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Characterization of Polyacrylate Samples*

The Characterization of Polyacrylate Samples by Light Scattering and Other Methods as a Basis for GPC Calibration

Dedicated to Prof. Dr. Herbert Willersinn on his 65th birthday

The conventional calibration of a gel permeation chromatograph for determining the molar masses of polymer samples requires a set of standards of similar chemical structure with a narrow distribution of molar masses determined by independent methods. The dearth of such standards for sodium polyacrylate makes it necessary to use indirect GPC calibration methods for these polymers, sometimes even using calibration substances of a different chemical structure. We investigated a series of sodium acrylate homopolymers and copolymers with a GPC apparatus, for which we had constructed calibration curves based on several different methods of determination. Parallel evaluation of the chromatograms with the individual calibration curves in some cases led to intolerable discrepancies exceeding 100% of the molar mass for the same GPC analysis. We obtained the best agreement between the results of GPC measurements and those of other methods with a calibration curve that was based on a mixture of sodium polyacrylates with a very broad distribution of molar masses. We had previously precisely determined the molar mass distribution of this calibration mixture by GPC coupled with light scattering. The accuracy of the results of light scattering and ultracentrifuge measurements is very dependent on the specific refractive index increments dn/dc used. Because of the complex structure of aqueous polyelectrolyte solutions in the presence of low-molecular-weight salts, there is a discrepancy between the gross dn/dc value measured directly in the polymer solution and the actual effective value in the light scattering experiment. It is therefore absolutely necessary to achieve osmotic equilibrium between the polyelectrolyte solution and the polymer-free salt-containing solvent used as an optical reference standard, by dialysis for an adequate time, before the dn/dc values are determined. The influence of dialysis on the measured dn/dc values is demonstrated with comparative measurements, and some of the serious falsifications in mean molar mass are discussed, which result if light scattering measurements are evaluated with uncorrected dn/dc values.

Die konventionelle Eichung eines Gel-Permeations-Chromatographen zur Molmassenbestimmung von Polymerproben benötigt einen Satz von eng verteilten, durch unabhängige Methoden bzgl. M_w charakterisierten Standards gleicher chemischer Struktur. Der Mangel an derartigen Standards für Natrium-Polyacrylat macht es notwendig, für diese Polymere indirekte GPC-Eichmethoden zu benutzen und dafür auch chemisch anders aufgebaute Eichsubstanzen einzusetzen. Wir untersuchten eine Reihe von Natrium-Acrylat-Homo- und Copolymeren mit einer GPC-Apparatur, für die wir Eichkurven nach mehreren unterschiedlichen Methoden konstruiert hatten. Die Parallel-Auswertung der Chromatogramme mit den einzelnen Eichkurven führte in einigen Fällen zu nicht mehr tolerierbaren Unterschieden von über 100 % bzgl. M_w für dieselbe GPC-Analyse. Die beste Übereinstimmung zwischen den Resultaten aus GPC-Messungen und anderen Methoden erhielten wir mit einer Eichkurve, die mit Hilfe einer sehr breit verteilten Natrium-Polyacrylat-Mischung aufgestellt worden war. Die Molmassenverteilung dieser Eichmischung hatten wir zuvor durch GPC-Lichtstreuungs-Kopplung absolut bestimmt. Die Richtigkeit der Ergebnisse von Lichtstreu- und Ultrazentrifugemessungen hängt entscheidend von den zur Auswertung benutzten spezifischen Brechungsindexinkrementen dn/dc ab. Wegen des komplexen Aufbaues von wäßrigen Polyelektrolytlösungen in Gegenwart von niedermolekularen Salzen besteht ein Unterschied zwischen dem an der Polymerlösung unmittelbar gemessenen Brutto- dn/dc -Wert und dem bei der Lichtstreuung tatsächlich wirkenden Wert. Es ist daher unbedingt notwendig, vor der Bestimmung von dn/dc -Werten die Polyelektrolyt-Lösung mit dem als optischen Vergleichsstandard benutzten polymerfreien salzhaltigen Lösungsmittel durch ausreichend lange Dialyse in ein osmotisches Gleichgewicht zu bringen. An Hand von Vergleichsmessungen wird der Einfluß der Dialyse auf die gemessenen dn/dc -Werte gezeigt und die teilweise gravierenden Verfälschungen des Massenmittels M_w diskutiert, die sich ergeben, wenn die Auswertung von Lichtstreuungen mit unkorrigierten dn/dc -Werten vorgenommen wird.

1 Introduction

The growing use of salts of polyacrylic acid and their copolymers in laundry detergents for reducing incrustation and preventing the redeposition of soil, and as a scale inhibitor and processing aid demands reliable methods for characterizing their mean molar masses and above all their molar mass distributions. Gel permeation chromatography (GPC) with

aqueous eluents has in the past proved to be a reliable and reproducible method for determining the molar mass distributions of salts of acrylic acid homo- and copolymers [1-5]. However GPC is not an absolute method; it requires calibration with standards that must first be characterized by independent absolute methods. In an ideal case, this calibration is carried out with a series of samples with the same chemical composition and structure as the polymer to be analyzed and with a narrow molar mass distribution. However, no such calibration substances are commercially available for salts of poly(acrylic acid). As described in Part 3.3, we therefore used several indirect calibration methods with differently structured commer-

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cially available calibration standards (polyethylene oxide (PEO), polyethylene glycol (PEG), sodium polystyrene sulfonate (NaPSS)) and with a set of sodium polyacrylate (NaPAA) standards with a broad distribution of molar masses and known weight-average molar masses, M_w . The NaPAA calibration curve was constructed according to methods described in the literature: Benoit's [6] universal calibration principle and/or iterative approximation of the overall calibration curve on the basis of the M_w values of samples with a broad distribution of molar masses. As discussed in Part 3.3, we obtained very divergent results with these calibration methods in the same GPC analysis.

