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SIZE EXCLUSION CHROMATOGRAPHY OF POLYAMIDES

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ABSTRACT

We report here a new chromatographic method for characterization of polyamides and polyether-block-amide copolymers by Size Exclusion Chromatography. First, it concerns absolute characterization of polyamide probes by classical light scattering and Ubbelohde viscometry measurements and the choice of narrow distribution standards to calibrate the GPC system. The GPC analysis of polyamides 6, 11, 12 and copolymers is based upon the dual detection refractometer/on-line continuous viscometer at 130°C using columns packed with cross-linked polystyrene gels, benzyl alcohol as mobile phase and polytetrahydrofuran standards for calibration. The main results are absolute average molecular weights and distribution curve, intrinsic viscosity and viscosity law. In addition, viscometric data produced evidence of long-chain branching occurring beyond a limiting molecular weight in some polyamide 12 samples.

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INTRODUCTION

Size exclusion chromatography is one of the most important methods for characterization of polymers, particularly polyamides. But characterization of polyamide solutions requires special attention because of their poor solubility, the toxicity of commonly used solvents and the lack of reference data for average molecular weights and intrinsic viscosity.

Molecular weight determination by size exclusion chromatography is generally achieved via three main ways (1) :

- *with low temperature solvents:*

- Fluoro-alcohols (1,1,1,3,3,3 hexafluoro-isopropanol, ...) are too expensive and strong acids (H_2SO_4 ...) are dangerous.
- Derivatization of amide groups by trifluoroacetylation (2) leads to solubilization in classical room temperature solvents (THF, CH_2Cl_2 , ...). This method presents important drawbacks preventing routine application, because of the instability of trifluoroacetylated polymers in presence of humidity.

- *with mixed solvents:*

- The preferential solvation brings trouble with a differential refractometer and results are difficult to interpretate.

- *with high temperature solvents:*

- It turned out that all classical solvents of aliphatic polyamides at high temperature have important drawbacks. Metacresol is toxic, hexamethylphosphorotriamide (HMPT) (3) seems potentially carcinogenic. Dimethylacetamide is corrosive, even with stainless steel 316L used in the chromatographic equipment. Ethylene glycol and derivatives are highly viscous.

A new approach of polyamide characterization was described by PASTUSKA (4) using a porous silica stationary phase and benzyl alcohol as mobile phase. This solvent seems more convenient since it does not present the previous drawbacks; but silica is a well-known packing which can give strong polar interactions with solutes. For these reasons, we have developed a new chromatographic system based on cross-linked polystyrene gel columns and benzyl alcohol as solvent.

We used two different kinds of detector sets which will be described later :

- SYSTEM I : for polyamides and copolymers
- SYSTEM II : mainly for copolymers

Absolute measurements, light scattering (LS) and Ubbelohde viscometry (UV) were carried out with internal polyamide samples, used as probes, to obtain reference data for checking our GPC system.

EXPERIMENTAL

Materials

- GPC and viscometry solvent was benzyl alcohol supplied by PROLABO (Paris - France), stabilized with 0.5 % di-tert-butyl-paracresol and filtered through MILLIPORE (Milford , MA-USA) membranes, type FH, porosity 0.5 μm .

- LS solvent was hexafluoroisopropanol supplied by FLUKA AG (Buchs - Switzerland) filtered on MILLIPORE membrane type FH, porosity 0.2 μm .

- Narrow distribution standards were purchased from Pressure Chemical Company (Pittsburg , PA-USA) for polystyrene and from Polymer Laboratory (Shropshire , UK) for polyethylene oxyde and polytetrahydrofuran.

- Polyamide probes were supplied by ATOCHEM (Paris , France).

Light scattering

Static measurements of dn/dc of different polymers were achieved with a BRICE-PHOENIX differential refractometer at 6328 Å. Light scattering measurements were performed at room temperature with a FICA 42000 spectrogoniometer equipped with an helium/neon Laser (5 mW, $\lambda = 6328 \text{ \AA}$).

Intrinsic viscosity

Experiments were carried out with an Ubbelohde capillary viscometer, with internal diameter 0.36 or 0.46 mm according to probes, at constant temperature, controlled with an oil bath. All measurements were made at 130°C and reproducibility was tested at least three times.

