R. Brüssau, N. Goetz, W. Mächtle and J. Stölting, Ludwigshafen, Germany

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 Ultrazentrifugenmessungen 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 wirksamen 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 Lichtstreumessungen 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.

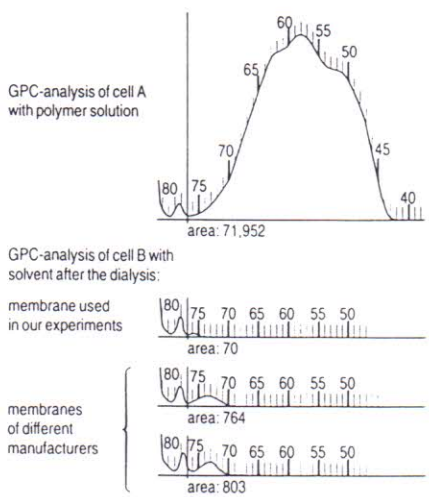

Fig. 1. Permeation of low molecular weight NaPAA-fractions during the dialysis experiment: Comparison of different membranes

2.2 Determination of the parameters, dn/dc and dρ/dc

The specific refractive index increments dn/dc were determined at 25°C at a laser wavelength of 633 nm with Brice-Phoenix and Shimadzu differential refractometers. The dialyses to equilibrium described in detail below were usually carried out in a Plexiglas® dialysis cell of our own design, based on the designs of *Vink* [7] and *Prokopova* [8].

The capacity of the two chambers was about 8 ml, the membrane was circular with a diameter of about 5 cm. The membrane material was selected after a number of initial trials with several different brands. The criteria for selection included the reproducibility of the dn/dc values with repeated measurements and the results of GPC analyses of the cell contents on the solvent side after dialysis (see below and Fig. 1). We selected "Thomapor-Dialyseschlauch Standard" made of cellulose with a nominal separation limit of M = 10000 to 15000; order No. 50432 from Reichelt, Heidelberg, Germany.

The specific density increment dρ/dc was determined on a *Kratky* balance: here too, the solution used was dialyzed to equilibrium against the solvent.

2.3 Low-angle laser light scattering (LALLS)

Most of the light scattering measurements were conducted on a Chromatix KMX 6 instrument. Six concentrations in the range 0.015 to 0.9% wt., depending on the molar mass of the sample, were measured at a scattering angle of 6–7° and the results extrapolated to concentration c = 0. The measurements were conducted in two different laboratories: Laboratory I used 0.5 M NaCl solution, while Laboratory II used the different solvents specified for each determination.

2.4 Gel-permeation chromatography (GPC)

We used four 600 × 7.5 mm columns packed with TSK-PW with the pore sizes G6000PW (2×), G4000PW (1×) and G3000PW (1×); these were all from batches manufactured before the end of 1984. For the experiments described here, we used an eluent consisting of 0.08 M tris(hydroxymethyl)aminomethane (= TRIS) + 0.15 M NaCl + 0.01 M NaN_3 adjusted to pH 7.0 with 0.1 M HCl prior to the final dilution with water.

This buffer is a compromise which was made to allow the determination of other water-soluble polymers in addition to polyacrylic acid salts under the same GPC conditions. A higher NaCl content would be desirable, as then extrapolation of the measured refractive index differences in the dn/dc determination at higher neutral salt contents would give better linearity and pass closer to the origin. However, with a NaCl content of 0.3 M NaCl, adsorption phenomena already take place in the GPC analysis of NaPSS and give meaningless deformations in the chromatogram. This only applies to the older TSK-PW column batches: the PW and PWXL columns currently supplied by Tosohaas require the addition of a polar organic modifier (e.g. 20% acetonitrile) to the aqueous eluent for the analysis of NaPSS to avoid total adsorption.

In spite of using a buffer solution as eluent, we tried to stoichiometrically neutralize all the polyacrylate samples prior to the GPC analysis: injection of the acid form sometimes gave deformed chromatograms with poor reproducibility.

A flow rate of 1 ml/min was used for the eluent and the analyses were conducted at room temperature. 0.2 ml of a 0.1% wt. solution of the polymer sample in the eluent was injected. An ERMA ERC 7510 differential refractometer was used as a detector.

2.5 GPC-LALLS coupling

The GPC apparatus that was coupled with the Chromatix KMX 6 laser light scattering instrument had a somewhat different combination of separation columns: four 600 × 7.5 mm columns packed with TSK G3000PW + TSK G4000PW + TSK G4000PW + TSK G6000PW, while the other conditions were practically identical.

Insofar as the second virial coefficient had not been determined from static light scattering measurements, it was taken as zero in the calculations. Because of the low concentration of the GPC eluates, the error is negligibly small.

When aqueous eluents are used in the GPC-LALLS apparatus, particular attention must be paid to corrosion. The light scattering detector is extremely sensitive to large particles and produces spikes considerably earlier than the differential refractometer, indicating the break-up of surfaces as a risk to corrosion at the joints of the LALLS cell, pump heads, pulsation dampers and other places.

2.6 Other methods

Some of the samples were measured by other independent methods:

- Membrane osmometry (MO)

measurements were conducted in 0.1 M NaCl at 25°C with a Knauer Digital instrument from Knauer, Berlin, using asymmetrical acetate membranes (exclusion limit approx. M = 10,000 g/mol). Because equilibrium is established very quickly with this instrument (one measurement takes about 5 min), permeating polymer samples can also be measured: the pressure drop is then obtained by extrapolation to time zero. The absolute error in the resulting M_n values is about ± 10%.

- Classical wide-angle light scattering (WALS)

with a FICA50 instrument at 25°C with measuring angles between 30° and 150° using 0.5 M NaCl as solvent.

- Analytical ultracentrifuge (AUZ) and molar mass determinations by the *Svedberg* method

The AUZ results given in Table 6 were determined by the sedimentation diffusion equilibrium method. The M_{SoDo} values also listed were determined by a complex combination of

- determination of the sedimentation coefficient S_o by AUZ
- determination of the diffusion coefficient S_o by quasi-elastic light scattering (QUELS) and
- determination of the specific density increment dρ/dc on the Kratky balance

using a formula given by *Svedberg* [9]. We did this to obtain an additional independent value for the molar mass; however it must be noted that the value obtained for M_{SoDo} depends somewhat on the width of the molar mass distribution.

