

Application Note

► Determination of molecular weight distribution of polyacrylonitrile

Category	polymer analysis
Matrix	-
Method	GPC
Keywords	polymers, molecular weight
Analytes	polyacrylonitrile (PAN)
ID	VCH1, 05/08(1)



Summary

A separation based on molecular size using GPC with organic eluents was demonstrated, along with a simple sample preparation procedure. Since this GPC application uses DMF and a small amount of lithium bromide as mobile phase, it will work on a standard HPLC system without any modifications. The molecular weight ranges (M_w) of the polyacrylonitrile samples analyzed were found to be in the middle of the linear calibration range.

Introduction

Polyacrylonitrile (PAN) is an important component of many industrial products including heavy-duty fibers, synthetic ropes, flame resistant plastics, and the impact resistant ABS plastics. PAN is also commonly used to produce fabric for clothing manufacture since its addition creates a material which is warming, soft and crease-resistant.

The properties of these fibers depend on the molecular weight and on the molecular weight distribution of the polymer chains. Producers of PAN fibers must therefore use quality control procedures to monitor these characteristics. GPC (gel permeation chromatography) is an excellent and simple means to determine the molecular weight distribution of PAN samples.

GPC separation is based on the interaction-free diffusion of sample molecules into the pores of the column packing material. For this application, we chose a medium polar column and a medium polar mobile phase. The GPC column was a polystyrene-divinylbenzene copolymer mixed-bed column with an exclusion limit of 20,000,000 Da.

The sample and calibration standard molecules must have the same steric properties for every single monomer mass because GPC separates based only on the molecular size. For this application, the calibration standard used was polymethyl methacrylate (PMMA) with a molecular weight range from 1890 Da up to 949,000 Da.

Experimental Sample Preparation

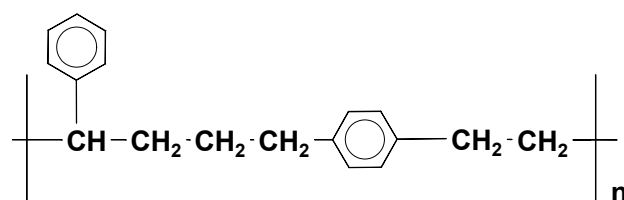
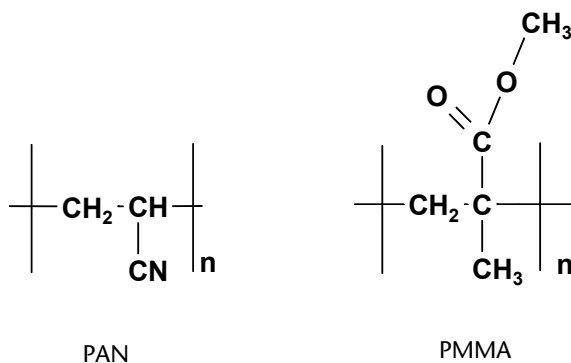
The calibration standards and samples must be carefully dissolved in a low concentration range, typically using the mobile phase. If the concentration of sample is too high, its high viscosity will decrease the rate of diffusion of the sample into the pores of the stationary phase, resulting in molecular weight results which are too low.

In this study, approximately 1.5 mg of PAN sample was mixed with 1 ml mobile phase. The mixture was heated at 50°C for 10 minutes and then carefully agitated.

Experimental Preparation of Standard Solution

Approximately 1.5 mg of each standard substance was weighed into a separate volumetric flask, heated at 50°C for 10 minutes and then carefully agitated.

