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Dec. 16-18, 2000, Kunming, China

Chen Fangeng and Jiang Huanfeng, eds

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DETERMINATION OF SOLVATION NUMBER OF NITROCELLULOSE IN THF BY QUANTITATIVE SEC

Rongshi Cheng, Yunjun Luo and Xiaohu Yan

College of Chemistry & Chemical Engineering,
Nanjing University, Nanjing 210093, CHINA
College of Material Science, South China University
of Technology, Guangzhou 510640, CHINA
E-mail: rscheng@scut.edu.cn

ABSTRACT

A quantitative method for the determination of the solvation number of macromolecule in solution is proposed. The method consists in measuring the specific refractive index increment (dn/dc) or the refractive index detector response constants of a given polymer solution with varying thermal histories. This method is applied to nitrocellulose solution in tetrahydofuran. The solvation number of the structural repeating unit of nitrocellulose equals fourteen, corresponding to 4 solvated solvent molecules are associating with each NO_2 group and other 2 molecules are associating with the two ether linkages.

INTRODUCTION

Since Berlin[1] introduced the cyclic freezing and thawing process to study the effect of cryogenic treatment on dilute polymer solutions, all of the later investigators claimed that long chain macromolecules will undergo degradation by freezing the solvent. This conclusion was reached from the measured viscometric[2-4] and size exclusion chromatographic (SEC)[5-9] data.

However, recent investigation [10] on this problem showed that the concept of cryogenic degradation is not true. The decrease of intrinsic viscosity and the increase of the SEC retention volume are actually caused by conformational change of the solvated macromolecules upon freezing due to coil collapsing and forming intrachian cohesional entanglements [10-13]. It is reasonable to imagine that the degree of solvation of a compact globule produced by intramolecular physical cross-linkages should also varies besides its conformational change. In the present work we proposed a method to determine the solvation number of nitrocellulose in tetrahydrofurane in the course of cyclic freezing-thawing treatments by adapting quantitative size exclusion chromatographic technique to measure the specific refractive index increments (dn/dc) change [14,15] which is sensitive to the degree of solvation of polymer in solution [16, 17].

EXPERIMENTAL

Materials

The nitrocellulose sample used in the present investigation is prepared and supplied by the Nanjing University of Science and Technology with nitrogen content of 13.12 %. A sample solution in tetrahydrofuran with $C = 1.996 \times 10^{-3}$ g/ml was prepared at 15 °C. by weighing both the sample and solution. A part of the solution was used to perform the SEC measurements and the other part was subjected to cyclic freezing-thawing treatments. The freezing-thawing process was carried out by immersion the solution vessel into liquid nitrogen until the whole solution solidified and then taken the vessel out off liquid nitrogen for thawing its content at room temperature. After 200 times of cyclic treatments, the thawed frozen solution was subjected to perform SEC measurement again. Afterwards immerse the remaining thawed frozen solution into a 65℃ water bath for 3 hours and then measure SEC profiles of the heated solution again.

SEC Measurements

A Waters-244 equipment with a Waters-401 differential refractive index detector was used for SEC measurements at 15°C. Tetrahydrofuran was used as eluent. The digitized SEC chromatograms were analyzed as described in the following section.

THEORETICAL

In this section, the theoretical background for measuring the solvation number of macromolecules in solution is summarized first.

Basic Concepts

1. The solvated solvents are firmly attached

to the polymer chain segments by certain attractive solvent-segment interactions and the solvated polymer chain moves as a whole in solution.

2. All the observable polymer solution properties are those of the solvated polymer chains, not the properties of the hypothetical "naked" chain without solvated solvents on it.

3. In calculating the polymer solution properties it is desirable to regard the solvated solvents as a constituents of the effective polymer chain.

Specific Refractive Index Increment

By the additive rule, the observed specific refractive index increment of a polymer solution

$$(dn/dc)_{obs} = w_p\,(dn/dc\,)_p + (1 - w_p)\,(\,dn/dc)_s \tag{1}$$

where w_p is the weight fraction of the polymer segments in the solvated chain , $(dn/dc)_p$ is the specific refractive index increment of the hypothetical i.e., non-solvated polymer chain and $(\,dn/dc)_s$ is the specific refractive index increment of the solvated solvent in the solution medium. If the medium is a single solvent, both the solvation and desolvation process do not change the composition and the refractive index of the medium, therefore

$$(dn/dc)_s = 0 \tag{2}$$

and

$$(dn/dc)_{obs} = w_p\,(dn/dc\,)_p \tag{3}$$

Since w_p and $(dn/dc\,)_p$ are usual not known exactly, the experimentally measured $(dn/dc)_{obs}$ is regarded as the specific refractive index increment of the polymer in literature which is smaller than $(dn/dc)_p$ due to w_p is always less than one. However, if the refractive index increment of nonsolvated polymer is accessible experimentally, the weight fraction of the solvated solvents on the solvated polymer chain may be calculated simply as