3 Procedure and discussion of the measurements

3.1 Determination of the auxiliary parameters dn/dc and dρ/dc

When light is scattered by a dilute polymer solution, the intensity R_Θ of the scattered light is proportional to the molar mass, M and the square of the specific refractive index increment dn/dc of the polymer:

$$R_\Theta \sim M \cdot (dn/dc)^2$$

To evaluate light scattering measurements, it is therefore necessary to know the dn/dc value for the polymer under investigation in the solvent used. The evaluation itself is carried out according to a scheme given by *Zimm*. When polyelectrolytes are investigated in pure water, the *Zimm* diagrams obtained are usually strongly distorted so that it is no longer possible to determine the molar mass, the second virial coefficient and the gyration radius by extrapolation of the concentration c and the angle of scattering Θ to zero. This interference is caused by the so-called polyelectrolyte effect [10, 11]: the intramolecular repulsion of groups with the same charge along the polymer chain leads to an expansion of the polymer coil. These effects are drastically reduced by the addition of low-molecular electrolytes. The low-molecular-weight ions shield the charges on the polymer chains and the polymer coil shrinks to a size found in uncharged polymer molecules. The intermolecular interactions are also reduced to an extent found in solutions of uncharged polymer molecules. At the same time an increase in the intensity of the scattered light by a factor of about ten is observed, compared with the electrolyte-free aqueous solution.

The addition of the low-molecular salt makes a multi-component system out of the binary system of polymer and solvent and effects are observed which indicate that the solvated shell of the polymer molecules has a composition different from that of the surrounding polymer-free salt solution or the polymer-free initial solvent mixture. This preferential solvation gives the polyelectrolyte solution different optical properties compared to those that would be expected from the overall composition of the solvent. In a single-component solvent, on the other hand, the composition of the solvated shell of the polymer molecules is of course identical with the composition of the polymer-free solvent, and the dn/dc value can be determined directly by comparison of the refractive indices of the polymer solution and the solvent.

Because of the preferential solvation that usually takes place in multi-component solvents, the free solvent that is not bound in the solvent envelope has a different composition from that of the original solvent mixture, that cannot be determined empirically. It is therefore no longer possible to use the original solvent direct as a reference standard for determining the dn/dc value. However, with an experimental trick, it is possible to obtain the necessary reference solution for measuring the dn/dc value. Dialysis of the polymer solution against a de facto infinitely large quantity of the original solvent mixture results in the restoration of the osmotic equilibrium between the solvated shell, the free solvent of the polymer solution and the original solvent, i.e. on completion of the dialysis, the free solvent of the polymer solution and the original solvent are practically identical again. When the polymer solution has been treated in this way, it is possible to determine the dn/dc value against the original solvent in a differential refractometer [5, 12–15]; such equilibrium dn/dc values are usually given the index μ.

The consequences of these effects are shown in Table 1 for a sodium polyacrylate sample (M_W approx. 455,000), that was measured in different aqueous salt solutions. Each sample was weighed out in the form of its sodium salt and the dn/dc value was measured against the original solvent with and without dialysis of the polymer solution. The light scattering measurements were conducted in the solvents given, without prior dialysis, and evaluated with the two dn/dc values. A dn/dc value of approx. 0.181 ± 0.002 ml/g was found for the dn/dc measurement on solutions that had not been equilibrated, almost independently of the nature of the low-molecular-weight electrolyte added. If this value is used uncritically in the evaluation of light scattering measurements, apparent molar masses between 290,000 and 579,000 are obtained for the same sample. However, after dialysis, significant differences in the $(dn/dc)_\mu$ values are obtained, depending on the low-molecular electrolyte used, though the M_W values calculated fall into a narrower range between 447,000 and 488,000.

The driving forces for these electrolyte shifts between the solvated shell and the free solvent can best be explained in terms of the *Donnan* effect: the charges on the polymer chain hinder the diffusion of ions of the same charge in the solvated shell. Because of the principle of charge neutrality, the motion of the counterions is also hindered. The result is that the solvated shell is deprived of low-molecular electrolyte [16]. Accordingly, a decrease in the $(dn/dc)_\mu$ values, compared with the

Table 1. Influence of the dialysis on the light scattering M_W-values of the sodium polyacrylate sample P 11

salt component in the aqueous solvent	(dn/dc)		M_w-result of light scattering calculated with		virtual excess Rayleigh factor
f = 1.319	without dialysis	with dialysis	(dn/dc) without	(dn/dc) with	$R^* = M_w \cdot (dn/dc)^2$
	(ml/g)	(ml/g)	dialysis		
0.3 M NaF	0.180	0.170	408,000	457,000	13,200
0.3 M NaCl	0.180	0.159	355,000	456,000	11,500
0.3 M NaBr	0.180	0.155	336,000	453,000	10,900
0.3 M NaJ	0.179	0.144	294,000	454,000	9,400
0.5 M NaCl	0.179	0.147	303,000	450,000	9,700
0.3 M LiCl	0.183	0.153	312,000	447,000	10,500
0.3 M KCl	0.181	0.159	351,000	455,000	11,500
0.3 M CsCl	0.182	0.179	447,000	462,000	14,800
0.3 M Na phosphate pH = 7.0		0.143		450,000	9,200
0.3 M $NaNO_3$		0.162		461,000	12,100
0.08 M TRIS* + 0.30 M NaCl	0.181	0.180	467,000	472,000	15,300
0.08 M TRIS* + 0.15 M NaCl	0.179	0.195	579,000	488,000	18,600
0.08 M TRIS*	0.181	(0.296)$			33,700

* TRIS = Tris(hydroxymethyl)-aminomethane neutralized by HCl to pH = 7.0
$ estimated, because the relationship between measured refractive index n and polymer concentration was not linear

initial values, is observed in alkyl halides with a greater refractive index n than water. As the table shows, the difference between the dn/dc values appears the greater, the larger the anion with the same charge as the polyelectrolyte (with constant cation) or the smaller the cation (with the same anion). It is clear from this that the repulsion of the co-ion is the smaller, the smaller it is in size and the better it can be shielded by a large counter-ion (in this case the cation). This provides a casual explanation of the small dn/dc differences in the presence of the bulky TRIS cation. *Budd* describes similar effects in tetramethylammonium chloride [17].