Size exclusion chromatography

The column set was composed of four μ -STYRAGEL columns packed with different porosity gels 10^5 , 10^4 , 10^3 , 500 A supplied by MILLIPORE-WATERS (Milford, MA-USA). The chromatograph was a WATERS model 150C instrument operated at 130°C and equipped with dual detection :

SYSTEM I : on-line continuous viscometer already described (5) and differential refractometer.

SYSTEM II : infrared spectrometer MIRAN 1A WILKS (Foxboro, USA) and differential refractometer.

Samples were injected at constant volume (400 μ l) with concentration values extending from 3.10^{-4} to 6.10^{-3} g.cm⁻³.

Data acquisition and treatment were carried out with a computing system composed of a KEITHLEY 195 digital voltmeter, a KEITHLEY 705 multichannel scanner (Cleveland, OH-USA) and a HEWLETT PACKARD HP 9836 computer (Palo Alto, CA-USA). Data storage and processing were performed using GPC software developed in our own laboratory.

RESULTS AND DISCUSSION

Absolute characterization of samples

We have chosen a set of representative polymers in the commercial range of polyamides as probes. Light scattering and Ubbelohde viscometry measurements were carried out with these samples to obtain references.

Examples of characterization are shown in Figures 1 and 2. The repetition of analysis brings out an accuracy of the results better than 5% for Ubbelohde viscometry and only about 10% for light scattering owing to the weak variation of the scattered light with angle for low molecular weight species such as polyamides.

Calibration of the GPC system (SYSTEM I)

Polystyrene standards

The comparison of data obtained from SYSTEM I and those determined by light scattering and GPC in HMPT (3) is shown in Table I. It demonstrates an abnormal behaviour of polystyrene in our

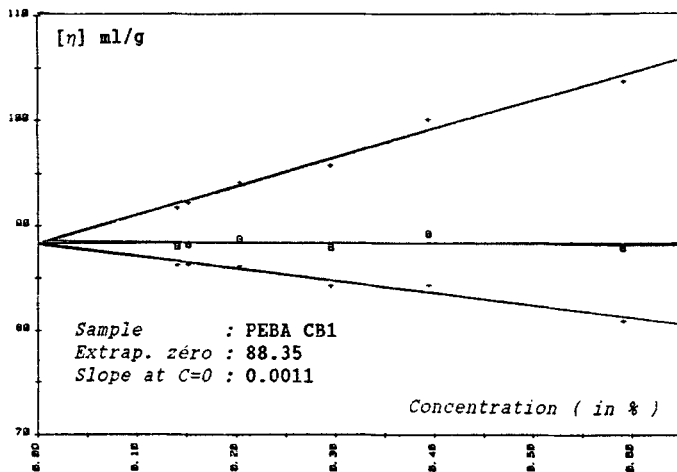


Figure 1 : Typical viscometry measurement carried out with a copolymer PEBA (polyether-block-amide).
 Solvent : benzyl alcohol, $\theta = 130^{\circ}\text{C}$, capillary $\Phi_{int} = 0.46$ mm.
 Upper curve : reduce viscosity, Lower curve : inherent viscosity, Intermediate curve : intrinsic viscosity.

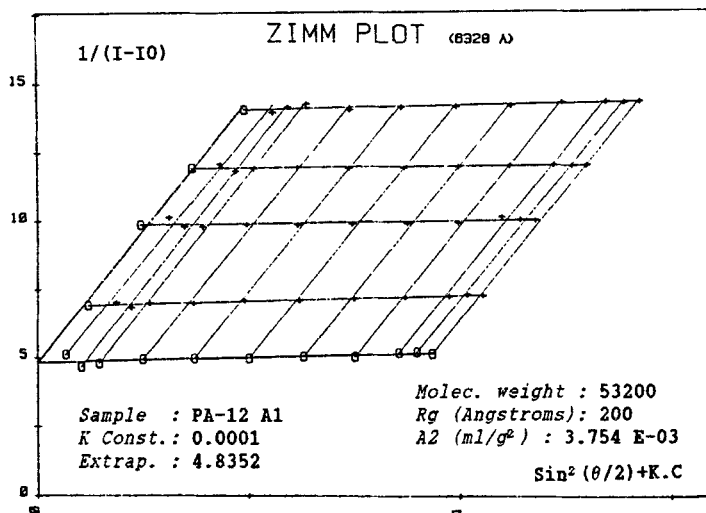


Figure 2 : Typical light scattering measurement carried out with a polyamide 12. Solvent : hexafluoroisopropanol. $\theta = 23^{\circ}\text{C}$, $\lambda = 6328$ A (polarized light). $M_w = 53280$ g mole⁻¹.

