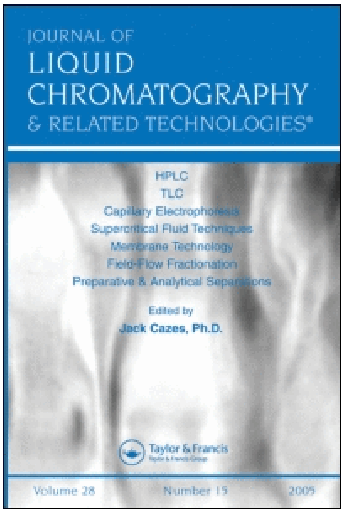

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Characterization of Polyether-Polyurethanes by Sec Coupled with Viscometry and Lalls

M. Žigon[a]; A. Mirčeva[a]; T. Malavašič[a]; Z. Griblšlć-Gallot[b]
[a] Polymer Department, National Institute of Chemistry, Ljubljana, Slovenia [b] Institute Charles Sadron (CRM-EAHP), Strasbourg, Cedex, France

To cite this Article Žigon, M. , Mirčeva, A. , Malavašič, T. and Griblšlć-Gallot, Z.(1993) 'Characterization of Polyether-Polyurethanes by Sec Coupled with Viscometry and Lalls', Journal of Liquid Chromatography & Related Technologies, 16: 17, 3813 — 3825

To link to this Article: DOI: 10.1080/10826079308019669

URL: http://dx.doi.org/10.1080/10826079308019669

JOURNAL OF LIQUID CHROMATOGRAPHY, 16(17), 3813-3825 (1993)

CHARACTERIZATION OF POLYETHER-POLYURETHANES BY SEC COUPLED WITH VISCOMETRY AND LALLS

M. ŽIGON[1], A. MIRČEVA, T. MALAVAŠIČ[1], AND Z. GRIBIŠIĆ-GALLOT[2]
[1]*National Institute of Chemistry*
Polymer Department
Hajdrihova 19, 61115 Ljubljana, Slovenia
[2]*Institute Charles Sadron (CRM-EAHP)*
6, rue Boussingault, 67083 Strasbourg-Cedex, France

ABSTRACT

Two- and three-component polyether-polyurethanes were characterized by means of size exclusion chromatography (SEC)-multidetector methods. SEC was coupled with three or two detectors in series, a continuous viscometer (CVM), a low angle laser light scattering (LALLS) photometer and a differential refractometer (DR), or with CVM and DR. Molecular weight (MW) averages were determined independently by SEC-LALLS and by SEC using universal calibration (SEC-UC).

MWs obtained by SEC-UC agreed with the corresponding SEC-LALLS MWs up to 60,000, but were higher for MWs over 60,000. This apparent increase in MW was attributed to the non-linearity of the calibration curve in the range of MW over 7.10^5. Due to high limiting viscosity number $[\eta]$ of polyurethanes as compared to polystyrenes with the same MW, there was a big influence of concentration effects upon SEC when using calibration curves. For an accurate SEC-UC determination of the MW distribution, the parameter $[\eta]\cdot c$ should be considered.

INTRODUCTION

Polyurethanes are technically important and commercially very interesting materials known for their excellent mechanical properties. Among versatile products, like foams, coatings, adhesives or elastomers, polyurethane elastomers represent a small group. They possess good elastic properties as a result of a physical network structure consisting of mixed soft and hard segment domains. The soft segments originate from polyether or polyester diols, and the hard segments from diisocyanates and aliphatic short-chain diols [1-5].

One of the significant characteristics of polyurethanes, next to composition, is the molecular weight distribution (MWD), which is usually determined by using size exclusion chromatography (SEC) coupled with a concentration detector that can be a differential refractometer (DR) or a UV spectrophotometer. Molecular weight (MW) averages are calculated by using calibration curves, related to monodisperse reference materials, and are relative values only [6]. SEC with two detectors, a continuous viscometer (CVM) and DR, enables the calculation of MW averages based on the universal calibration concept using hydrodynamic volume as a universal calibration parameter: a plot of log $[\eta]\cdot M$ against elution volume V_e gives a common curve for polymers of different chemical nature and molecular architecture [7]. Absolute MWs, without any need of calibration, are provided by SEC coupled with a low angle laser light scattering (LALLS) photometer and DR or UV spectrophotometer as a concentration detector [8, 9].

