluent. Comparison of the results from rheology and

GPC showed that the MW and MWD of cellulose could be roughly inferred from their rheological data. Although the differential MWD obtained from the rheological method was bell shaped and can not reflect the fine characteristics of cellulose as GPC, it may be feasible to compare the MWDs of cellulose by using the rheological method. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 598–603, 2004

Key words: cellulose; molecular weight distribution; rheology; gel permeation chromatography

INTRODUCTION

The viscose rayon process is declining in commerce because of pollution problems and the complexity of this process. Much work has been performed to develop a nontoxic and easy dissolution system of cellulose. During the past 30 y, a considerable research effort has been made to find new direct solvents for cellulose. Among them, *N*-methyl morpholine *N*-oxide (NMMO) stands out as being the most promising solvent.¹ The lyocell process consists of cellulose regeneration from cellulose / NMMO monohydrate solution by ejecting from a spinneret whereby the solution is drawn through an air gap and coagulated in water or an aqueous NMMO solution. Comparisons of lyocell with viscose rayon show that the lyocell fiber has excellent properties and the process is simple and environmentally friendly.

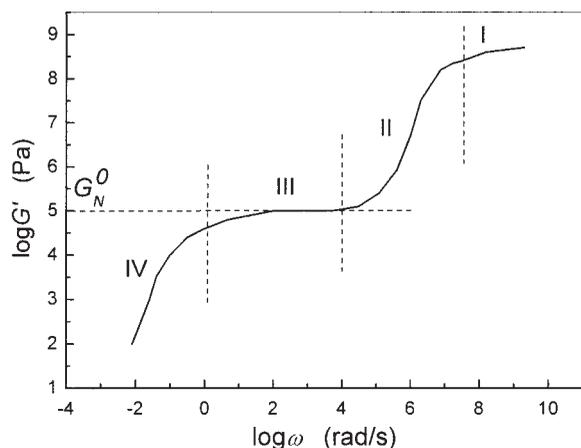
The molecular weight (MW) and the MW distribution (MWD) of cellulose, which is a raw material of lyocell fiber, are very important parameters. Different kinds of cellulose or the same kind of cellulose from different sources may have different MWDs and different spin abilities that would result in different mechanical properties of resulted lyocell fibers. In general, the MWD is determined by gel permeation chromatography (GPC). A commonly used solvent for

GPC characterizations of cellulose is lithium chloride / *N,N*-dimethylacetamide (LiCl / DMAc).² However, it is difficult to dissolve directly cellulose in LiCl / DMAc. Cellulose must be activated before its time-consuming dissolution process, which may be sometimes 5 days long.³

Recently, a new method for determining the MWD of polymer from its dynamic rheological property has been developed.^{4–11} In 1985, Wu¹² made MWD calculations from storage modulus G' and stress relaxation modulus $G(t)$ using approximations derived from the Doi-Edwards description of chain dynamics. Wu's method seemed to predict accurately the MWD of polymer with narrow distribution. However, often, it leads to a distorted shape of the MWD for the sample with bimodal distributions. Therefore, Tuminello⁶ developed a theory based on a series of assumptions. According to his method, the MWD can be characterized well from rheological data.

Gu¹³ thought Tuminello's theory was suitable for the case of the concentrated cellulose / NMMO solution. He investigated the relative widths of MWDs of several kinds of cellulose from the rheological data by using Tuminello's method. However, Gu's results, determined from the rheological method, were not compared with the MWDs obtained from GPC. In this study, we predict the MWDs of four cellulose samples from the rheological data of cellulose / NMMO solutions and make a comparison with the results from GPC to substantiate the feasibility of the rheological method.

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I- Glassy state, II-Transition, III-Plateau, IV-Terminal zone

Figure 1 G' master curve for a typical linear polymer.

Theory^{6,14}

The behavior of storage modulus (G') vs. frequency (ω) for a typical linear polymer is illustrated in Figure 1.