$$w_s = 1 - w_p = [\,(dn/dc)_p - (dn/dc)_{obs}]\,/\,(\,dn/dc\,)_p \tag{4}$$

For a fully extended and solvated polymer in solution, the weight fraction of solvated solvents on the chain may be expressed as

$$w_s = n\,x\,M_s\,/\,(\,n\,x\,M_s + x\,M_0\,) \tag{5}$$

where M_0 and M_s are the molar mass of monomer and solvent respectively, x is the degree of polymerization of polymer and n is the solvation number i.e. the number of solvent molecules joined with a structural repeating unit. Combining Eq. 4 and Eq. 5, we have

$$n = (\,M_0/M_s\,)\,[\,(dn/dc)_p - (dn/dc)_{obs}]\,/\,(\,dn/dc\,)_p \tag{6}$$

by which the solvation number n could be evaluated with known $(dn/dc)_{obs}$ for fully solvated and $(dn/dc)_p$ for non-solvated polymer.

In the case of partially solvated chain caused by intrachin segmental cohesion or short range crystallization, the observed dn/dc should higher than that of the fully solvated chain. By the similar reasoning, a quantitative estimation of these structural content is possible.

For partially solvated polymer solution

$$(dn/dc)_{obs} = w_{p\_partial}\,(dn/dc\,)_p \tag{3a}$$

where

$$w_{p\_partial} = x\,M_0\,/\,[\,x\,M_0 + n\,x'\,M_s\,] \tag{7}$$

in which x' denotes the number of solvated segments in a chain. As the weight fraction of non-solvated segments in a chain

$$W_{non} = 1 - x'\,/\,x \tag{8}$$

hence the weight fraction of polymer segments in a partially solvated polymer chain

$$w_{p\_partial} = M_0\,/\,[M_0 + n(\,1 - W_{non})\,M_s\,] \tag{7a}$$

and the observed (dn/dc) for such solution

$$(dn/dc)_{obs} = (\,dn/dc\,)_p\,M_0\,/\,[M_0 + n(\,1 - W_{non})\,M_s\,] \tag{9}$$

If both $(dn/dc)_p$ and solvation number n are known, we have

$$W_{non} = 1 - [M_0/n\,M_s][(dn/dc)_p - (dn/dc)_{obs}]\,/\,(dn/dc)_{obs} \tag{10}$$

Since the solvaton number could be estimated from the $(dn/dc)_F$ of fully solvated and non-solvated polymer solution by Eq. 6 as

$$n = [\,M_0\,/\,M_s\,]\,[\,(dn/dc)_p - (dn/dc)_F]\,/\,(\,dn/dc\,)_F \tag{6a}$$

Combining above two Equations, we have

$$W_{non} = [1 - (dn/dc)_F\,/(dn/dc)_{obs}]\,/\,[1 - (dn/dc)_F\,/(dn/dc)_P] \tag{11}$$

by which the relative portion of the non-solvated segments of the dissolved polymer in solution could be estimated with the aid of dn/dc measurements for fully solvated and non-solvated solutions.

Response Constant of SEC

The response height H monitored by differential refractive index detector of a size exclusion chromatograph (SEC) equipment is proportional to dn/dc of the solution. Since both the response heights and concentrations of eluted solution are functions of elution volume V

$H(V) = k\,(dn/dc)\,c(V)$ (12)

in which k is a instrument constant of the detector. Hence the total area of the chromatogram

$A=\bullet H(v)dV=k(dn/dc)\bullet c(V)\,dV = k\,(dn/dc)\,w_{inj}$ (13)

is proportional to the mass of of injected solute w_{inj},which in turn is a known quantity equals to the product of the concentration c_{inj} and volume V_{inj} of the injected sample solution

$w_{inj} =\bullet\, c(V)\,dV = c_{inj}\,V_{inj}$ (14)

Defining the response constant of the detector, K, as the product of instrument constant k and the refractive index increment of the sample solution, by Eq. 13 we have

$K = k\,(dn/dc) = A / w_{inj}$ (15)

which is simply the ratio of total area of chromatogram to the injected sample mass and readily determinable by injecting known amounts solute into the SEC column and measuring the total area of the chromatograms obtained. If a solute with known specific refractive index increment is chosen as standard sample,and its response constant

$K_s = (A / w_{inj})_s = k\,(dn/dc)_s$

(16)

is also detemined under the same experimental condition (gain factor, flow rate, recorder chart speed etc.) , since the instrument constant k of a given detector is unique regardless what solvent is used, combining Eq. 15 and Eq. 16 we have

$dn/dc = (K / K_s)\,(dn/dc)_s$

(17)

It indicates that using size exclusion chromatography with differential refractive index detection is an alternative way for measuring the specific refractive index increment of polymer solution.