There are scarce literature data about the determination of the MW averages of polyurethanes by absolute detection techniques [5, 10-13]. In some cases, the limiting viscosity number $[\eta]$ and $\bar{M}_w$ were determined for individual fractions of a polyurethane sample; considering the Mark-Houwink-Sakurada (MHS) viscosity equation [14], the MHS parameters K and α were determined. SEC-LALLS was used for the comparison with SEC using polystyrene calibration and with SEC using a broad MWD reference compound calibration [12], as well as for monitoring the polymerization of triisocyanate and diol [13].

In this work, the characterization of two- and three-component polyether-polyurethanes by SEC-multidetector methods is presented. By using three detectors in series - a continuous viscometer, a low angle laser light scattering photometer and a differential refractometer, it was possible to determine the limiting viscosity number, the MW averages, the polydispersity index, and the MHS parameters. The purpose of this work was the comparison of MWs obtained by SEC-LALLS with the values obtained by SEC-CVM using the universal calibration.

EXPERIMENTAL

Materials

Polytetramethylene oxide with $\bar{M}_n$=2038 (PTMO, BASF), bis(iso-cyanato)-toluene (TDI) with 80% of 2,4-TDI and 20% 2,6-TDI isomers (Soda So), 2,4-TDI (Fluka), hexamethylene diisocyanate (HDI, Fluka), isophorone diisocyanate (IPDI, Fluka), 1,4-butane diol (BD, Aldrich), trimethylol propane (TMP, Perstrop Polymer), and, as a catalyst, dibutyltin dilaurate (Acima) were used. BD was dried over molecular sieves 4A, TMP in a vacuum drier, and PTMO by heating for two hours at 65°C under vacuum. Tetrahydrofuran (THF, Kemika) was distilled and dried over anhydrous sodium sulfate. THF used for SEC was distilled over sodium wire and filtered over Millipore filter FGLP with pore size 0.2 μm.

Synthesis

The two-component polyurethanes (PU) were synthesized in THF solution at 70°C, while the three-component PU elastomers (known also as segmented polyurethanes, SPU) were synthesized by using a standard prepolymer process [15]. Both samples were precipitated by hexane. The composition of the reaction mixtures is given in Table 1. In some cases an excess of the diisocyanate was added in order to obtain higher MWs. Eventual unreacted -NCO groups were blocked by 2-butanonoxime.

Equipment

The measurements were performed on two different chromatographic devices using THF as effluent at a flow rate 1 mL/min at 25°C. The solution concentration was about 2% (w/v) for chromatograph A, and from 0.08 to 0.9% (w/v) for chromatograph B. The injection volume was 100 μL.

A. Waters liquid chromatograph, model 150C, coupled with three detectors in series, a home-made continuous viscometer [16], a low angle laser

TABLE 1
Composition of Polyether-Polyurethanes and Their Refractive Index Increment Values

Sample	Composition	Molar Ratio	PTMO Weight Fraction	dn/dc mL/g
PU-T1		1:2	0.958	0.072
PU-T2	TDI:PTMO	1:1.5	0.946	0.073
PU-T3		1.1:1	0.913	0.080
PU-T4	2,4-TDI:PTMO	1:1.5	0.946	0.073
PU-T5		1.1:1	0.913	0.081
PU-H1		1:2	0.960	0.068
PU-H2	HDI:PTMO	1:1.5	0.947	0.069
PU-H3		1.1:1	0.915	0.072
PU-I1		1:2	0.947	0.068
PU-I2	IPDI:PTMO	1:1.5	0.931	0.069
PU-I3		1.1:1	0.891	0.072
SPU1	TDI:PTMO:BD	2:1:1.1	0.817	0.089
SPU2	TDI:PTMO:BD	3:4:1	0.883	0.082
SPU3	2,4-TDI:PTMO:BD	2:1:1.1	0.817	0.090
SPU4	2,4-TDI:PTMO:BD	3:4:1	0.883	0.082
SPU5	TDI:PTMO:TMP	2:1:1.1	0.801	0.087
SPU6	2,4-TDI:PTMO:TMP	2:1:1.1	0.801	0.087
PTMO 2000				0.066
TDI*				0.24
HDI*				0.15
IPDI*				0.13