TABLE I
 Comparison between data obtained with SYSTEM I and other
 characterization methods (polystyrene calibration)

SYSTEM I : benzyl alcohol 130°C					GPC - HMPT 100°C		LS
Samples	V peak cm ³	$\bar{M}_w \cdot 10^{-3}$ g.mole ⁻¹	$\bar{M}_n \cdot 10^{-3}$ g.mole ⁻¹	$[\eta]$ cm ³ .g ⁻¹	$\bar{M}_w \cdot 10^{-3}$ g.mole ⁻¹	$\bar{M}_n \cdot 10^{-3}$ g.mole ⁻¹	$\bar{M}_w \cdot 10^{-3}$ g.mole ⁻¹
NBS 706	28.68	237	112	52	-	-	257.8
A1	28.66	106	46	84.7	52	25	53.3
A2	28.78	68	41	82.6	46	23	44.3
B1	30.14	40	28	44.6	23	11	23

chromatographic conditions. The affinity of polystyrene for stationary phase is stronger than for mobile phase, leading to increased elution volumes. Accordingly, molecular weights of polyamides (samples A1, A2, B1) are found approximately twice their absolute values determined by other methods. Nevertheless, results for NBS 706 polystyrene sample are found to be quite correct owing to the similarity of interactions.

Polyethylene oxide standards

A second way was to use polyethylene oxide standards which are available in a wide range of molecular weights and are soluble in benzyl alcohol. Unfortunately, intrinsic viscosity measurements indicated that random degradation occurs, mainly with high molecular weight samples ($\bar{M}_w > 10^5$ g.mole⁻¹), even for the shortest possible dissolution time. Molecular weight values obtained with SYSTEM I, calibrated with polyethylene oxide standards, are shown in Table II and are generally overestimated; the higher the molecular weight, the greater is the discrepancy.

Polytetrahydrofuran standards

Finally, we have developed our calibration method with polytetrahydrofuran standards, which does not present the previous

TABLE II

Comparison between data obtained with SYSTEM I and other characterization methods (polyethylene oxide calibration)

SYSTEM I : benzyl alcohol 130°C					GPC - HMPT 100°C		LS
Samples	V peak cm ³	$M_w 10^{-3}$ g.mole ⁻¹	$M_n 10^{-3}$ g.mole ⁻¹	$[\eta]$ cm ³ .g ⁻¹	$M_w 10^{-3}$ g.mole ⁻¹	$M_n 10^{-3}$ g.mole ⁻¹	$M_w 10^{-3}$ g.mole ⁻¹
A1	28.66	89	30	84.7	52	25	53.3
A2	28.78	58	29	82.6	46	23	44.3
B1	30.14	30	12	44.6	23	11	23

drawbacks. Results obtained from SYSTEM I calibrated with these standards are given in Table III and are in good agreement with those obtained by other methods.

We have plotted in Figure 3, the universal calibration curve obtained for a series of monodisperse polytetrahydrofuran standards.

Size exclusion chromatography of polyamides

Average molecular weights

Typical results obtained for various samples of polyamide 6, 11, 12 are presented in Table IV. They exhibit a good accuracy, mainly for polyamide 11 and 12 and point out the potential of our new system for molecular characterization of the polyamide family.

Characterization of oligomers

The particular molecular weight distribution of polyamides requires good column reliability. The analysis of low molecular weight compounds (Figure 4) demonstrates a good selectivity for our system in this range, suitable for the determination of polyamide distribution curves and consequently, for checking the polycondensation reaction.

TABLE III

Comparison between data obtained by absolute methods (LS-UV), HMPT-GPC and GPC in SYSTEM I (polytetrahydrofuran calibration)

SYSTEM I benzyl alcohol 130°C				GPC - HMPT 100°C		LS HFIP 25°C	UV Ubbeloh. 150°C
Samples	$M_w \cdot 10^{-3}$ g.mole ⁻¹	$M_n \cdot 10^{-3}$ g.mole ⁻¹	$[\eta]$ cm ³ .g ⁻¹	$M_w \cdot 10^{-3}$ g.mole ⁻¹	$M_n \cdot 10^{-3}$ g.mole ⁻¹	$M_w \cdot 10^{-3}$ g.mole ⁻¹	$[\eta]$ cm ³ .g ⁻¹
A1	51.7	26.3	87.4	51.7	25.5	53.3	84.1
A2	45.3	27.3	82.6	46.3	22.7	44.3	80.3