To find the causes of these divergencies, we first measured a number of commercially available and laboratory polyacrylic acid products by independent absolute methods (low-angle laser light scattering (LALLS) and GPC-LALLS). In the course of this work, we encountered a series of trivial questions in connection with the characterization of polyelectrolytes which, in practice, are given too little thought even today, but which, if they are ignored, can lead to serious misinterpretations.

The best agreement between the GPC results and the M_w values obtained independently by light scattering and other methods was obtained by constructing the calibration curve for a NaPAA sample containing a broad molar mass distribution, whose integral distribution curve had been determined by GPC-LALLS.

2 Experimental conditions

2.1 Description of the samples

We investigated a series of laboratory samples and commercially available products (marked P ...); unless stated otherwise, the determinations were conducted on stoichiometrically neutralized sodium salts. The M_w values lay between about 2,000 and 460,000. We further analyzed a number of acrylic acid-maleic acid copolymers (marked C ...) in the two proportions, AS:MS = 70:30 and 50:50 (% wt.); see Table 5 for details on all the samples.

The solids contents of the samples, most of which were in solution, were determined by drying at 120°C for 24 hours in a vacuum drying cabinet; any low-molecular salts present were ignored. Attempts to determine these components, which are sometimes present in technical-grade products, by subsequent incineration of the organic components failed, as NaCl, for example, already evaporates under the incineration conditions required.

We wanted to determine a sample of polyacrylic acid both in the form of its sodium salt in aqueous solution and in the form of an ester in an organic solvent. Unfortunately, the reaction with diazomethane did not result in complete methylation; the reaction with BF_3 in *n*-butanol, on the other hand, was always accompanied by the formation of very high-molecular-weight components or microgels: light scattering measurements gave molar masses that were too high by a factor of 10 even after membrane-filtration of the sample solutions.

We obtained the commercially available calibration substances from the following companies:

– Polyethylene glycol (PEG) $HO-[CH_2-CH_2-O]_nH$

as Kit PEG10 from Polymer Laboratories ($M_w = 106-12,600$),

– Polyethylene oxide (PEO) $H-[CH_2-CH_2-O]_nH$

as Kit TSK PEO from Toyo Soda Co. ($M_w = 18,000-990,000$); according to the package insert, these samples decompose

gradually and have a limited shelf life. This decomposition, which mainly affects the higher molecular samples, is said to be retarded by storing the product under nitrogen at 0°C. As the history of these samples between characterization and receipt by the GPC laboratory is nearly always unknown, this decomposition represents a limitation in the use of the product as a calibration standard. Further, we found discrepancies in the transition range between the PEG and the PEO sets, which we also found in subsequent sets that we purchased.

– Sodium polystyrene sulfonate

(undialyzed) from Pressure Chemical Comp. in the form of 11 individual samples with M_w values of the sodium salt form between 1,600 and 1,060,000; these samples are prepared by polymer-analogue sulfonation of polystyrene samples that have been prepared by anionic polymerization. According to the manufacturer, the degree of sulfonation is measured by determining the sulfur, and the NaPSS molar mass calculated from the original molar mass of the polystyrene. The "undialyzed" grade that we used contains up to 40% Na_2SO_4 .

– "Polyacrylic acid"

from Polysciences Inc.; molar mass M_w between 2,000 and 1,300,000; the samples are referred to as "acid" and, with one exception, are supplied as concentrated aqueous solutions (25–65% wt.); however, the pH values of the different samples lie between 2.8 and 9.0: according to the supplier, the solutions are made alkaline with NaOH to achieve better solubility, i.e. the products are neutralized to an unknown extent and it is therefore practically impossible to measure the basic molar mass – as discussed in Part 3.2 – by light scattering; it was not possible to find out definitely from the manufacturer, whether the molar mass data referred to the acid or to the sodium salt form. The samples have a broad molar mass distribution; in two deliveries of the product with a nominal molar mass of 250,000, with different lot numbers, we also found major differences in the molar-mass distributions. The dn/dc value of 0.179 ml/g in 1.0 M NaCl given by the manufacturer and used by him to evaluate the light scattering results would indicate that this parameter was determined without previous dialysis to equilibrium.

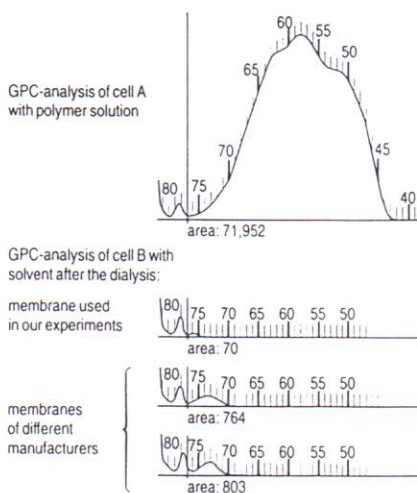


Fig. 1. Permeation of low molecular weight NaPAA-fractions during the dialysis experiment: Comparison of different membranes