RESULTS AND DISCUSSION

The digitized SEC chromatograms of nitrocellulose with varying injection amount for the original, thawed frozen and heated solution are shown in Fig. 1. It could be seen that though the absolute injection amounts are similar, the response sensitivities are quite different as indicated by the height and area of the chromatograms of these three solutions. The chromatograms of the thawed frozen solution have the largest heights and areas while the heated solutions have the smallest heights and areas. The dependence of the area of chromatograms of these solutions on the injected sample amounts is shown in Fig. 2. The detector response constants of these solutions deduced from the slopes of the straight lines passing through the origin point are listed in Table 1.

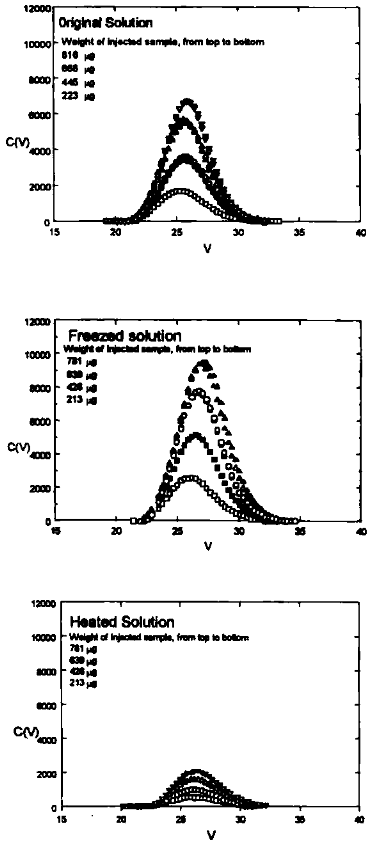

Fig. 1 The digitized SEC chromatograms of tetrahydrofuran solutions of nitrocellulose with varying thermal histories and injection amounts

Table 1 The response constants of nitrocellulose solutions in THF with varying thermal histories

Nitrocellulose Solutions	Response Constants
Original	1.20×10^5
Thawed Frozen	1.74×10^5
Heated	0.40×10^5

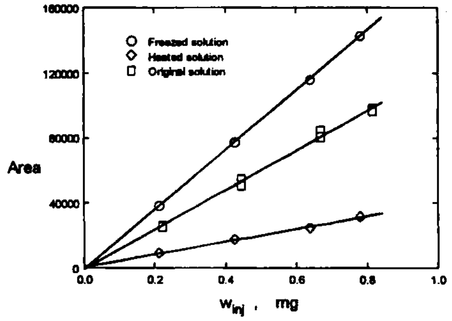

Fig. 2 Dependence of the area of the chromatograms of nitrocellulose solutions on the injected sample amounts

As discussed in the preceding section, the D.R.I. detector response constant is directly proportional to the specific refractive index increment of the injected solution. The thawed frozen solution has the highest while the heated solution has the least response constant. It is reasonable to assume that the nitrocellulose chains in these two solutions are existing in collapsed compact globule state and fully solvated coil state respectively. By inserting the corresponding response constants into Eq. 17 and then into Eq. 6 we have

$$n = \frac{M_0}{M_S} \cdot \frac{K_{frozen} - K_{heated}}{K_{heated}}$$

Using this equation with the molar masses of tetrahydrofuran and structural repeating unit M_0 =297.14 and M_s =72.09, we are able to calculate n, i.e. the solvation number of the structural repeating unit of nitrocellulose. It equals to 14. At first sight the Fig. '14' is rather large. However, considering a structural repeating unit of nitrocellulose consists of three huge nitro groups and two ether linkages, this Fig. is reasonable also. If assigning one and four solvent molecule(s) are associated with each ether linkage and nitro group respectively, the total number of the associating solvated solvent molecules per repeating unit is just 14.

The response constant as well as dn/dc of the original solution is situated between the two limiting values of that of the heated and frozen solutions. It suggests that the solution prepared at room temperature is partially solvated. Using Eq. 11 with the same reasoning, the relative portion of the non-solvated segments of the dissolved nitrocellulose in solution could be evaluated. In the present case we obtain **W_{non} = 0.87.**

The results presented above shows that the proposed method for measuring solvation number is successful for nitrocellulose solution.

