

Solution Properties of Polyurethanes Studied by Static Light Scattering, SEC-MALS, and Viscometry[†]

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[†] Dedicated to the memory of Prof. Dr. Tatjana Malavašič

Abstract

Solution behaviour of PUs of different composition in DMF, LiBr/DMF, and THF was studied by a static light scattering (LS), size exclusion chromatography coupled to a multi-angle light scattering (SEC-MALS), and viscometry. The influence of PU chemical composition, kind of a solvent, and addition of simple salts on PU hydrodynamic volume was investigated. The values of the second virial coefficient (A_2) determined by LS measurements indicated that THF is a better solvent for the flexible soft segments, whereas LiBr/DMF is better for the hard segments in the PU chains. Since the A_2 values of PUs indicated that LiBr/DMF is a worse solvent than THF, the hydrodynamic volumes of all investigated PUs were smaller, as indicated by smaller values for the radius of gyration (R_g) and intrinsic viscosities $[\eta]$ of PUs in LiBr/DMF. The PU molar mass averages and R_g determined in THF (LiBr/DMF) were comparable regardless of the method used (LS or SEC-MALS) and did not depend on solution concentration, indicating that PUs were dissolved on a molecular level. In DMF, peculiar dilute solution behaviour was observed for all PUs investigated. The PU molar mass averages, R_g , and $[\eta]$ were higher than those determined in LiBr/DMF indicating that the PUs in DMF associated to a certain degree dependent on the chemical composition of PU.

Key words: polyurethanes, dilute solution properties, molar mass averages, molar mass distribution, size exclusion chromatography (SEC), light scattering, viscometry

Introduction

Linear segmented polyurethanes (PUs) are multiblock copolymers produced by the addition reaction of an oligomeric diol (polyether or polyester), a diisocyanate and a low molar mass diol as the chain extender.¹ The portion of the polymer chain originating from the oligomeric diol is usually called the soft segment, whereas the hard segments are composed of the reaction products of the diisocyanate and chain extender. Hard and soft segments differ in polarity and capability for hydrogen bond formation. In a solid state, these two kinds of segments tend to phase separate, which gives rise to the interesting and useful properties of these materials. Therefore, the investigations concerning structure–properties relationship of these materials have been the object of an enormous number of papers. On the other hand, a relatively limited amount of data concerning the solution properties of PU has been found in the literature. Particularly rare are literature data regarding the determination of absolute PU molar mass averages and their influence on PU properties.^{2–15}

PU molar mass averages are usually determined by conventional size exclusion chromatography (SEC). Thus, the obtained molar masses are relative values related to the polymer standards used for the column calibration. Since SEC separates macromolecules according to their hydrodynamic volume in a given solvent, which is, in addition to molar mass, strongly influenced by various macromolecular interactions (intra- or intermolecular),^{16–19} it is difficult to evaluate and compare the relative molar masses of PU samples with different chemical composition. The usefulness of SEC technique can be enhanced by the use of a universal calibration concept, which accounts for the differences in the intrinsic viscosities of polymer standards and PU samples of the same molar mass.^{2–6, 10} A deficiency of the universal calibration approach for PU is that the method does not account for composition distribution, which may be present in copolymers synthesized from three or more monomers. Namely, composition distribution, as well as molar mass, influences the intrinsic viscosity of copolymers. SEC coupled to a light scattering detector together with a concentration detector provides absolute polymer molar masses,

without any need for calibration.^{7–15} The variation in average copolymer composition with molar mass can be taken into account using a third detector (UV or IR spectrometer) monitoring only the presence of one segment type.

Most work concerning the absolute PU molar mass averages has been focused on the viscosity and light scattering characterization of individual PU fractions in order to correlate the intrinsic viscosities toward molar masses using the Mark-Houwink-Sakurada equation (MHS). The MHS parameters K and α have been determined for many PU/solvent systems.^{2–8} The SEC-multidetector method was used for the comparison and evaluation of SEC using polystyrene (PS) calibration and SEC using the universal calibration method.^{9,10} The dilute solution behaviour of PUs of different chemical composition was also investigated by SEC coupled to a multi-angle light scattering photometer (MALS),^{11–15} which enables the determination of absolute PU molar mass averages as well as a z-average root-mean-square radius of gyration, $\langle R_g^2 \rangle_z^{1/2}$ (written as R_g).