Chemical Structures



poly (styrene-divinylbenzene) copolymer

Method Parameters

Column	2 x Shodex GPC KD-806M, 10 µm, 300 x 8 mm
Precolumn	Shodex GPC KD-G, 8 µm, 10 x 4.6 mm
Mobile phase	Dimethylformamide (DMF) + 10 mmol LiBr
Flow rate	0.4 ml/min
Injection volume	100 µl
Column temperature	50 °C
System pressure	29 bar
Detection	RI (refractive index)
Run time	70 min

Results

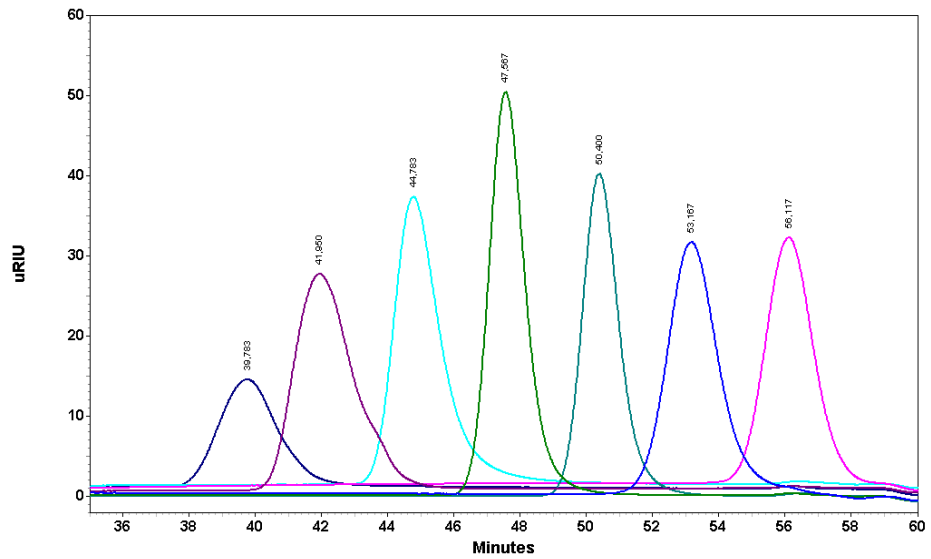


Fig. 1 Overlay of 7 PMMA calibration standards

Substance	t _R (min)	Molecular weight
PMMA standard 1	39.783	949000 Da
PMMA standard 2	41.950	451000 Da
PMMA standard 3	44.783	139000 Da
PMMA standard 4	47.567	52600 Da
PMMA standard 5	50.400	20800 Da
PMMA standard 6	53.167	7100 Da
PMMA standard 7	56.117	1890 Da

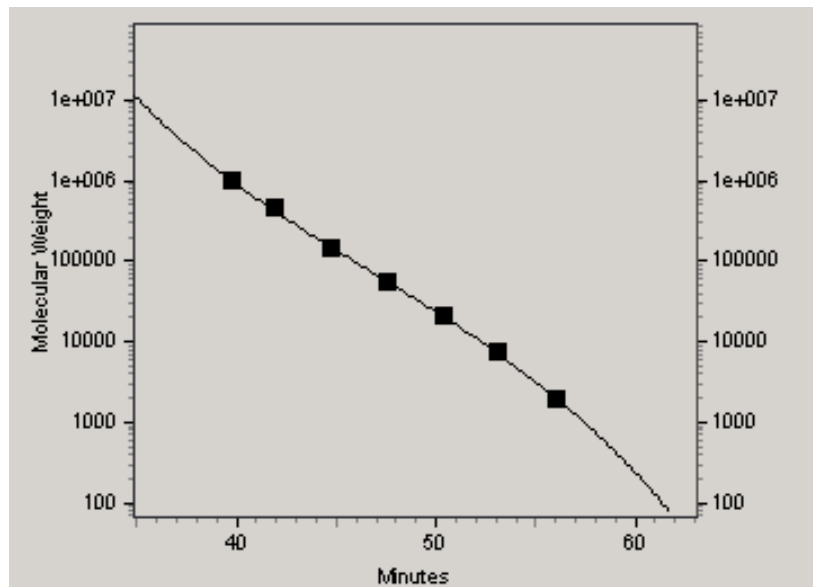
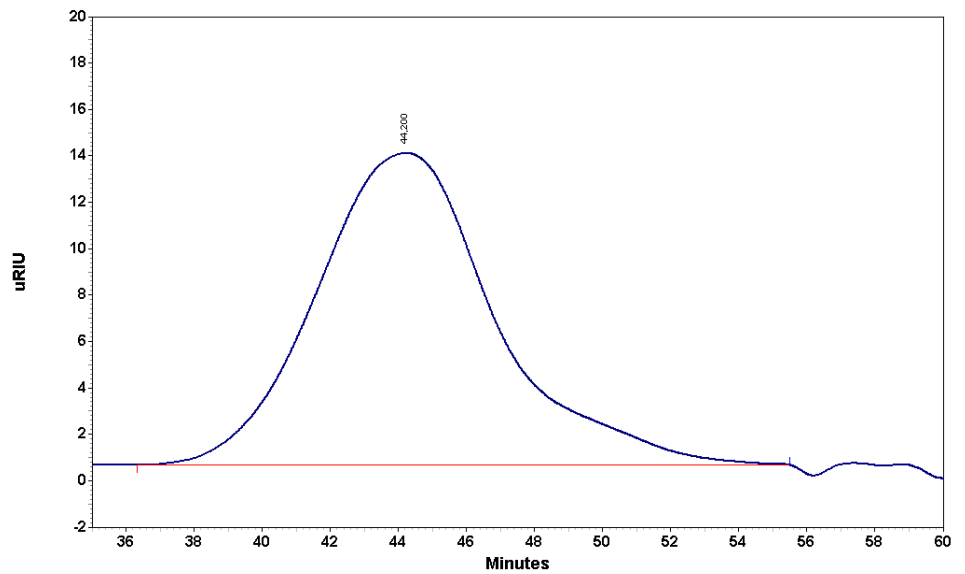