As can be seen from the two experiments with 0.3 and 0.5 M NaCl, the effect does not decrease with increasing salt concentration, it actually increases (further examples, see [14] p. 77) and it therefore has an inverse relationship to the decrease in radius of the coils and to the intermolecular interactions. The directly measured (dn/dc) values can a priori only be expected to be identical with the $(dn/dc)_\mu$ values at very small charge densities on the polyelectrolyte molecule and at very small ion concentrations in the solvent, according to [14].

The quantities of salt exchanged between the solvated shell and the surrounding free solvent and those exchanged in the dialysis with the original solvent are not negligibly small and can be clearly detected in experiments: if the dialysis is conducted in a symmetrical cell with two chambers of equal size, once equilibrium has been established, a clear difference in the refractive indices between the chamber contents on the solvent side and the original solvent not subjected to dialysis can be observed.

The question arises, whether it is also necessary to conduct the light scattering measurements with multi-component solvents on dialyzed polymer solutions. Practice has shown that there are no differences in the light scattering effect. By way of explanation, it should be noted that the observed scattered light is the difference between the polymer molecule/solvated shell complex that scatters strongly and the scatter of the surrounding solvent. The scatter effect of this mixed solvent is low and, because of the low molecular masses of its components, only changes slightly if its composition is changed ([14] p. 80 and [18] p. 185 ff.). It must therefore be expected that the shifts in composition under consideration here have no noticeable light scattering effect.

We conducted dialysis experiments according to two different methods. In the first, approx. 100 ml of polyelectrolyte solution was filled into a dialysis tube and suspended in about 900 ml of solvent for about 72 hours. However, this ratio of quantities cannot be regarded as an "exhaustive dialysis against a practically infinitely large quantity of solvent". The external solvent was therefore used after the dialysis as a reference standard for the $(dn/dc)_\mu$ measurement and as a diluent in the preparation of a series of dilutions of the dialyzed polymer solution.

In the second method, we conducted the dialysis in the osmometer-like chamber described above. A separate dialysis experiment was run for each concentration and the $(dn/dc)_\mu$ measurement was conducted on the contents of pairs of cells that belonged together.

With both methods, it is necessary to use the liquid from the solvent cell as the refractive index standard, as measurable shifts occur in the composition of the solvent during the dialysis, compared with the original solvent. Though the specific refractive index increment is then measured on a solution of slightly different composition, the change in the dn/dc value as a function of the composition of the solvent, which is in osmotic equilibrium with the polyelectrolyte solution, is so small that it can be ignored ([18] p. 184 and [14] p. 80).

The manufacturers' data on the permeation limits of the dialysis membranes are frequently of little use in their selection for a specific polymer/solvent system. We therefore investigated the contents of the dialysis cell on the solvent side with the very sensitive Optilab Multiref 902 interferometric refractive index detector following GPC, in some initial trials. In the examples shown in Fig. 1, between 1 and 0.1 % of the polymer from the sample with M_W = 455000 had diffused to the solvent side, depending on the membrane used. The chromatograms show that these components originate from the bottom end of the molecular weight range of the polymer. With low-molecular-weight samples and with polymers with a broad distribution of molecular weights and a high proportion of low molecular weights, conventional membranes allow diffusion of the polymer to the solvent side in quantities that can no longer be tolerated.

If a membrane with smaller pores is selected to avoid this diffusion of polymer, not only an exchange of low-molecular salts but a migration of water from the solvent cell to the polymer solution are frequently observed. This undesirable dilution of the polymer solution cannot be determined with accuracy and is very difficult to recognize when a membrane tube is used for dialysis, unless very large volumes are exchanged. We therefore preferred to conduct the dialysis in the small osmometer-like chambers in which very small changes in volume resulting from these effects can be observed in the meniscus of the liquids in the capillary filling tubes.

If, for the reasons discussed above, the dialysis of a particular polymer sample cannot be properly conducted, a method described by *Vrij* and *Overbeek* [19] may be helpful. In this method, the light scattering of a polyelectrolyte sample is first measured in a series of different salt solutions and the dn/dc values obtained without dialysis are used for their evaluation, giving the apparent molar masses M_W^* of this polymer sample. The molar masses obtained for the different salt solutions are then plotted as $\sqrt{M_w^*}$ against the product $M_{salt} \cdot (dn/dc)_{salt}$ derived from the molar mass M_{salt} and the specific refractive index increment $(dn/dc)_{salt}$ of the salt used in each case. In the case of the sodium halides, NaF, NaCl, NaBr and NaI, the sodium polyacrylates of interest here give a straight line that intersects the y axis at $\sqrt{M_w}$, the true molar mass of the polymer, when it is extrapolated to $M_{salt} \cdot (dn/dc)_{salt} = 0$. To carry out this extrapolation, the so-called preferential adsorption coefficient ζ according to [19] for the salts used must be the same. In our case we found an average value of 0.010 ± 0.001 mol/ml for the individual salts, which was independent of the NaPAA samples used and their molar masses. Thus, ζ is the same for all the sodium halides. However, this condition is not always fulfilled. For instance, we were unable to carry out this extrapolation with solutions of the four alkali chlorides LiCl, NaCl, KCl and RbCl.

We used the M_W values calculated according to *Vrij* and *Overbeek* in sodium halide solutions to verify the $(dn/dc)_\mu$ values. We obtained values that were within 2–3 % of those given above for the sample with a molecular weight of 455000. We also applied the *Vrij-Overbeek* method to this sample, which was easy to dialyze. Extrapolation gave a molecular weight of 442000 – a difference of −3 % to the values obtained from the $(dn/dc)_\mu$ values measured by dialysis, which is also satisfactory.