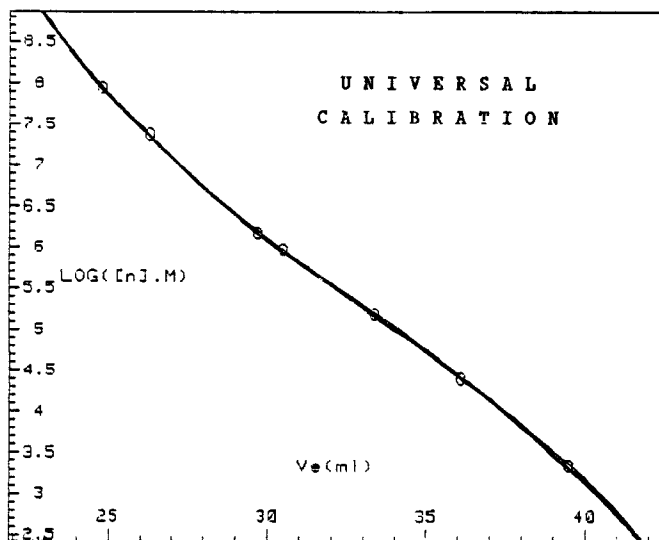


Figure 3 : Universal calibration curve obtained with commercial polytetrahydrofuran standards.

TABLE IV

Average molecular weights and intrinsic viscosities of polyamide samples

SYSTEM I : benzyl alcohol 130°C					GPC - HMPT 100°C		LS	UV
Samples	V _{peak} cm ³	M _w 10 ⁻³ g.mole ⁻¹	M _n 10 ⁻³ g.mole ⁻¹	[η] cm ³ .g ⁻¹	M _w 10 ⁻³ g.mole ⁻¹	M _n 10 ⁻³ g.mole ⁻¹	M _w 10 ⁻³ g.mole ⁻¹	[η] cm ³ .g ⁻¹
PA 12 A1	28.66	51.7	26.3	87.4	51.7	25.5	53.3	84.1
PA 12 A2	28.78	45.3	27.3	81.6	46.3	22.7	44.3	80.3
PA 11 B1	30.14	22.8	11.2	44.6	23.1	11	23	45
PA 06 01	29.72	26.2	9.5	48.3	31.3	15.1	30.7	50

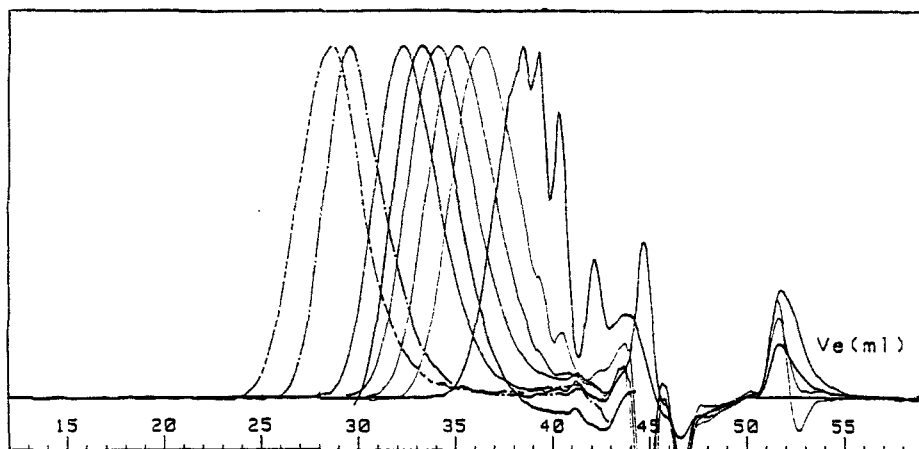


Figure 4 : Evidence of the column set selectivity in the whole range of polyamide molecular weights.

Viscosity law

For some polyamide 12 samples, chiefly for highly polymerized compounds, the experimental viscosity law presents a deviation from the straight line corresponding to the linear polymer, which exceeds the experimental error. Coefficients of MARK-HOUWINK's relationship are given by the lower part of the curve (Figure 5) :

$$[\eta] = 8.13 \cdot 10^{-2} \cdot M^{0.66}$$

The upper part is curved in the high molecular region, which demonstrates that long chain branching occurs in polyamide 12 after a limiting molecular weight around 50,000. All the analyses performed with polyamide 11 lead to a linear viscosity law, except when polycondensation is achieved with a multifunctional monomer (i.e. secondary amino 11-undecanoic acid). For polyamide 6, very few data are available for a strict conclusion. We are now trying to confirm these observations by NMR and FTIR spectroscopy and rheological measurements.