Two relaxation processes are obvious: the glass to rubber transition and the terminal zone relaxation. The glass transition is a consequence of submolecular units moving in the same time frame as the measurement frequency (ω). At high frequencies the apparatus sees the material as a glass because the submolecular units can not move as rapidly as ω . However, at lower frequencies the material appears less rigid as the movement of the submolecular unit is in the same time frame as ω . At much lower frequencies, a plateau region is observed because of the presence of the transient entanglement network. The plateau modulus (G_N^0) can be defined as the maximum of G' when the chains entirely disentangle in the high-frequency limit of the terminal zone. As the frequency is decreased, G' decreases monotonically, and this initial decrease reflects the disentangling of the chains with the lowest MW. As the frequency is decreased further, chains with progressively higher MW are able to disentangle on this timescale until all chains are disentangled. At the lowest frequencies, the disentanglement of this network results in terminal zone relaxation. The length of the plateau, plus the breadth and shape of terminal zone relaxation, are strong functions of the MWD. Therefore, all the information about MW and MWD is in the plateau and terminal zones. In addition, quantitative scaling to MW can be accomplished using the well-known relationships¹⁵:

$$1/\omega = K (MW)^{3.4} \quad (1)$$

where ω is frequency and K is a constant.

To determine a quantitative estimate of MWD, how to relate the concentration of each MW component with the $G'(\omega)$ curve is a problem. Wu¹² and Menefee assumed the cumulative MWD (CMWD) was approximately proportional to G'/G_N^0 vs. ω . This assumption leads to a distorted shape of the MWD, for a sample, with bimodal distribution. Tuminello⁶ developed a theory and assumed

1. The unrelaxed chains at a particular frequency are "diluted" by the relaxed chains, which are acting like a nonentangling solvent.
2. Each monodisperse MW fraction, in which MW is M_i , has a single relaxation frequency (ω_i) below which it makes no contribution to the modulus. Here, the polydisperse nature of the relaxation time distribution is partially ignored for a monodisperse polymer.

Then, an approach is derived from the theoretical and experimental analysis of concentrated polymer solutions, which predicts

$$C^2 = G_N^{00}/G_N^0 \quad (2)$$

where C is volume fraction of polymer and G_N^{00} , and G_N^0 are diluted and undiluted plateau moduli, respectively.

A direct analogy then can be made between G_N^{00} , the plateau modulus of the diluted polymer, and $G'(\omega_i)$, the elastic modulus at frequency ω_i . Because G_N^{00} is a plateau modulus, it represents the contribution of all unrelaxed chains to the elastic modulus of the "terminal zone." Analogously, all chains with MW $\geq M_i$ (unrelaxed chains) would contribute to $G'(\omega_i)$ as follows:

$$W_u = [G'(\omega_i)/G_N^0]^{0.5} \quad (3)$$

where W_u is the weight fraction of unrelaxed chains and $[G'(\omega_i)/G_N^0]^{0.5}$ is defined also as the square root of the reduced modulus elsewhere.^{14,16}

Therefore, the contribution of the unrelaxed chains (MW $> M_i$) to the storage modulus is proportional to the square of the weight fraction of unrelaxed chains.

We assume the density is not a function of the MW of polymer; therefore,

$$W_u = C \quad (4)$$

Because the cumulative MW (CMW) is defined as the cumulative weight fraction of chains up to a specified MW, then

$$CMW = 1 - W_u = 1 - [G'(\omega_i)/G_N^0]^{0.5} \quad (5)$$

TABLE I
Codes and Characteristics of Cellulose Samples

| Cellulose samples | $[\eta]$ (L/g) | \overline{DP}_v^a | Pulp type | Hemicellulose/cellulose content | Source |
|-------------------|----------------|---------------------|-------------------------------------|---------------------------------|--------|
| 1 | 0.346 | 691 | Cotton pulp | 0.015 | China |
| 2 | 0.412 | 823 | Cotton pulp for producing tire cord | 0.013 | China |
| 3 | 0.361 | 722 | Wood pulp | 0.088 | USA |
| 4 | 0.300 | 600 | Softwood kraft pulp | 0.153 | USA |

^a \overline{DP}_v is the degree of polymerization determined by viscosimetry.

The relation between the viscosimetric values and \overline{DP}_v is $[\eta] = K_m \times \overline{DP}_v$ and $K_m = 5 \times 10^4$

The cumulative MWD (CMWD) can be obtained by plotting $CMW = 1 - [G'(\omega_i)/G_N^0]^{0.5}$ from eq. (5) vs. $\log(MW)$. Because the coefficient K in the eq. (1) is a constant, the shape of CMW vs. $\log(1/\omega)$ is the same as the CMW vs. $\log(MW)$. Therefore, even though the value of K is unknown, the shape of CMWD also can be estimated by plotting CMW vs. $\log(1/\omega)$. Moreover, the shape of the differential MWD (DMWD) curve can be obtained by numerical differentiation of CMWD with respect to $\log(1/\omega)$.