The aim of the present work was to investigate PU dilute solution behavior depending on PU chemical composition, type of solvent (tetrahydrofuran, THF, as a low polarity solvent and *N,N*-dimethylformamide, DMF, as a high polarity solvent), solution concentration, and addition of simple salts. For this purpose we synthesized segmented non-carboxylated and carboxylated PUs, as well as the model compounds representing hard and soft segments in PU chains. With static light scattering measurements we were able to determine the PU weight average molar mass (\overline{M}_w), radius of gyration (R_g), and second virial coefficient (A_2) in a given solvent. From the comparison of A_2 values between PU samples of different chemical composition we inferred the solvent quality. SEC-MALS allowed us to determine PU molar mass averages (MMA), molar mass distribution (MMD), RMS radius averages, RMS radius distribution, and, in addition, the conformation of PU macromolecules in a given solvent. We investigated the dependence of reduced viscosity on concentration by viscosity measurements. The intrinsic viscosities ($[\eta]$) of PUs were estimated by the extrapolation of reduced viscosity to zero concentration. Since hydrodynamic volume (V_h) is proportional to the product of $[\eta]$ and molar mass, we estimated the influence of PU chemical composition and the kind of solvent on its V_h from the PU $[\eta]$.

Experimental

Materials and Polymer Synthesis

Segmented PU were synthesized from an aliphatic or aromatic diisocyanate (1,6-hexamethylene diisocyanate; HDI, Fluka or methylene bis(*p*-phenylene isocyanate; MDI, Aldrich), polyether diol (poly-

(tetramethyleneoxide); PTMO, $\overline{M}_n=1000$ g/mol, BASF), and low molar mass diols (2,2-dimethyl-1,3-propanediol; NPG, Fluka or/and 2,2-bis(hydroxymethyl) propionic acid; DMPA, Jansen) in *N,N*-dimethylformamide (DMF with water content below 0.005%, Aldrich). The molar ratio of diisocyanate to polyether diol to chain extender(s) was 3:1:2 (in case of both chain extenders used, the molar ratio between NPG:DMPA was 1:1). The chain extension reaction was catalyzed by dibutyltin dilaurate (DBTDL, Acima). The model compound representing the soft segments was synthesized from diisocyanate and polyether diol (molar ratio 1:1), whereas the model compounds representing the hard segments were prepared from diisocyanate and monomeric chain extenders, NPG or DMPA (molar ratio 1:1). Non-carboxylated PUs are designated as H-D0 (prepared with HDI) and M-D0 (prepared with MDI), while carboxylated PU is designated as M-D50, where “50” stands for the molar percentage of DMPA in the chain extender mixture. Polymers were precipitated by pouring their DMF solutions into distilled water and dried under a vacuum at 50°C, until the ¹H signals of water and DMF in the NMR spectra disappeared. The detailed preparation of the samples was described in our previous paper.¹¹

Characterization

Static light scattering measurements were obtained for PU solutions using a multi-angle light scattering instrument equipped with a He-Ne laser, $\lambda_0=633$ nm (Wyatt Technology Corp.). Measurements were made on highly diluted fractions eluting from a size exclusion chromatograph consisting of a Hewlett Packard pump series 1100, injector Rheodyne, and an Optilab-DSP interferometric refractometer (DR) as a concentration detector (Wyatt Technology Corp.). A PLgel 5 μ m column Mixed C of 30 cm length with a precolumn (Polymer Laboratories) was used. The mobile phase was tetrahydrofuran (THF, $\epsilon_{25}=7.6$, water content <0.05%, Fluka) stabilized with 0.025% BHT; the flow rate was 1.0 mL/min and *N,N*-dimethylformamide (DMF, $\epsilon_{25}=36.7$, water content <0.01%, Aldrich) or DMF with added LiBr (0.1M); the flow rate was 0.8 mL/min. The masses of the PU injected into the column were typically $(1.5–3.0)\times 10^{-3}$ g (solution concentration: 1.5–3.0% w/v, injection volume 100 μ L). Data acquisition and evaluation were carried out using Astra 4.73.04 software (Wyatt Technology Corp.).