Size exclusion chromatography of PEBA (SYSTEMS I AND II)

Polyether-block-amide copolymers (PEBA) are of commercial interest as thermoplastic elastomers. They are synthesized from polyamide 12 and polytetramethylene glycol prepolymers. Each prepolymer's physico-chemical properties are well known, but no fast and easy molecular characterization method exists for copolymers. Due to the poor sensitivity of end group analysis (quantity and chemical nature of chain ends) and the general complexity of copolymer studies, we tried to demonstrate the potential of system I for the characterization of PEBA samples. Our probes were supplied by ATOCHEM and are named CB1 and CC1.

Weight-average molecular weights and intrinsic viscosities, measured by SYSTEM I, are in good agreement with data obtained by absolute methods LS-UV (Table V).

But regularity of the functionality composition of a copolymer is essential to the assumption of the constancy of the refractive index increment dn/dc necessary to perform GPC calculations. Consequently, it was essential to check the chemical composition as a function of molecular weight with a second kind of coupling technique involving an

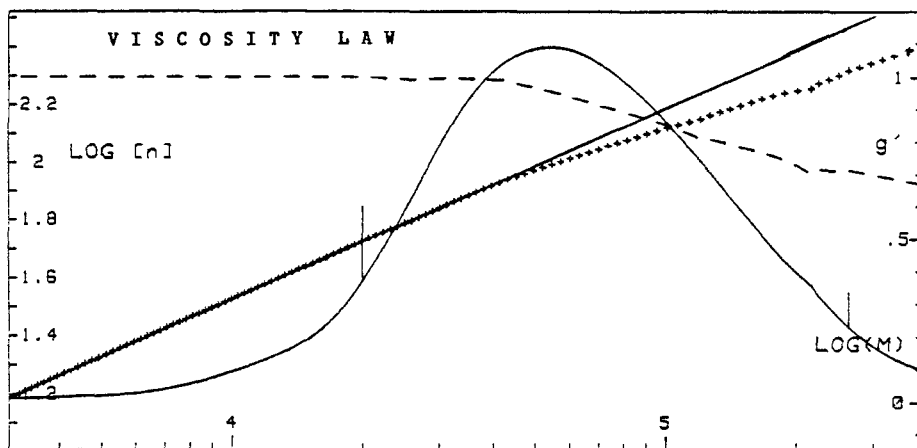


Figure 5 : Viscosity law of a polyamide 12 sample.

- (—) viscometric trace
- (---) linear viscosity law
- (+++) experimental viscosity law
- (-·-) branching parameter g' variations versus molecular weight.

TABLE V

Comparison of PEBA M_w values obtained by SYSTEM I with refractometer as concentration detector and by absolute methods

SYSTEM I : benzyl alcohol (130°C) (refractometer)		LS HFIP 25°C	UV Ubbeloh. 130°C	
Samples	$M_w \cdot 10^{-3}$ $g \cdot mole^{-1}$	$[\eta]$ $cm^3 \cdot g^{-1}$	$M_w \cdot 10^{-3}$ $g \cdot mole^{-1}$	$[\eta]$ $cm^3 \cdot g^{-1}$
PEBA CB1	50.5	90.9	53	92
PEBA CC1	42	85.8	-	85.3

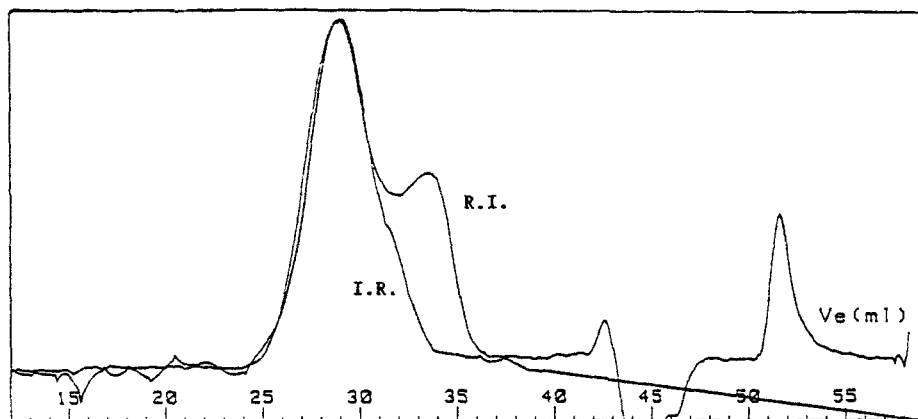


Figure 6 : Heterogeneity in a PEBA sample detected by the indirect method.