EXPERIMENTAL

Rheological experiment

Materials

Aqueous NMMO from BASF (Ludwigshafen, Germany) had an initial water content of 50% (wt) as determined by refractometry. A calibration curve of the index of refraction of aqueous NMMO solution, as a function of water content, was established beforehand in our laboratory.

n-Propyl gallate was used as an antioxidant for stabilizing the \overline{DP} of cellulose during the dissolving process.

Four cellulose samples, obtained from different areas, were used in this study. The cuprammonium hydroxide solution method¹⁷ was used for determining the intrinsic viscosity ($[\eta]$) or \overline{DP}_v of cellulose. Table I gives the identifying code and description for each sample.

Preparation of cellulose / NMMO / H₂O solution

The mixture of cellulose pulp NMMO / H₂O, with a certain amount of water and a little additive, was put into a dissolving apparatus and then stirred continually under the temperature of 100°C by using an oil bath. Extra water in the cellulose / NMMO / H₂O system was distilled under vacuum. The mixture gradually turned into a brown clear homogeneous solution, and the solution with 9% (wt) cellulose in NMMO·H₂O could be obtained.¹⁸

Rheological measurements

The rheological measurements were made on the RS1 Rheometer (Thermo Haake, Karlsruhe, Germany) in frequency scanning mode, and a cone plate (Ti, 35 / 1°) was used. The dynamic rheological properties (storage modulus G' , loss modulus G'' , and complex dynamic shear viscosity η^*) were determined at different frequencies under a certain amplitude of strain. Frequency scanning was made from 0.25 ~ 628 rad / sec and the measurements were performed at 75, 90, and 105°C, respectively. The data analysis was performed using RheoSoft software (Thermo Haake, Karlsruhe, Germany).

GPC CHARACTERIZATION

Materials

N,N-dimethylacetamide [DMAc; high-performance liquid chromatography (HPLC) grade] was obtained from Fluka (Buchs, Switzerland). Lithium chloride (LiCl, analytical reagent grade) was oven dried and then stored in a desiccator. Polystyrene standards were purchased from Waters (Milford, MA, USA) with nominal MWs of 1.3×10^4 , 6.55×10^4 , 1.85×10^5 , 6.68×10^5 , 1.01×10^6 , and 2.54×10^6 , respectively.

Dissolution of cellulose in LiCl / DMAc¹⁹

The cellulose samples were dissolved in LiCl / DMAc in the following way: 10 mg of sample was weighed into a 10-mL centrifuge tube into which 5 mL of distilled water was added and left overnight to allow the fibers to be swollen thoroughly. The samples were centrifuged at 4000 rpm for 15 min, after which the supernatant was decanted and 5 mL of DMAc was added. After 15 min of heavy stirring, the centrifugation and decantation were repeated. The whole solvent exchange procedure was repeated five times. Finally, 1.25 mL of 8%(w / vol) LiCl in DMAc was added, stirred for 60 sec and left for approximately 48 h to dissolve completely, with occasional mild stirring. The solutions then were diluted to 20 mL with

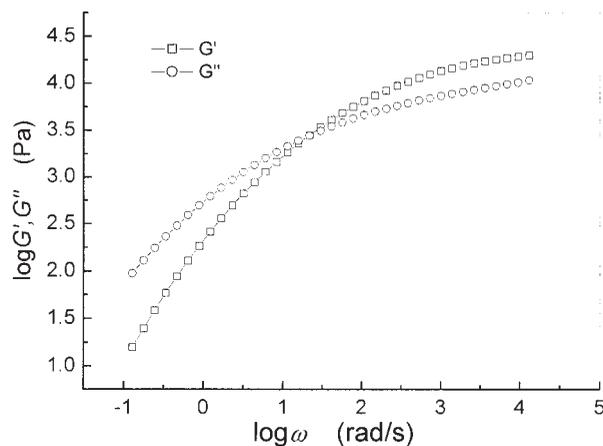


Figure 2 Dynamic moduli master curve for sample 1.