Already today, GPC analyses are frequently used to calculate the dn/dc value of a polymer from the peak areas of a chromatogram detected with a differential refractometer. As discussed by *Berkowitz* [20], the value found in this manner is identical to that found after equilibrium dialysis in the measurement of polyelectrolytes with salt-containing eluents, i.e.

Table 2. $(dn/dc)_\mu$ values as a function of the monomer ratio

Sample	Composition	$(dn/dc)_\mu$ in 0.3 M NaCl [ml/g]	$(dn/dc)_\mu$ in 0.08 M TRIS buffer with 0.15 M NaCl pH = 7.0 [ml/g]
Na polyacrylate	100 AS/ –	0.159	0.195
Copolymer	70 AS/30 MS	0.146	0.178
Copolymer	50 AS/50 AS	0.141	0.171

Table 3. LALLS determinations on commercially available products

Sample	M_W Manufacturer's data (as NaPAA)	M_W, LALLS evaluated by $(dn/dc)_\mu$ (as NaPAA)
Na polyacrylate	1,300	2,000
Na polyacrylate	2,600	5,600
Na polyacrylate	5,900	7,600
Na polyacrylate	60,000	133,000
Na polyacrylate	110,000	274,000
Copolymer 70 AS/30 MS	20,000	106,000

the GPC method is a further alternative to the dialysis of salt-containing polyelectrolyte solutions.

The need to conduct a dialysis to equilibrium prior to the dn/dc determination of polyelectrolytes in aqueous salt solutions discussed above also applies to the determination of the specific density increment d_ρ/dc that is required for evaluating the AUZ measurements and for the *Svedberg* method. See [17] and ([14] p. 105) for further details.

We found a linear relationship between the specific refractive index increments $(dn/dc)_\mu$ and the composition of the monomer for the sodium salts of polyacrylic acid-maleic acid copolymers (see Table 2 and Fig. 2).

As can be seen from the dates of the references quoted above, the necessity of conducting a dialysis to equilibrium prior to the dn/dc determination in solvent mixtures has been accepted in the literature for some time. However, subsequent measurement of the M_W values of a number of commercially available products and their comparison with the manufacturer's data shows that there are still laboratories that are reluctant to undertake the extra work. As a result the M_W values quoted are too low and this error can be compounded if GPC calibration curves are used, which are not evaluated properly.

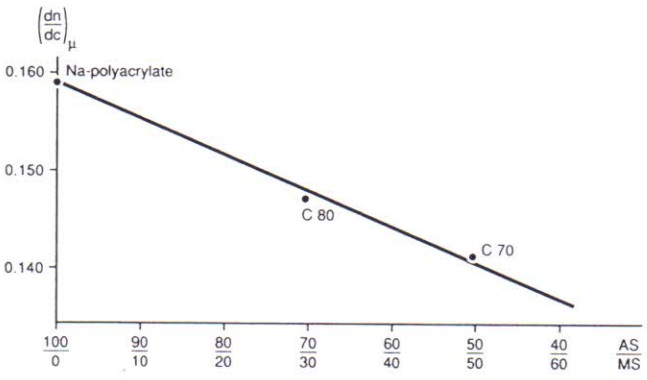

Fig. 2. Specific refractive index increments and polymer composition of Na-salts of acrylic acid-maleic acid-copolymers

3.2 *Light scattering measurements*

Polyacrylic acid, as a technical-grade product, is marketed as a free acid, as a stoichiometrically neutralized salt or in a partially neutralized form adjusted to a particular pH value. Products that have been neutralized simultaneously with different cations are also available. We were interested to know, what influence the ions in a sample had on the results of light scattering measurements and whether there were any restrictions on the low-molecular electrolytes added to the solvents used in the experiments.

Referring again to Table 1, we see that the polyacrylate sample used was in the form of the sodium salt and was weighed out and investigated in the different aqueous neutral salt solutions in this form. In the following, we refer only to those measurements in which osmotic equilibrium had been established between the polymer solution and the reference solvent prior to the dn/dc determination, i.e. those in which $(dn/dc)_\mu$ values were determined.

Let us first consider all the measurements in which the same cation (here, Na^+) was always added to the solvent. The M_W values found vary independently of the anions (halides, phosphate and nitrate) used within ± 0.9% of the average value of 454,000. This narrow range of variation means that the choice of anion in the solvent has practically no influence on the molar masses found. However, the variation in the associated $(dn/dc)_\mu$ values shows that it is absolutely essential to use exactly the same electrolyte additive for the determination of $(dn/dc)_\mu$ and the light scattering measurements and to establish osmotic equilibrium in the solutions prior to the dn/dc measurement.

It is interesting in this connection to know whether the low-molecular ions present have any effect on the intensity of the scattered light. To determine this, we calculated a virtual scattered light intensity R* from

$$R^* = M_W \cdot (dn/dc)_\mu^2$$

with the usual light scattering equation (ignoring the 2nd and higher virial coefficients)

$$\frac{K \cdot c}{R_\Theta} = \frac{1}{M_w}$$

in which

$$K = (2\pi^2 n^2/\lambda^4 N) \cdot (1 + \cos^2\Theta) \cdot (dn/dc)^2 = K^* \cdot (dn/dc)^2,$$

assuming normalized conditions, in which

$$K^* \cdot c \equiv 1$$

(See last column in Tables 1 and 4).

Depending on the anion of the sodium salts added, we obtained values between 9,000 and 13,000. A clear trend emerged in the intensity of the light scattered at a constant angle of 6–7°, which decreased with increasing size of the anion. This change is almost completely compensated when the appropriate $(dn/dc)_\mu$ value is used in the evaluation.