* calculated values by using equation (1)

light scattering photometer Chromatix CMX-100 and a standard Waters differential refractometer; a series of PL-gel columns with granularity of 10 μm and with pore diameters 10^6, 10^5, 10^4, 10^3 and $5x10^2$ Å were used.

B. Modular liquid chromatograph consisting of a Knauer pump, model 64, a 712 WISP Waters sample injector module, a home-made continuous viscometer and an R-401 Waters differential refractometer; a series of PL-gel SEC columns with granularity of 10 μm and with diverse pore diameters were used: 10^6, mixed, 10^5, 10^4, 10^3 and $5x10^2$ Å.

Prior to the SEC-LALLS characterization, the refractive index increment of the polyurethanes was measured in THF solutions by a Brice-Phoenix differential refractometer working at the same wavelength (632,8 nm) and temperature as used with the LALLS photometer.

RESULTS AND DISCUSSION

Refractive Index Increment (dn/dc)

Table 1 reviews the composition and the measured dn/dc values of the synthesized polyurethanes and PTMO. Because of a high weight fraction of PTMO having a low dn/dc, the values of polyurethanes are low, less than 0.1 mL/g. According to the additivity rule, dn/dc of a copolymer is a sum of the products of dn/dc and weight fraction for the particular monomer or homopolymer [12, 17, 18]:

$$(dn/dc)_{copolym} = \sum_{i=1}^{n} W_i \cdot (dn/dc)_i \qquad (1)$$

where $\Sigma W_i = 1$. The dn/dc values of diisocyanates TDI, HDI and IPDI were calculated by using equation (1). These values are much higher than of PTMO.

SEC-CVM-LALLS Characterization

Owing to the fluctuations in the copolymer composition and molecular weight (MW), the weight average molecular weight ($\bar{M}_w$) of copolymers, determined by light scattering, is an apparent $\bar{M}_w$ [18]. Every i-th fraction of a copolymer eluting from a SEC column at i-th elution volume V_i exhibits a distribution both in composition and in MW. With polyurethane samples, the situation can be even more complicated, since the polyols used for the synthesis exhibit themselves a distribution in MW. Additionally, due to high reactive isocyanate groups, side reactions are possible. Therefore, $\bar{M}_w$ of polyurethane samples, determined by SEC-LALLS, is denoted as $\bar{M}_{app}$.

TABLE 2
Limiting Viscosity Number, Molecular Weight Averages, Polydispersity Index, and MHS Parameters of Polyurethanes Determined by Using the SEC-Multidetector Method

Sample	$[\eta]$ (mL/g)	$\bar{M}_{app}$	$\bar{M}_n$	$\bar{M}_{app}/\bar{M}_n$	α	K
PU-T1	31.5	9,500	9,000	1.1	0.78	0.028
PU-T2	35.8	11,000	7,300	1.6	0.75	0.032
PU-T3	149.2	72,000	45,000	1.6	0.66	0.083
PU-T4	33.9	7,900	6,800	1.2	-	-
PU-T5	90.2	62,000	51,000	1.2	-	-
PU-H1	30.9	7,500	6,400	1.2	0.64	0.124
PU-H2	38.6	26,000	24,000	1.1	-	-
PU-H3	223.0	137,000	113,000	1.2	0.59	0.225
PU-I1	28.5	14,000	8,100	1.7	-	-
PU-I2	31.3	14,000	13,000	1.1	0.77	0.019
PU-I3	115.1	56,000	47,000	1.2	0.69	0.062
SPU1	66.2	29,000	18,000	1.6	0.67	0.073
SPU2	95.5	50,000	27,000	1.9	-	-
SPU3	50.2	32,000	26,000	1.3	-	-
SPU4	63.2	27,000	19,000	1.4	-	-
SPU5	75.4	53,000	21,000	2.5	-	-
SPU6	51.8	36,000	22,000	1.7	-	-