DMAc to give a final concentration of 0.5 mg / mL of cellulose in 0.5% LiCl in DMAc. Then, the solution was filtered through a 0.45- μm Acrodisc (Gelman Sciences, Ltd., Ann Arbor, MI, USA) membrane filter.

GPC analysis

The MWDs for the four cellulose pulps were determined by GPC in a liquid chromatography (Waters 1525) with a refractive index detector (Waters 2410). The mobile phase of 0.5% LiCl / DMAc (wt / vol) was pumped into the system at a flow rate of 1 mL / min. Columns were styragel 10^4 and 10^5 (Waters) preceded by a guard column. The system was operated at 50°C controlled by a column heater (Waters column temperature system). Injection volume was 200 μL on the basis of injection of 100 μL per column. Run time was 45 min. A linear calibration curve was constructed with polystyrene standards (MW = 2.54M–13 K) dissolved directly in 0.5% LiCl / DMAc. Data acquisition and MWD calculations were performed using Breeze software (Waters, Milford, MA, USA).

RESULTS AND DISCUSSION

MWD of cellulose from rheological data

It is known that the melting point of NMMO monohydrate is about 74°C, below which NMMO monohydrate will crystallize.²⁰ On the other hand, the solvent might decompose at a testing temperature higher than 180°C. Therefore, the temperature range for rheological measurements is limited. To avoid the crystallization and decomposition of NMMO monohydrate and to ensure that the samples are tested in their linear viscoelastic regions, the testing temperatures are set at 75, 90, and 105°C, respectively. The curves at 90°C are chosen as the reference for all solutions prepared from different pulp samples. By using the time-temperature

equivalence principle, the curves obtained at other temperatures can be superimposed on the reference curves, and the resultant master curves can be obtained at the reference temperature. Therefore, the experimental range will be enlarged considerably. The resulted master curve for G' and G'' at the reference temperature of 90°C for sample 1 is shown in Figure 2. According to the dynamic rheological master curve and eq. (4), the square root of the reduced modulus $[G'(\omega_i)/G_N^0]^{0.5}$ can be calculated. There are some functions for fitting the data of square root of the reduced modulus and $\log \omega$. Tuminello⁶ described one fitting function as follows:

$$[G'(\omega_i)/G_N^0]^{0.5} = \sum_i A_i [1 + \tanh(B_i(X + C_i))]/2 \quad (6)$$

where $X = \log \omega$. The MWD calculated from this fitting function often results in bimodal distributions for samples with a narrow distribution or a skewed and asymmetrical distribution appearing in the low MW region. Letton⁷ proposed that the cubic spline can be used to fit the data and a bell-shaped MWD can be obtained. For this study, Letton's method was chosen and the fitted curve of square root of the reduced modulus vs. $\log \omega$ for sample 1 is illustrated in Figure 3. The calculated cumulative and differential curves for sample 1 are shown in Figures 4 and 5.

The abscissa can be converted from $\log(1/\omega)$ in Figures 4 and 5 into $\log(\text{MW})$ by using eq. (1). However, it is impossible for us to get the exact value of the constant K because of the lack of a monodisperse cellulose.¹³ Because $\log(1/\omega)$ is proportional to $\log(\text{MW})$, the region of high value of $\log(1/\omega)$, i.e., low-frequency region or the right side of the curves in Figures 4 and 5, corresponds to the high MW composition of the system and vice versa. The MWDs for all

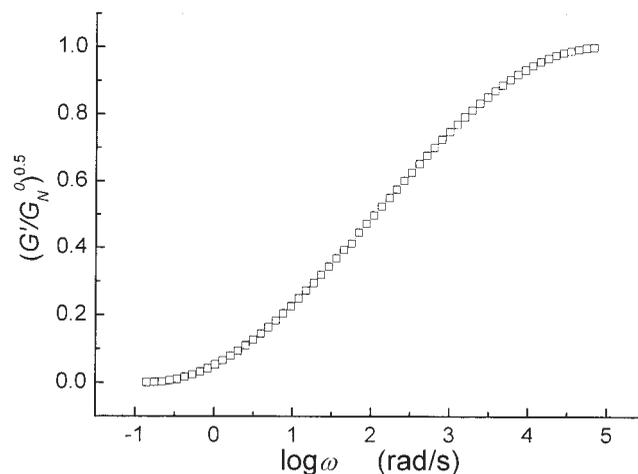


Figure 3 Square root of the reduced modulus $(G'/G_N^0)^{0.5}$ vs. $\log \omega$ for sample 1.