If the cation is changed (the Cl^- anion being used in each case), the situation is somewhat different: the M_W values for Na^+, Li^+ and K^+ as cations in the low-molecular electrolyte

Table 4. Influence on the neutralization conditions on the light scattering M_W-results of polyacrylic acids

Sample	Solvent	(dn/dc) with dialysis (ml/g)	$M_{W,-COOH}$ calculated from LALLS-measurements	$M_{W,-COOLi}$ recalculated from $M_{W,-COOH}$-value	$M_{W,-COOK}$ recalculated from $M_{W,-COOH}$-value	virtual excess Rayleigh factor $R^* = M_W \cdot (dn/dc)^2$
P 11_{acid} neutralized						
by LiOH	0.3 M LiCl	0.205	226,000	245,000		9,500
by KOH	0.3 M KCl	0.200	230,000		352,000	9,200
P 08_{acid} neutralized						
by LiOH	0.3 M LiCl	0.203	122,000	132,000		5,000
by KOH	0.3 M KCl	0.195	127,000		194,000	4,800

added are practically identical under the above experimental conditions. Only in the presence of the larger Cs^+ and $TRIS^+$ cations significantly higher M_W values and virtual scattering intensities, R* are obtained. This effect is increased when a TRIS buffer and, at the same time, a lower Na^+ concentration are used. We must therefore expect that the Na^+ ions of the polyacrylate sample used are at least partly exchanged with the cations of the solvent and that these large cations are registered in the light scattering measurement as an increase in molar mass. This observation agrees with an earlier finding by *Hermans* [21] that the influence of a counter-ion on the molecular weight value of a polyelectrolyte, determined by light scattering, can only be ignored if the counter-ion is small enough.

We conducted several further experiments, in which we used different cationic counter-ions on two samples of polyacrylic acid. We weighed these samples in the form of the acid, then neutralized them stoichiometrically with KOH and LiOH respectively, adding LiCl and KCl as low-molecular electrolytes (see Table 4). In the $(dn/dc)_\mu$ and light scattering measurements; these samples were in the form of the lithium and potassium salts, so that their molar masses differed by a factor of 1.41. However, evaluation of the measurements gave practically the same M_W results, which, as we had expected from other measurements, were similar to the values for the acid form. From this it can be deduced that the actual form of the molecule present during the measurements has no effect, as long as a polymer-analogue transformation is involved that is equally applicable to the $(dn/dc)_\mu$ and light scattering measurements. The measured $(dn/dc)_\mu$ values are specific for such factors as whether the polymer is weighed in the acid form and neutralized with KOH, and the presence and concentration of any salts in the solution measured. These are by definition different from the constants determined starting with potassium polyacrylate under otherwise identical conditions.

These results are an experimental confirmation for *Eisenberg*'s statements ([14], p. 78), that, because of the form of the light scattering equation,

$$R_\Theta = K^* \cdot M_w \cdot (dn/dc)_\mu^2 \cdot c,$$

any multiplication of c and M_W with the same scaling factor is cancelled out again in the evaluation. Again, it is essential that the same factor is used in the dn/dc and light scattering determinations and that the polymer solution and reference solvent are in osmotic equilibrium in the dn/dc determination.

What can we deduce from these observations for light scattering investigations in technical polyacrylate samples, if the degree of neutralization and the type and composition of the (counter-)cations are unknown or uncertain? If the repeatedly mentioned conditions

- $(dn/dc)_\mu$ and light scattering measurements under the same conditions,
- polyelectrolyte solution and reference solvent in osmotic equilibrium prior to the dn/dc measurement,
- cations of the neutral salt used in the solvent not too large,

are fulfilled, the light scattering measurement gives the exact molar mass of the sample in the form weighed. However, it is only possible to calculate from this the molar mass of the basic molecule in its acid form, if the exact degree of neutralization and the composition of the cations are known.

3.3 GPC and GPC-LALLS measurements

As already stated in the introduction, there are no substances with a narrow molar mass distribution available for polyacrylic acid and its copolymers for conventional GPC calibration. A number of other, indirect methods are described in the literature, which use other data to make it possible to construct the log M versus V_e calibration curve. We calibrated our GPC apparatus by four such indirect methods, which we discuss below together with their results:

3.3.1 Method 1: Calibration with a Na polyacrylate sample with a broad molecular weight distribution and known integral M distribution

This method of calibration requires a calibration substance with a broad distribution of molecular weights, whose integral distribution curve is known and which is chemically and structurally identical with the polymer to be investigated. The cali-

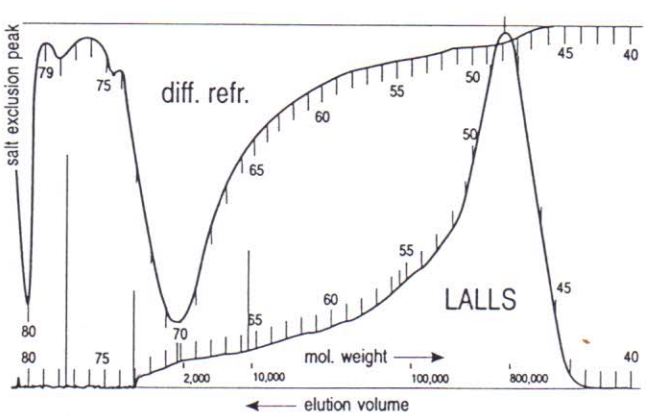

Fig. 3. Combined GPC-LALLS-analysis of a Na-PAA-mixture

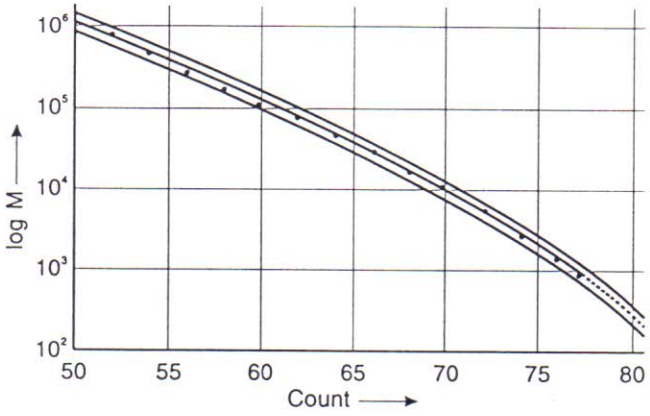

Fig. 4. Calibration of a GPC-column-combination for Na-polyacrylate ·–·– (mittlere Kurve) method 1: calibration by a broad distributed Na-PAA-mixture; —— (äußere Kurve) ± 20% confidence belt