The results of SEC-CVM-LALLS characterization are summarized in Table 2. As expected, $\bar{M}_{app}$ of the two-component polyurethanes (PU) increases with the increased molar share of a diisocyanate, $\bar{M}_{app}$ being the highest for HDI-PTMO reaction products.

The polydispersity index ($\bar{M}_{app}/\bar{M}_n$) of the polyurethanes shows a narrow molecular weight distribution (MWD). For the PU samples, $\bar{M}_{app}/\bar{M}_n$ is about 1.5 and for the three-component polyurethanes (SPU) between 1.5 and 2.0; the only exception are the SPU synthesized with tri-functional TMP instead of di-functional BD. It should be mentioned that SEC-LALLS gives a somewhat lower polydispersity index than other methods [16, 19].

From the viscosity law (the MHS viscosity equation), by correlating the limiting viscosity number $[\eta]$ and $\bar{M}_{app}$, the MHS parameters K and α were

TABLE 3
Dependence of Weight Average Molecular Weight Determined by SEC Using Universal and Polystyrene Calibrations on the Concentration of Polyurethane Solutions in THF

Sample	Concentration (mg/mL)	SEC-UC		SEC-PS
		$\bar{M}_w$	$[\eta]$ (mL/g)	$\bar{M}_w$
PU-T3	0.84	97,000	146.8	187,000
	3.96	100,000	144.4	193,000
	7.70	85,000	144.3	170,000
PU-H3	0.80	230,000	226.3	370,000
	4.18	198,000	228.5	364,000
	7.30	161,000	210.9	303,000
PU-I3	0.86	55,000	106.6	114,000
	5.38	54,000	96.9	106,000
	7.64	49,000	99.1	100,000
SPU4	1.30	31,000	54.0	56,000
	5.10	25,000	62.9	54,000
	9.16	24,000	60.9	51,000

calculated (Table 2). As already noticed [12], α decreases with the increasing diisocyanate content.

When the MHS parameters are known, $\bar{M}_w$ can also be calculated by using the universal calibration [7]. For this calculation, it has to be taken into consideration that the concentration of samples and reference materials has a big influence on their elution volume, and therefore also on the calculated $\bar{M}_w$ [20]. For polyurethanes, the calculated $\bar{M}_w$ were lower than $\bar{M}_{app}$ of the SEC-LALLS determination, which indicated strong concentration effects.

SEC-CVM Characterization

SEC coupled with CVM and DR was used to calculate MW averages based on the universal calibration (SEC-UC). In order to compare the results of SEC-LALLS and of SEC-UC determinations, the PU samples,

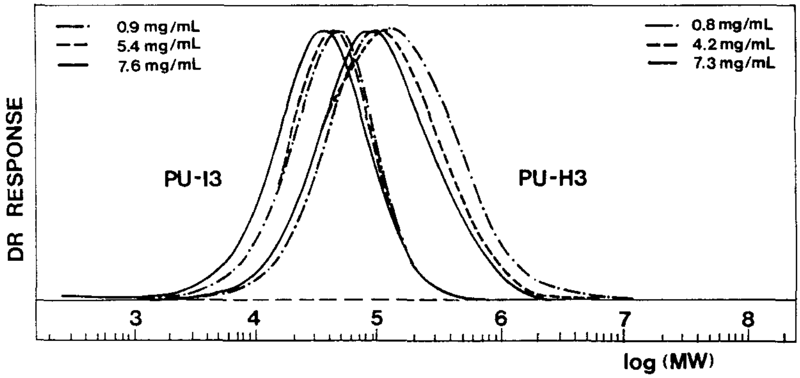

FIGURE 1: SEC-CVM and DR curves of the samples PU-I3 and PU-H3 with various concentrations of THF solutions.

based on three different diisocyanates, with the molar ratio of diisocyanate to polyol 1.1:1, and one SPU sample were chosen (Table 3). The influence of concentration effects on MW was studied by preparing three concentrations of the samples in THF, being varied between 0.8 and 9 mg/mL, regarding the concentration of polystyrene standards (4-5 mg/mL).