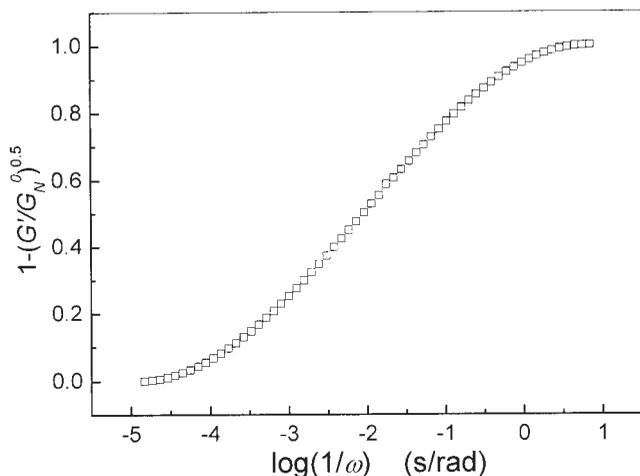


Figure 4 Cumulative relative MWD for sample 1.

four samples are illustrated in Figure 6, and the peak value and the width of the $\log(1/\omega)$ are listed in Table II. It can be found, from Figure 6 and Table II, that the narrowest MWD appears in sample 2, next is sample 1, and then sample 3, and the MWD of sample 4 is the broadest. In addition, because the MW of cellulose is proportional to $\log(1/\omega)$, it can be concluded that the order of relative MW is sample 2 > sample 3 > sample 1 > sample 4. This corresponds with the results determined from the cuprammonium hydroxide solution.

MWD of cellulose from GPC

The solubility of the samples in LiCl / DMAc is different. Cotton pulps can be dissolved completely in LiCl / DMAc. However, wood pulps, especially softwood kraft pulps, are not completely soluble in LiCl / DMAc in contrast to cotton pulps,³ and the small quantity of undissolved fraction contains mannan, lig-

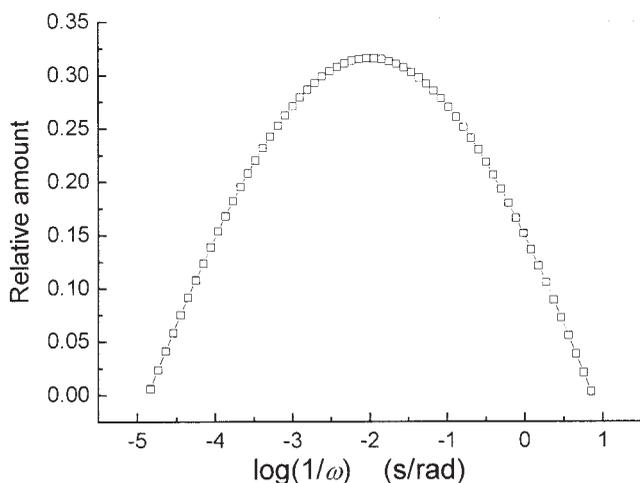


Figure 5 Differential relative MWD for sample 1.

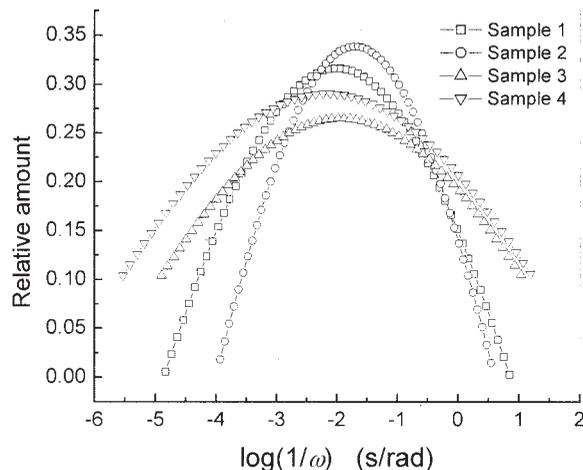


Figure 6 Differential relative MWDs for four samples from the rheological method.

nin, and nitrogen.²¹ Nevertheless, the solvent also has been used for GPC characterizations of softwood kraft pulp.^{22,23}

Because of the lack of commercial cellulose standards with narrow distribution, polystyrene standards were used for calibration. The differential MWDs of the four cellulose samples are illustrated in Figure 7.