CONCLUSION

Based on the results obtained, following conclusions are reached:

1 Nitrocellulose in tetrahydrofuran undergoes compact globule formation upon deep freezing. It ones again confirms the incorrectness of the concept of cryogenic degradation of polymer in solution.
2 (dn/dc) is sensitive to the state of solvation of macromolecules in solution. The observed dn/dc of the compact globule may be regarded as the dn/dc of the naked chain in solution without a solvated solvent dress.
3 By the proposed method, it is able to determine the solvation number of the structural repeating units of nitrocellulose in THF solution. It equals 14, corresponding to 4 solvent molecules are associating to each nitro- group and other 2 solvent molecules are associating to the ether linkages.

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A MODIFIED DFRC METHOD FOR LIGNIN STRUCTURAL ANALYSIS

Tsutomu Ikeda, John F. Kadla, Hou-min Chang and Hasan Jameel

Department of Wood and Paper Science
North Carolina State University,
Raleigh, NC, 27695,USA
E-mail: Hou-min_chang@ncsu.edu

ABSTRACT

A modified DFRC (Derivatization Followed by Reductive Cleavage) method has been developed to allow quantitative determination of monomeric products of three different structural origins in lignin: phenolic β-O-4, etherified α-O-4 and etherified β-O-4 structures. The modified DFRC method was used to study the effect of ball milling on the structure of lignin. While rotary ball milling for 7 days has little effect on lignin structure, vibratory ball milling for 48 hours may cause substantial structural changes including condensation. MWL may not be representative of the total lignin in wood.

INTRODUCTION

In the study of native lignin wood chemists have been faced with two challenges: the isolation of native lignin without incurring structural changes, and suitable methods for its structural characterization. Milled wood lignin (MWL) has traditionally been used for structural characterization of lignin in its native state.

The yield of the MWL obtained according to the original Björkman method was usually about 25% (1). It has been suggested that this isolated MWL originates from the middle lamella or at least that lignin from this morphological region is over-represented in the samples (2). On the other hand, Whiting and Goring reported that MWL originates mainly from the secondary wall (3). With strong milling and extension of milling time, MWL yield increases to about 50% (1). Such a lignin would be more representative of the total lignin in wood. However chemical modification of the lignin during milling might be severe. Milling is expected to cause chemical changes in the lignin. Björkman and Person, Chang et al have reported a slight increase in the carbonyl content (4,5), an increase in phenolic hydroxyl content and a decrease in molecular weight (5) as a result of vibratory ball-milling. There has not been a systematic study done on the extent of structural changes in lignin during milling.

A new lignin characterization method, the DFRC method, has been recently developed by Lu and Ralph (6,7,8). It includes two key steps (i) solubilization of lignin by bromination and acetylation with acethyl bromide and (ii) reductive cleavage of the β-aryl ether bonds in lignin with zinc dust. Identification of the resulting monomeric and dimeric degradation products by gas chromatograph (GC) gives valuable information on the structure lignin. We have modified the DFRC method to enable us to identify and quantify the phenolic β-O-4, etherified α-O-4 and etherified β-O-4 structures. In this paper, we describe the modified method and show some preliminary results on the effect of ball milling on lignin structure.

EXPERIMENTAL

Materials

Loblolly pine (*Pinus taesa* L.) sapwood ground to pass a 42 mesh screen in a Wiley mill was first extracted with ethanol/benzene (1:2, v/v) in a soxhlet apparatus for 24 hours and then with ethanol for an additional 24 hours (Wiley milled wood). After first air-drying, then drying in a desiccator over P_2O_5, the Wiley milled wood (100 g) was then placed in a 1 gallon porcelain jar together with glass marbles under a nitrogen atmosphere. The jar was placed on a rotary mill for 7 days (Rotary ball-milled wood). The rotary ball-milled wood (10 g. each) was then ground in a vibratory ball mill (Siebtechnik GMBH, 433 Mulheim 011380, Germany) under a nitrogen atmosphere for 48 hours using stainless steel balls (Vibratory ball-milled wood). Milled wood lignin (MWL) was isolated from the vibratory ball-milled wood according to the method of Björkman (1).

Methylation

Diazomethane in ether (40 ml) was produced from N-Nitroso-n-methylurea (2g). The diazomethane ether solution (40 ml) was added to a dioxane/methanol (2:1,v/v) suspension (60 ml) of milled wood (5g) and stirred for 6 hours at room temperature. The ether phase was removed by evaporation and fresh diazomethane (40ml) was added. This treatment with diazomethane was repeated 8 times. After the last treatment with diazomethane, the whole solvent was removed by evaporation, and the milled wood was washed with methanol/ether (1:1,v/v) 3 times before being air-dried (methylated milled wood).

In the case of MWL (2 g), it dissolved in the dioxane/methanol (2:1,v/v) solution (40 ml), however a small amount of precipitation appeared upon the addition of the diazomethane ether solution (40 ml). After 6 hours of stirring, the whole solvent was