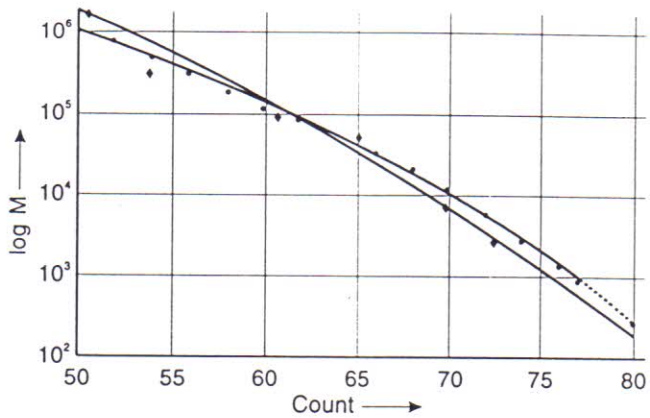

Fig. 5. Calibration of a GPC-column-combination for Na-polyacrylate ♦–♦ (Kurve von links oben nach rechts unten) method 2: iterative approximation using broad distributed Na-PAA-samples with known M_W-Values; ·–·– (Kurve von links unten nach rechts oben) calibration curve according to method 1

bration substance is analyzed on the GPC apparatus to be calibrated and the calibration curve is obtained by comparison of the distribution of the molar masses and of the peak area according to methods described in the literature [22, 23, 24].

We prepared a sample with a very broad distribution of molecular weights from four NaPAA samples with molecular weights between 2,700 and 160,000 for a calibration standard and determined the integral distribution curve by GPC-LALLS as described above. The ratio of the standards was selected such that the calibration mixture gave a good detector signal s over the entire molar mass range both with the differential refractometer ($s \sim c$) and with the LALLS detector ($s \sim c.M$). These differences in ratio of detector signal to concentration are the reason that the maximum is at the low molar mass end of the chromatogram when a differential refractometer is used as detector, while that of the LALLS curve is at a high molar mass (see Fig. 3).

In the upper molecular weight range, the calibration curve was confirmed by analyzing a sample of molar mass = 140,000 that had been characterized in the same manner. The lower limit of this calibration curve lies at a molar mass between 800 and 1,000. The low molecular weight range was therefore extended by extrapolation to the elution volume of the Na-salt of the monomer or the Na propionate eluted immediately before the monomer. The result is the calibration curve shown in Fig. 4, where the circles represent points plotted from the calibration values and the continuous curve was determined from three intervals using a spline algorithm. To gain an impression of the accuracy of this semi-logarithmic representation in the comparison with the calibration curves described below, we included the ± 20% band for the calculated calibration curve in Fig. 4.

We have used this calibration method for some two years. The difference resulting from different interpretation of the points in the vicinity of strongly curved boundaries, the area of overlap of the two calibration substances and in the boundary intervals obtained by extrapolation is in the 5–10% range for the molecular weights of samples with peak maxima near to the critical areas.

This method of calibration has one disadvantage, as do all calibration methods that are based on broad-distribution calibration standards: the effects of the *Tung* peak spreading are partly eliminated and smaller heterogeneity factors, M_W/M_n, are obtained than with a conventional GPC calibration curve based on a narrow range of standards. Regrettably, the extent of the elimination cannot be determined precisely, as it depends on a number of parameters in a manner that is difficult to define, e.g. on the ratio of the peak broadening in the GPC-LALLS calibration apparatus and that in the chromatograph to be calibrated. Further, the relationship of the mean molar masses of the calibration standard and their distribution to those of the sample also have an influence.

3.3.2 Method 2: Calibration with a set of broad-distribution polyacrylic acid standards with a wide range of known molar masses, M_W

A number of polyacrylic acid standards with a wide range of known molecular weights have been commercially available since about 1985. A series of such samples can also be used iteratively to construct a GPC calibration curve, if their molar masses cover a large enough interval:

(a) The samples are analyzed with the GPC instrument to be calibrated; an initial approximate calibration curve is obtained by taking the peak maximum as representing the weight-average molecular weight, M_W.
(b) The chromatograms are evaluated with the n^{th} approximation of the calibration curve.
(c) The $(n+1)^{th}$ approximation of the calibration curve is constructed from the elution volumes in place of the weight-average molecular weight values calculated with the aid of the n^{th} approximation of the calibration curve (as x axis) and the known weight average molecular weight values on the y axis.
(d) Steps (b) and (c) are iterated until the n^{th} and $(n+1)^{th}$ approximations of the calibration curves practically agree.

The resultant calibration curve (diamonds) obtained for our GPC apparatus is compared with that obtained by Method 1 in Fig. 5. The curves intersect at approx. M = 100,000; here too, there is a relatively wide range of uncertainty over the position of the calibration curve in the peripheral areas where there are no plotted points. Further it is not possible to assume that all the calibration points are simultaneously correct, as otherwise an undulating calibration curve would be obtained, which would not make sense. From the relative positions of the two calibration curves, M_W values that are 40% lower in the low-molecular range than the values obtained with the calibration curve from Method 1 and M_W values up to 30% higher in the high-molecular range are to be expected. We suspect that the cause is inaccurate calibration data for the standards used (see above).

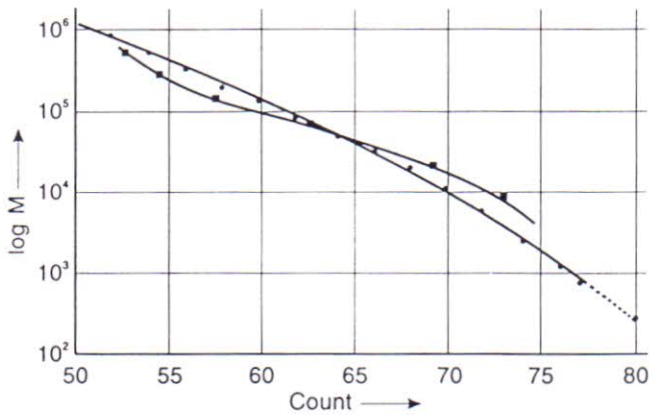

Fig. 6. Calibration of a GPC-column-combination for Na-polyacrylate —▮▮— method 3: universal calibration according to Benoit by narrow distributed Na-polystyrenesulfonate-samples; —·— calibration curve according method 1