Fig. 2 Calibration curve of 7 PMMA standards

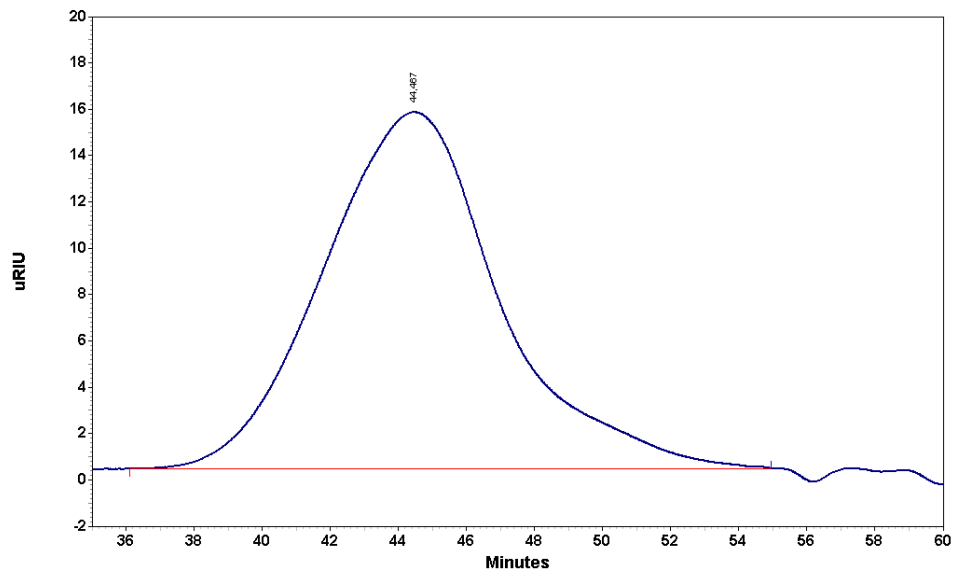
Parameter	Value
calibration type	narrow
fit type	cubic
correlation factor	0.9995

Fig. 3
PAN sample 1



Parameter	Value
weight average molecular weight	255345 Da
number average molecular weight	95425 Da
peak molecular weight	178608 Da
polydispersity index	2.68