The Dawn-DSP photometer was calibrated with spectrometric grade toluene and the normalization of the detectors was performed with standard monodisperse polystyrene of low molecular weight, which does not show angular dependence of the light scattering signal. Standard monodisperse polystyrene was also used for interdetector volume determination.

The molar mass (M) and the root-mean-square radius of gyration (R_g) were evaluated at selected intervals along the distribution eluting from the column using well-known expressions of classical light scattering.^{20–24}

$$\frac{Kc}{R(\theta)} = \frac{1}{MP(\theta)} + 2A_2c \quad (1)$$

where:

$$P^{-1}(\theta) = 1 + \frac{16\pi^2 n^2 R_g^2 \sin^2(\theta/2)}{3\lambda^2} + \dots \quad (2)$$

and:

$$K = \frac{4\pi^2 n^2 (dn/dc)^2}{\lambda^4 N_A} \quad (3)$$

The symbols are: λ is the wavelength of the incident light, 632.8 nm, n is the refractive index of the solvent and $R(\theta)$ is the excess Raileigh factor (minus the solvent) at scattering angle θ . The concentration, c , of the polymer for each elution volume was determined using Optilab-DSP interferometric refractometer. PU differential refractive index increments (dn/dc) were measured separately on an Optilab-DSP refractometer. The molar mass averages were obtained from light scattering measurements on fractions eluting from the size exclusion chromatograph supposing that each slice, i , along the chromatogram contained molecules of a single, or at least very narrow, molar mass, M_i . Therefore, once a separation had been achieved and the collected data processed, the MMA were calculated from the following relations:

$$\overline{M}_n = \frac{\sum_i M_i N_i}{\sum_i N_i} = \frac{\sum_i c_i}{\sum_i (c_i / M_i)} \quad (4)$$

$$\overline{M}_w = \frac{\sum_i M_i^2 N_i}{\sum_i M_i N_i} = \frac{\sum_i (c_i M_i)}{\sum_i c_i} \quad (5)$$

$$\overline{M}_z = \frac{\sum_i M_i^3 N_i}{\sum_i M_i^2 N_i} = \frac{\sum_i (c_i M_i^2)}{\sum_i c_i M_i} \quad (6)$$

The second term in equation 1 can be neglected, since the concentrations of eluting polymer were very low.

The Optilab-DSP interferometric refractometer was used for measuring the PU differential refractive index increments (dn/dc) at the same wavelength as operating the Dawn-DSP laser photometer ($\lambda_0=633$ nm). Data acquisition and evaluation utilized DNDC 5.00 software. Due to the fluctuation in chemical composition and molar mass of PU, as well as the fact that only an average dn/dc of the sample and not the dn/dc of the individual fractions could be used, SEC-MALS gave actually only the apparent weight average molar mass (\overline{M}_w) of segmented PU.

The Dawn-DSP laser photometer was also used for static light scattering measurements on the

unfractionated PU at higher concentrations, but still in the dilute region. The weight average molar mass, \overline{M}_w , the z -average root-mean-square radius of gyration (R_g), and the second-order virial coefficient, A_2 , are directly determined from the Zimm plot. Such a plot has two limiting curves, which within the experimental error intersect the ordinate at the same point representing the weight average molar mass, $1/\overline{M}_w$. The scattering curve at zero scattering angle, $\theta=0$, gives quantitative information on the interparticle interactions, with A_2 at its initial part at low concentration. The angular dependent scattering data at $c=0$ is a curve that gives information on the size and shape of the individual macromolecules, as shown by the parameter R_g . The temperature and the solvents used were the same as those in the SEC-MALS measurements.

PU solution viscosities were measured using an Ubbelohde capillary viscometer in a thermostatic water bath held at 25 ± 0.05 °C. A Ubbelohde capillary of 0.46 mm was used for PU solutions in THF, while a capillary of 0.53 mm in diameter was used for PU solutions in DMF and LiBr/DMF. The flow times of PU solutions and solvents were corrected for the kinetic energy effects. The preparation of the samples and a detailed measurement procedure are described in our previous paper.¹²

The ¹H and ¹³C NMR spectra were recorded using a Varian VXR 300 NMR spectrometer in a 10% solution of PU samples in THF-d₄, DMF-d₇ and LiBr/DMF-d₇. TMS was used as an internal reference.