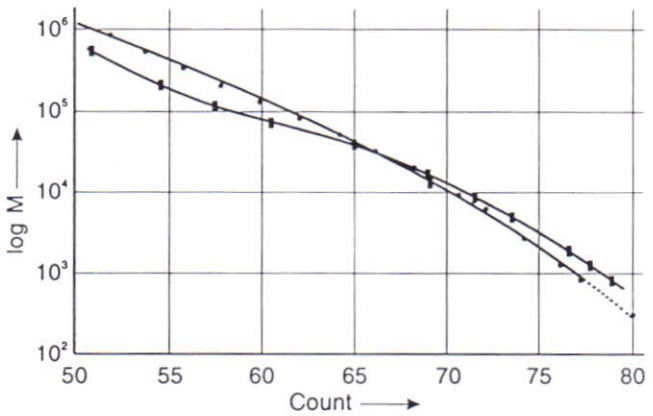

Fig. 7. Calibration of a GPC-column-combination for Na-polyacrylate —▮▮— method 4: universal calibration according to Benoit by narrow distributed Polyethyleneglycol-samples; —·— Calibration curve according method 1

3.3.3 Method 3: Conversion of a Na polystyrene sulfonate calibration to a Na polyacrylate calibration curve

As demonstrated in a number of literature sources, the *Benoit* [6] universal calibration principle can be applied both to NaPAA [1, 2, 3, 5] and to NaPSS [2, 3]. Thus, assuming that both polymers are eluted under the same experimental conditions according to an ideal GPC mechanism, it should be possible to convert a NaPSS calibration curve to a NaPAA calibration curve point by point according to the *Benoit* formula,

$$[\eta]_{NaPSS} \cdot M_{NaPSS} = [\eta]_{NaPAA} \cdot M_{NaPAA}.$$

Using the viscosity measurements of *Spatorico* and *Beyer* [1], we obtained the calibration curve (squares) in Fig. 6, with the calibration curve from Method 1 (circles) for comparison. The curves cross each other at several points; the size of the deviations to be expected with the samples analyzed depends on the distribution of their molecular weights. Without a large number of further measurements, it can currently not be determined, whether the deviations in the NaPSS calibration are the result of inaccurate calibration data supplied by the manufacturer or the non-fulfilment of the conditions required for applying the *Benoit* method.

3.3.4 Method 4: Conversion of a polyethylene oxide calibration curve to a Na polyacrylate calibration curve

Polyethylene glycols (PEG) and polyethylene oxides (PEO) are a class of calibration substances that are frequently used for aqueous eluents. They are commercially available with very narrow molar mass distributions from the monomer range to molar masses of about $7 \cdot 10^6$. We first attempted to interconvert the two calibration curves for $M_{PEO,PEG}$ and M_{NaPAA} with an empirical factor, f using a calibration principle

Table 5. Influence of the calibration method on the GPC-M_W-results

Sample	Mw – values (in sodium polyacrylate units = NaPAA)					
	independent measurements		GPC – analysis data conversion using a calibration curve constructed by			
	LALLS	GPC-LALLS	method 1 Na-PAA-mixture	method 2 broad distr. stds.	method 3 univ. cal. Na-PSS	method 4 univ. cal. PEO/PEG
Sodium Homopolyacrylates						
P 22	8,100	8,500	8,500	7,000	14,900	9,700
P 84		4,400	4,470	3,380	9,700	5,900
P 10	2,000	1,800	2,610	2,030	5,600	3,600
P 20			5,600	4,600	10,500	6,700
P 35	7,600	7,700	8,200	6,900	14,500	9,500
P 40			133,000	179,000	100,000	82,000
P 21		274,000	300,000	594,000	450,000	177,000
P 11	456,000	459,000	437,000	712,000	575,000	220,000
broad distributed Na-PAA calibration mixture		35,300	32,600	42,900	32,700	22,300
P 47		142,000	149,000	217,000	135,000	86,000
Copolymers AS:MS = 70:30						
C 70	85,000	95,000	68,000	88,000	57,000	46,000
C 80			85,000	112,000	68,000	55,000
C 75	106,000		87,000	121,000	77,000	54,000
Copolymer AS:MS = 50:50						
C 36	63,000	68,000	49,100	58,000	43,600	36,000

similar to *Moore's* from the early days of GPC, which used the equation

$$M_{NaPAA} = f \cdot M_{PEO}.$$

However we found that this factor depended on the molar mass and that it increased from values around 0.6 at M = 1,000 to 1.7 at M = $1 \cdot 10^6$. This method of conversion would be strictly valid if the exponents of the *Mark-Houwink* equation for the two polymers in the solvent used were identical; however, this condition is not fulfilled here: the *Mark-Houwink* α-exponent for PEO and PEG in aqueous solutions with a low content of neutral salts of monovalent ions is 0.60 to 0.70 [25, 26]. Under the same conditions, the α-value for NaPAA is larger than 0.75 [3, 5]. However, these minor differences in the α-values are already too great to be able to convert the calibration curve with adequate accuracy using a constant factor that is independent of the molar mass. This calibration method cannot therefore be used.

The validity of *Benoit's* universal calibration principle is also described for PEO and PEG in aqueous eluents [5, 25, 27]. Although *Bailey* [28] observed a depression of the viscosity when salts were added to aqueous solutions of PEO, according to *Dubin* [25], this effect is so small for the concentrations of salts of monovalent ions usually used in GPC, that it is possible to use the *Mark-Houwink* coefficients for PEO and PEG in pure water in *Benoit's* calibration curve conversion. We therefore combined *Kato's* [26] results for the high-molecular range with those of *Dubin* [25] for the low-molecular range in our experiments and obtained the following values for PEO and PEG in H_2O at 25°:

$$[\eta] = 4.77 \cdot 10^{-4} \cdot M^{0.671} \text{ (dl/g)}.$$

From measurements by *Kato* [5] of the viscosity of NaPAA at different salt contents between 0.05 and 0.5 M NaCl, we determined the *Mark-Houwink* coefficients for 0.15 M NaCl by linear interpolation and obtained

$$[\eta] = 1.53 \cdot 10^{-4} \cdot M^{0.786} \text{ (dl/g)}.$$

By determining [η] in several NaPAA samples in aqueous 0.15 and 0.3 M NaCl solutions with and without 0.08 M TRIS base and which were partially neutralized to pH 7.0, we were able to demonstrate that these concentrations of TRIS had no influence on the resulting intrinsic viscosity.