Fig. 4
PAN sample 2



Parameter	Value
weight average molecular weight	245775 Da
number average molecular weight	94818 Da
peak molecular weight	162372 Da
polydispersity index	2.59

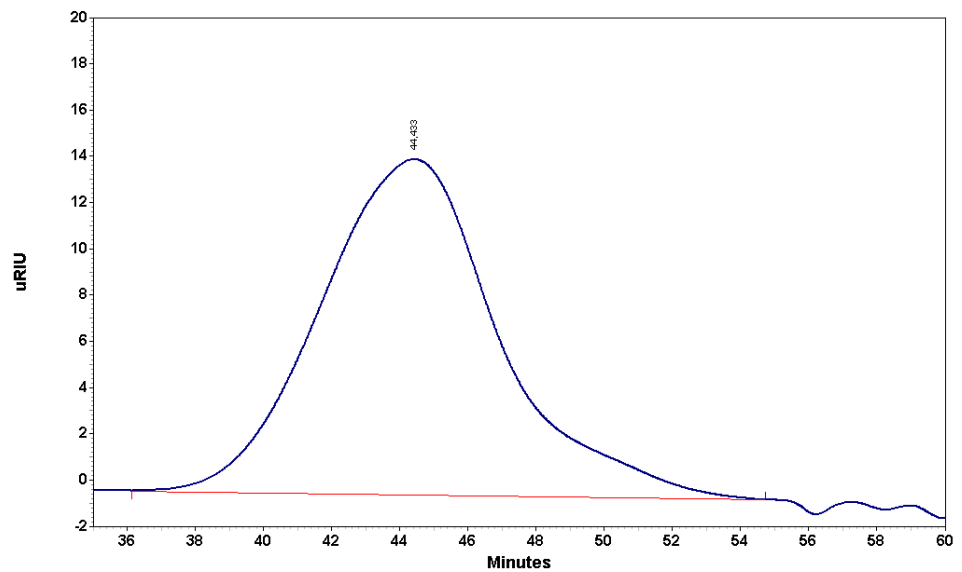


Fig. 5
PAN sample 3

Parameter	Value
weight average molecular weight	254967 Da
number average molecular weight	98665 Da
peak molecular weight	164313 Da
polydispersity index	2.58

Conclusion

A separation based on molecular size with good peak resolution is easily accomplished for the PAN samples by GPC using the Shodex KD-806M column and Smartline HPLC system with RI detection. The robustness of this method is reflected in the linear calibration curve over a wide molecular weight range.

It is important to note that the DMF mobile phase was spiked with 10 mmol/l lithium bromide to cover active end groups on the stationary phase. A mobile phase without lithium bromide shows poor results.

References

SHOWA DENKO K.K., Standard Operation Procedure GPC KD-800 Series 13 - 17

Physical Properties of Recommended Column



The column used is a polystyrene-divinylbenzene copolymer mixed-bed column, designed for use with dimethylformamide mobile phase.

Stationary phase	poly (styrene-divinylbenzene) copolymer
USP code	-
Particle size	10µm (precolumn: 8 µm)
Form	spherical
Exclusion limit	20,000,000 Da
Dimensions	2 x 300 x 8 mm ID (precolumn: 10 x 4.6 mm ID)
Max. temperature	60 °C
Max. pressure	30 bar
Max. flow rate	1.5 ml/min
Order number	B98 (precolumn: B98-1)

Recommended Instrumentation



This application requires an isocratic HPLC system equipped with degasser, autosampler, column oven and RI detector. Other configurations are also available. Please contact KNAUER to configure a system that's perfect for your needs.

Description	Order No.
Smartline Pump 1000, incl. 10 ml pump head	A50303
Smartline Manager 5000 with degasser	A5316
Smartline Autosampler 3950	A5005
Smartline Column Thermostat	A0585
Smartline RI Detector 2300	A5160
ChromGate software	A1493
ChromGate GPC option	A1470
PMMA calibration standard M-75 (1.68 – 1580 kDa)	B98-2

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