The SEC curves of the samples PU-I3 and PU-H3 (Figure 1) show that the influence of the solute concentration on elution volume increases with increasing MW; this phenomenon is well known [20]. For PU-H3, the SEC curves differ for all the three concentrations, while for PU-I3, the SEC curves with concentrations about 1 and 5 mg/mL partly overlap. The influence of the solute concentration on calculated $\bar{M}_w$ can be observed from the results in Table 3. For $\bar{M}_w$ up to 100,000, the difference for the calculated SEC-UC values between the lowest and the highest concentration is about 15%, while for $\bar{M}_w$ over 150,000, the difference approaches 50%.

To avoid the influence of concentration effects on SEC-UC results, $\bar{M}_w$ was extrapolated to zero concentration (Figure 2) [21], and the values obtained compared to the SEC-LALLS values (Table 4). The SEC-LALLS and SEC-UC values for samples PU-I3 and SPU4 are in good accordance, whilst the SEC-UC values for samples PU-T3 and PU-H3 are higher than those of SEC-LALLS. This apparent increase in MW was attributed to the non-linearity of the

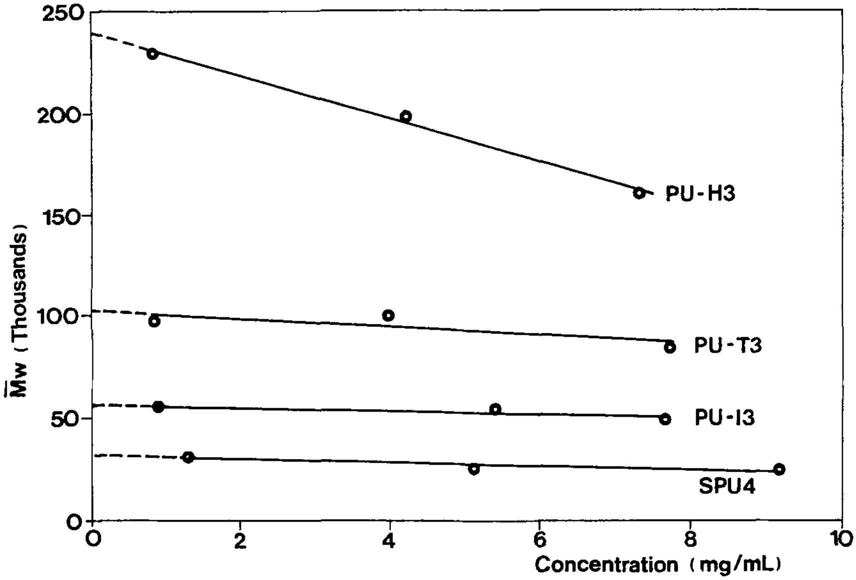

FIGURE 2: Dependence of the weight average molecular weight of some synthesized PU and SPU samples on the concentration of THF solutions.

TABLE 4

Weight Average Molecular Weight of Some Polyurethane Samples Determined by SEC-LALLS and SEC Using Universal and Polystyrene Calibrations with Extrapolation to Zero Concentration

Sample	$\bar{M}_w$			
	SEC-LALLS	SEC-UC	SEC-PS	SEC-PS_{corr}
PU-T3	74,000	102,000	200,000	110,000
PU-H3	137,000	241,000	392,000	220,000
PU-I3	56,000	57,000	116,000	59,000
SPU4	27,000	32,000	57,000	30,000

TABLE 5
Comparison of the Elution Volume of Polyurethane and Polystyrene Samples with Approximately Equal Hydrodynamic Volumes