Results and Discussion

In DMF, all investigated PUs show peculiar dilute solution behavior. In SEC, carboxylated PU elutes from the column at very small elution volumes, near the high molar mass exclusion limit of the column, whereas the SEC curves of non-carboxylated PUs and the model PU, MDI-PTMO, show bimodal molar mass distributions. The LS signal of PU fractions, which eluted from the column first, is very intense and shows pronounced angular dependence.¹³ Non-linear angular dependence of the scattered light is also characteristic for the PUs measured by static light scattering (Zimm plot²⁵ in Figure 1). Such behavior is typical of solutions containing very high molar mass species, which in the case of PUs in DMF originated from the association of macromolecular chains.¹³ The determined PU molar mass averages and R_g are higher than the corresponding values determined in THF or LiBr/DMF (Tables 1, 2). The values determined by SEC-MALS are also higher than those determined by LS. The dependence of the degree of association on solution concentration, temperature, and PU composition is described in our previous paper.¹³

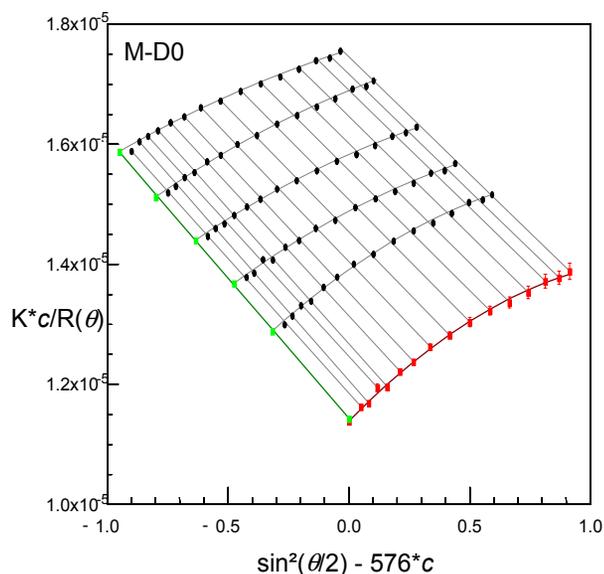


Figure 1. Zimm plot of non-carboxylated PU M-D0 in DMF. M-D0: $R_g = 37 \pm 1$ nm, $\bar{M}_w = (8.77 \pm 0.04) \cdot 10^4$ g mol $^{-1}$, $A_2 = (1.35 \pm 0.02) \cdot 10^{-3}$ mol mL g $^{-2}$.

The peculiar dilute solution behavior of PUs in DMF is also demonstrated by viscosity measurements (Figure 2). The concentration dependencies of PU reduced viscosities are not linear. The upward discrepancies from the straight lines were observed in very dilute regions, below approx. 0.1 g/dL. Other authors have observed similar dilute solution behavior of non-ionic PUs in polar amide solvents.^{26–30} The association of PUs was prevented by the addition of LiBr to DMF.

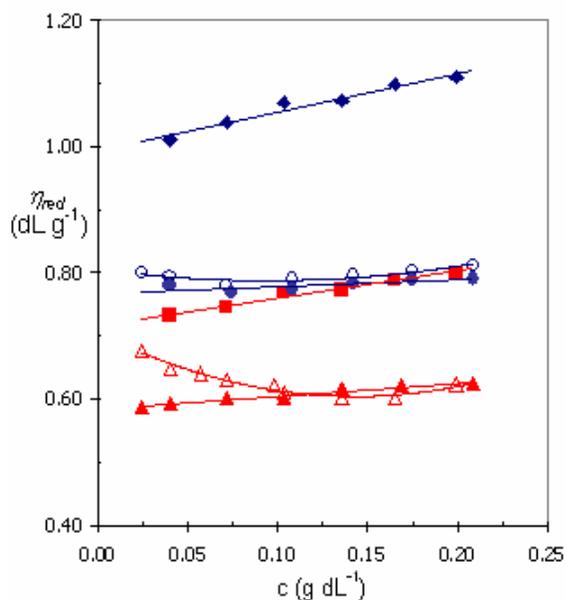


Figure 2. Reduced viscosity, η_{red} , of non-carboxylated PU M-D0 and carboxylated PU M-D50, as a function of solution concentration in THF, DMF, and LiBr/DMF; \blacklozenge : M-D0 in THF; \circ : M-D0 in DMF; \bullet : M-D0 in LiBr/DMF; \blacksquare : M-D50 in THF; \triangle : M-D50 in DMF; \blacktriangle : M-D50 in LiBr/DMF.