- RI : refractive index detector
- IR : infrared spectrometer detector

TABLE VI

Comparison between data obtained from SYSTEM I with infrared spectrometer as concentration detector and from absolute characterization methods

SYSTEM I benzyl alcohol (130°C) (infrared spectrometer)			LS HFIP 25°C	UV Ubbeloh. 130°C
Samples	$M_w \cdot 10^{-3}$ g.mole ⁻¹	$[\eta]$ cm ³ .g ⁻¹	$M_w \cdot 10^{-3}$ g.mole ⁻¹	$[\eta]$ cm ³ .g ⁻¹
PEBA CBl	49.5	91	53	92
PEBA CCl	38.4	87.3	-	85.3

infrared spectrometer set at the absorption wavelength of carbonyl groups. This detector provides information only on polyamide sequence concentration.

Indirect method (SYSTEM I)

We replaced the refractometer (RI) with an infrared detector (IR) and we compared chromatograms through the viscometric signal. Molecular weights and viscosity are calculated in the same way and compared with those obtained by refractometer/viscometer coupling. Figure 6 represents an example of chemical heterogeneity in a PEBA sample synthesized in our laboratory.

Experimental average molecular weights and intrinsic viscosities determined through SYSTEM I are in good agreement with those obtained by absolute methods (Table VI).

Direct method (SYSTEM II)

An on-line detection with two concentration detectors avoids the problem of signal adjustment and permits the direct calculation of the

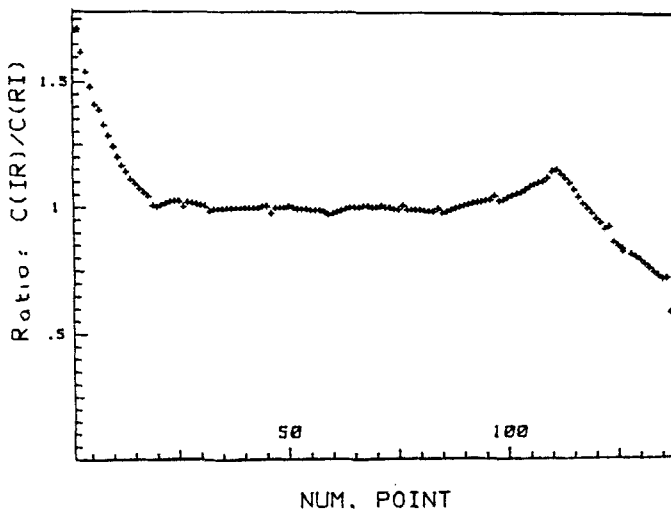


Figure 7 : Variation of the R ratio (C(IR)/C(RI)) for a PEBA sample as a function of the number of points in the chromatogram.

ratio R of concentration given by IR and RI detectors as a function of the number of points in the chromatogram. As the ratio R is generally constant along the distribution, we can deduce that the copolymer composition is homogeneous (Figure 7).

In conclusion, SYSTEM II is well suited for the study of copolymer composition, but when this composition is determined to be constant, SYSTEM I is the best method for molecular weight measurements, viscosity law determination and long-chain branching characterization. We are now trying to develop this method for a complete study of various PEBA samples.

CONCLUSION

Based on the above results, we can conclude that our new chromatographic system is well-suited for polyamide and copolymer molecular characterization. Weight-average molecular weights, intrinsic viscosity, distribution curve, viscosity law are obtained in good agreement with those determined by absolute methods. Our results are also consistent with data obtained by GPC in HMPT. We are now trying to confirm long-chain branching in polyamide 12 samples by other spectroscopic and rheological methods because a few reliable data for this phenomenon have been already reported. Work is in progress, but it will be necessary to investigate, more systematically, hydrodynamic behaviour of copolymers which seems to be dependent on several factors such as respective weight fractions of prepolymers, amide and ether block lengths and chemical nature of chain ends.

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