Sample	$\bar{M}_w.10^5$	$[\eta]$ mL/g	$[\eta]\cdot M.10^7$ mL/g	Conc. mg/mL	$[\eta]\cdot c$	V_e mL
PU-H3	1.37	223.0	3.1	4.18	0.93	37.1
PS	3.20	113.2	3.6	8.02	0.91	37.0

calibration curve in the range of $[\eta]\cdot M$ over 10^8 (MW over 7.10^5), and to the fact that the SEC curve in the region of $[\eta]\cdot M$ over 10^9 (MW over $2.24.10^6$) falls out of the calibration curve. Some causes for the non-linearity of the calibration curve have been discussed elsewhere [22-24].

The strong concentration effects being reflected in a big difference of the SEC-UC values between the lowest and the highest concentration (Table 3), were correlated with the two to three times higher $[\eta]$ of polyurethanes as compared to $[\eta]$ of polystyrenes at the same $\bar{M}_w$; the latter was calculated from the MHS viscosity equation with known MHS parameters. To confirm such an interpretation, an experiment based on the universal calibration concept [7] was performed. For this experiment, the samples PU-H3 with $\bar{M}_w$ 137,000 and polystyrene (PS) with $\bar{M}_w$ 320,000 were selected, PU-H3 having higher $[\eta]$ than PS despite the lower MW (Table 5). In order to avoid concentration effects or to keep them on the same level, instead of the usual parameter $M\cdot c$, the dimensionless parameter $[\eta]\cdot c$ was taken into account [25]. The value about 0.9 was chosen on the basis of an acceptable signal to noise ratio for the PU-H3 sample. Due to differences in experimental conditions, this value was higher than reported for an aqueous SEC separation [25]. The comparison of the elution volume of the two samples has confirmed the validity of the universal calibration concept in this particular case. However, for an accurate SEC-CVM characterization of polyurethanes, both the parameter $[\eta]\cdot c$ and the limiting viscosity number are essential.

The results obtained by SEC-LALLS and by SEC-UC were also compared with the most employed SEC using a common polystyrene calibration

(SEC-PS). MW averages were approximately two to three times higher than the SEC-UC and SEC-LALLS values as a consequence of differences in chemical composition and therefore in chain dimensions of polyurethanes and polystyrenes (Tables 3 and 4). Higher SEC-PS results had already been mentioned in literature for the three-component polyether-polyurethanes based on methylene-bis(4-phenyl isocyanate) (MDI), butandiol and PTMO [12]; after correction by the ratio of the limiting viscosity number of polystyrenes to polyurethanes at the same MWs, which was between 0.6 and 0.9, the $\bar{M}_n$ values agreed with the SEC-LALLS values, whilst the $\bar{M}_w$ values were slightly higher. With our experimental conditions, the viscosity ratio was between 0.5 and 0.6, and, after correction, the $\bar{M}_w$ values agreed with those of the SEC-UC determination (Table 4).

CONCLUSIONS

Two- and three-component polyether-polyurethanes were characterized by SEC-multidetector methods. By using a continuous viscometer (CVM), a low angle laser light scattering (LALLS) photometer and a differential refractometer (DR), connected in series, it was possible to determine the limiting viscosity number, the molecular weight (MW) averages, the polydispersity index, and the MHS parameters K and α. The comparison of MWs obtained by SEC-LALLS with MWs obtained by SEC using universal calibration (SEC-UC) indicated good agreement for MWs of up to 60,000; over 60,000, the SEC-UC values were higher than those of SEC-LALLS. The apparent increase in MW was attributed to the non-linearity of the calibration curve, based on polystyrene standards, in the range of MW over 7.10^5. The high limiting viscosity number $[\eta]$ of polyurethanes, as compared to polystyrenes with the same MWs, was related to the strong concentration effects which influenced the MW calculation when calibration curves were used. For an accurate SEC-CVM characterization, the parameter $[\eta]\cdot c$ must be considered.