We obtained the NaPAA calibration curve shown in Fig. 7 with these *Mark-Houwink* coefficients using the *Benoit* method from GPC analyses of the PEO and PEG calibration standards. Comparison with the NaPAA calibration curve obtained with Method 1 shows that both methods of calibration give the same results only in the range M = 10,000 to 50,000. Above this range, the values given by the calibration method 4 are too small, while below it the molar masses are too high. Thus, for low-molecular samples we obtained M_W values that were up to 50% too high, while in the high-molecular range, the M_W values were too small by the same proportion. For example, we found $M_{W,GPC}$ = 225,000 for the sample with M_W = 455,000 referred to in Part 3.1. The calibration curve established according to Method 1 with a broad-distribution calibration mixture gives the considerably more accurate value of 437,000.

We did not carry out any further tests to determine the causes (e.g. imprecise data from the manufacturer or the literature, a greater influence of the salt or TRIS content than expected, non-ideal GPC mechanism) for the discrepancies in converting the PEO calibration curve. As Table 5 shows, Method 1, our method of choice, i.e. the construction of a NaPAA calibration curve with the aid of one or more broad-distribution calibration standards, whose molar mass distribution has been established by GPC-LALLS, provides the best results. With this method of establishing a calibration curve, the GPC-M_W values agree best with the M_W values obtained independently by light scattering measurements. We now use this method on a routine basis in our laboratory for calibrating GPC analyses of water-soluble polyacrylates.

Apart from the above, we also evaluated the GPC analyses of a number of acrylic acid-maleic acid copolymers using the calibration curve established by Method 1. The composition and results can also be found in Table 5. The M_W values found are always significantly smaller than those found by static light scattering measurements and by GPC-LALLS. On average, there is a difference of 20%. If we consider that the GPC mechanism fractionates the molecules according to the size of the polymer coils they form in solution, and that the calibration was conducted with Na homopolyacrylate, the finding could indicate that, in the form of the salt with the same molar mass, the maleic acid copolymer molecules in the TRIS buffer used possess a smaller volume than the homopolyacrylate molecules. For a more precise characterization, it would therefore also be necessary to calibrate samples by GPC-LALLS for use in Calibration Method 1 for each single copolymer composition.

In the tables mentioned so far, the GPC results have only been compared with those of low-angle laser light scattering. However, we used further independent measuring methods (see Table 6) for four technical-grade products and found satisfactory agreement with the NaPAA homopolymer. The GPC results for the copolymers were also evaluated with the sodium homopolyacrylate calibration curve according to Method 1. As expected, the M values for these two samples were too low. The difference between the membrane osmometer and GPC-M_n values shows that even if Method 1 is used for calibration, the influence of peak widening is not entirely eliminated and the M_n values are too low while the M_W/M_n values, in consequence, are too high.

Table 6. Comparison of the results got by independent methods

Sample		M_n		M_{s,D_n}	M_W					(Mw/Mn)
	PAA:MS	MO	GPC	AUZ/QUELS	AUZ	WALS	$LALLS_{lab1}$	$LALLS_{lab2}$	GPC	GPC
P 22	100/0	5,100	3,700	6,900	9,300	8,000	8,800	8,100	8,500	2.3
P 11	100/0	43,000	26,000	240,000	390,000	450,000	430,000	456,000	437,000	17
C 80	70/30	14,000	6,900	73,000	86,000	76,000	83,000	85,000	68,000	9.9
C 36	50/50	14,500	7,500	59,000	70,000	55,000	56,000	63,000	49,000	6.5

All M-values are in sodium polyacrylate-units (= Na-PAA)

4 Summary

The absolute accuracy of the GPC results cannot be better than the precision of the calibration substances used. It is only possible to construct calibration curves, using *Benoit's* universal calibration principle with current commercially available calibration substances and the *Mark-Houwink* coefficients given in the literature, if certain approximations are made. The GPC results obtained only agree with independently measured M_W values over relatively limited molar mass ranges.

The best agreement with independent measurements was achieved with a calibration method that used broad-distribution standards with a known integral distribution curve.

The influence of the neutral salts added to the aqueous polyacrylate solutions in the light scattering measurements can be eliminated over a wider range, if a number of secondary conditions are fulfilled. Above all, it is absolutely necessary to determine the specific refractive index increments dn/dc, that are required for evaluation, with the polymer solution in osmotic equilibrium with the neutral salt solution used as a solvent.

A comparison of the GPC results for maleic acid-acrylic acid copolymers with independent measurements showed that for a given molar mass, the copolymers were eluted later. With the Na homopolyacrylate calibration curve, we obtained M_W values that were about 20% too small for the 70/30 and 50/50 compositions.

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The authors of this paper

Dr. *Rudolf J. Brüssau*, born 1936, studied Physical Chemistry at the J. W. Goethe-University in Frankfurt am Maîn. Since 1967 he has been working at the Kunststofflaboratorium of BASF Aktiengesellschaft in the field of polymer characterization. His areas of interest are GPC of polyelectrolytes and especially multiple detection in GPC.

DI. *Norbert Goetz*, born 1936, studied at the Fachhochschule of Nürnberg. After concluding his studies in 1959, he worked in the Kunststofflaboratorium of the BASF Aktiengesellschaft.

Dr. *Walter Mächtle*, born 1938, studied Physics at the University Stuttgart from 1959 to 1965. Ph. D. at the Deutsches Kunststoffinstitut in Darmstadt. 1970 he joined the BASF and has been working in the Kunststofflaboratorium on the field of characterization of polymers and polymer dispersions.

Dr. *Jürgen Stölting*, born 1936, studied Physics at the Philipps-University in Marburg. After concluding his studies in 1968, he joined the BASF in 1969, where he has been working in the Kunststofflaboratorium in the fields of rheology and characterization of polymer solutions.

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