The results, obtained from the rheological method and GPC, are listed in Table II. It can be seen that the results determined by GPC, i.e., the MWDs of samples 3 and 4 are broader than samples 1 and 2, sample 2 is the narrowest, and sample 4 is the broadest are consistent with the results from the rheological method. This is reasonable, from consideration of the sources of the samples: it is noted in Table I that samples 3 and 4 are wood pulps, and samples 1 and 2 are cotton pulps. In general, the MWD of wood pulp is broader than cotton pulp. Sample 2 has been processed beforehand for producing tire cord; therefore, it has the narrowest MWD. Moreover, more information also can be obtained from the results of GPC. For example, sample 1 has an asymmetrical distribution, and the moderate and low MW components are the major composition. The whole MWD resembles a blended peak composed by moderate and the high MW components. Sample 2 shows a symmetrical distribution. In addition, the MWDs of samples 3 and 4 are skewed and asymmetrical. Distinct distortions in the low MW region of the MWD for both samples indicate the presence of a high hemicellulose content as seen in Table I.²³ However, such useful information can not be reflected from the MWD curves obtained from the rheological method directly. It shows that further modification still is needed for the rheological method to be used.

In this study, the obtained data from GPC are relative values because of the use of polystyrene stan-

TABLE II
Comparison of the Results Obtained from the Rheological Method and GPC

| Cellulose samples | Rheological method | | GPC | | | | |
|-------------------|--------------------------------|--------|------------------------------------|------------------------------------|---------------------------|---------------------------------------|-------------------|
| | Peak value of $\log(1/\omega)$ | Width | \overline{M}_n ($\times 10^4$) | \overline{M}_w ($\times 10^4$) | M_p^a ($\times 10^4$) | $D = \overline{M}_w / \overline{M}_n$ | \overline{DP}_v |
| 1 | -1.9966 | 6.9654 | 30.97 | 71.70 | 65.84 | 2.32 | 691 |
| 2 | -1.6959 | 5.4648 | 36.78 | 76.79 | 74.99 | 2.09 | 823 |
| 3 | -1.9258 | 7.8830 | 17.56 | 75.97 | 73.28 | 4.33 | 722 |
| 4 | -2.1597 | 8.6622 | 15.26 | 76.48 | 63.50 | 5.01 | 600 |

^a Molecular weight of peak.

dards; nevertheless, the GPC method is an effective way to compare the samples and observe the differences of MW and MWD of cellulose. However, the relative data can not reflect the real MW characteristics of cellulose; so, the data from GPC can not be used to calibrate the results from the rheological method. Even so, the comparison of results, from the rheological method and GPC, shows that it may be feasible to compare the MWD of cellulose by using the rheological method.

CONCLUSION

In this study, we compared two methods for measuring MW and MWD of cellulose, i.e., GPC and a rheological method. The MWDs of four cellulose samples were predicted from the rheological behavior of cellulose / NMMO / H₂O solutions and compared with MWDs characterized by GPC. The results show that the MWs and the MWDs of cellulose can be roughly inferred from their rheological data. However, the

MWD predicted from the rheological method can not reflect finer characteristics of MWD of cellulose as does GPC. In spite of that, it may be feasible and convenient to compare the MWDs of cellulose by using a rheological method.

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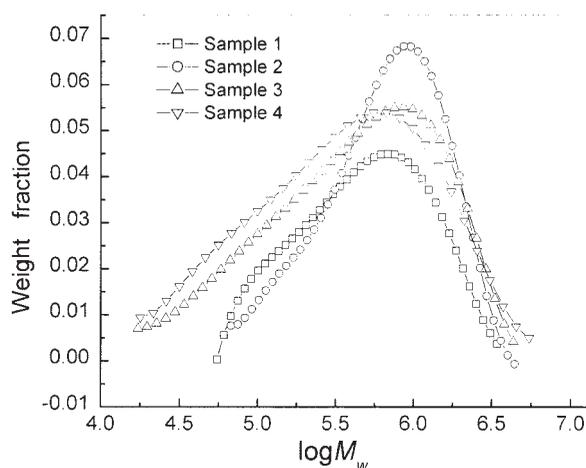


Figure 7 Differential MWDs for four samples by GPC.