ACKNOWLEDGMENT

One of the authors (M.Ž.) is grateful to the Commission of the European Communities for granting the post-doctoral fellowship at the Institute Charles Sadron.

REFERENCES

1. J. H. Saunders, K. C. Frisch, Polyurethanes: Chemistry and Technology, Part I and II, Interscience Publishers, New York, 1962 and 1964.

2. G. Oertel, ed., Polyurethane Handbook, Hanser Publishers, Munchen, 1985.

3. G. Woods, The ICI Polyurethane Book, ICI Polyurethanes and J. Wiley & Sons, Inc., Chicester, 1987.

4. J. K. Backus, C. D. Blue, P. M. Boyd, F. J. Came, J. H. Chapman, J. L. Eakin, S. J. Harasin, E. R. McAfee, C. G. McCarty, N. H. Nodelman, J. N. Rieck, H. G. Schmelzer, E. P. Squiller, "Polyurethanes", in Encyclopedia of Polymer Science and Engineering, Vol.13, J. I. Kroschwitz, exec. ed., J. Wiley & Sons, Inc., New York, 1988, pp. 243-303.

5. Z. S. Petrović, J. Ferguson, Prog. Polym. Sci., 16: 695-836 (1991).

6. See for example N. C. Billingham, "Characterization of High Polymers by Gel Permeation Chromatography", in Practical High Performance Liquid Chromatography, Heyden & Son Ltd., New York, 1976, pp. 167-191, or M. G. Styring, A. E. Hamielec, "Determination of Molecular Weight Distribution by Gel Permeation Chromatography", in Determination of Molecular Weight, A. R. Cooper, ed., John Wiley & Sons, Inc., New York, 1989, pp. 263-300.

7. Z. Grubisic, P. A. Rempp, H. Benoit, J. Polym. Sci., Part B, 5: 753-759 (1967).

8. A. C. Ouano, W. Kaye, J. Polym. Sci.: Polym. Chem. Ed., 12: 1151-1162 (1974).

9. R. C. Jordan, J. Liq. Chromatogr., 3: 439-463 (1980).

10. K. Kamide, A. Kiguchi, Y. Miyazaki, Polym. J., 18: 919-925 (1986).

11. S.I. Ali, S. Ali, Acta Polym., 42: 597-599 (1991).

12. D. C. Lee, T. A. Speckard, A. D. Sorensen, S. L. Cooper, Macromolecules, 19: 2383-2890 (1986).

13. Z. S. Petrović, W. J. MacKnight, Polym. Bull., 27: 281-287 (1991).

14. P. J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, New York, 1953, p. 310.

15. D. Lyman, J. Polym. Sci., 45: 49-59 (1960).

16. A. Halbwachs, Z. Grubisic-Gallot, Macromol. Chem., Rapid Commun., 7: 709-712 (1966).

17. W. H. Stockmayer, L. D. Moore, Jr., M. Fixman, B. N. Epstein, J. Polym. Sci., 16: 517-530 (1955).

18. W. Bushuk, H. Benoit, Can. J. Chem., 36: 1616-1626 (1958).

19. A. C. Ouano, J. Chromatogr., 118: 303-312 (1976).

20. Z. Gallot, Thesis, University of Strasbourg, 1970.

21. M. J. R. Cantow, R. S. Porter, J. F. Johnson, J. Polym. Sci., Polym. Lett., 4: 707-711 (1966).

22. J. G. Rooney, G. Ver Strate, "On Line Determination by Light Scattering of Mechanical Degradation in the GPC Process", in Liquid Chromatography of Polymers and Related Materials III, J. Cazes, ed., Marcel Dekker, Inc., New York, 1981, pp. 207-235.

23. G. W. Rand, A. K. Mukherji, J. Polym. Sci: Polym. Lett. Ed., 20: 501-508 (1982).

24. Z. Grubisic-Gallot, private communication.

25. G. Volet, Thesis, University of Paris 6, 1990; J. Lesec and G. Volet, to be published.

Received: April 20, 1993
Accepted: May 11, 1993