The \bar{M}_w and R_g values determined by static light scattering measurements on unfractionated PUs in LiBr/DMF (Figure 3, Table 1) or THF (Figure 4, Table 1) are in good agreement with the corresponding average values obtained by summation of the slices in the SEC-MALS measurements (Table 2). In both solvents, the molar mass averages are not dependent on solution concentration, indicating that PUs are dissolved on a molecular level. The differences in \bar{M}_w between PU of different chemical composition are attributed to the side reactions occurring during PU synthesis. The isocyanate group reacted to some extent with water and/or the carboxylic group of DMPA yielding urea as a by-product, as shown by the NMR spectra of PUs.

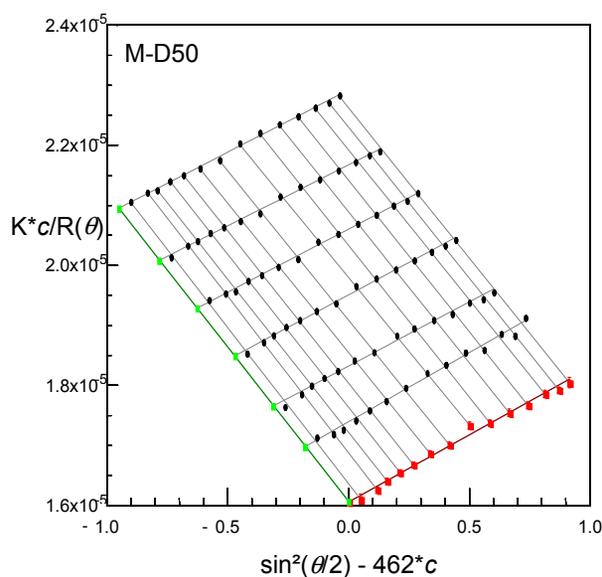
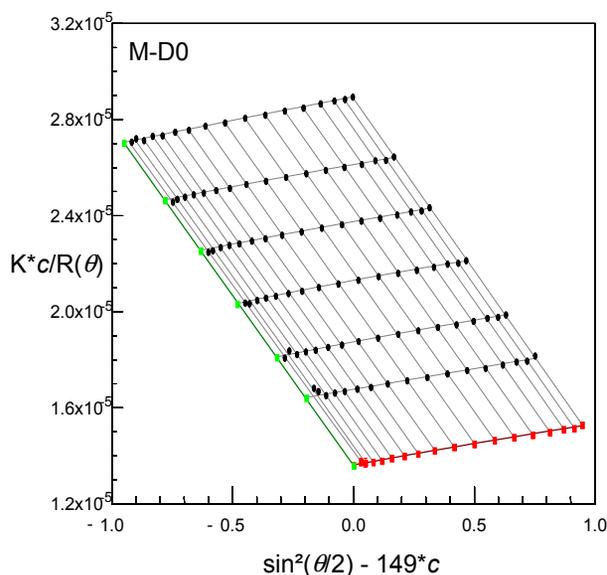


Figure 3. Zimm plots of non-carboxylated PU M-D0 and carboxylated PU M-D50 in LiBr/DMF. M-D0: $R_g = 23 \pm 1$ nm, $\bar{M}_w = (7.35 \pm 0.04) \cdot 10^4$ g mol $^{-1}$, $A_2 = (1.06 \pm 0.01) \cdot 10^{-3}$ mol mL g $^{-2}$. M-D50: $R_g = 22 \pm 1$ nm, $\bar{M}_w = (6.23 \pm 0.01) \cdot 10^4$ g mol $^{-1}$, $A_2 = (1.19 \pm 0.01) \cdot 10^{-3}$ mol mL g $^{-2}$.

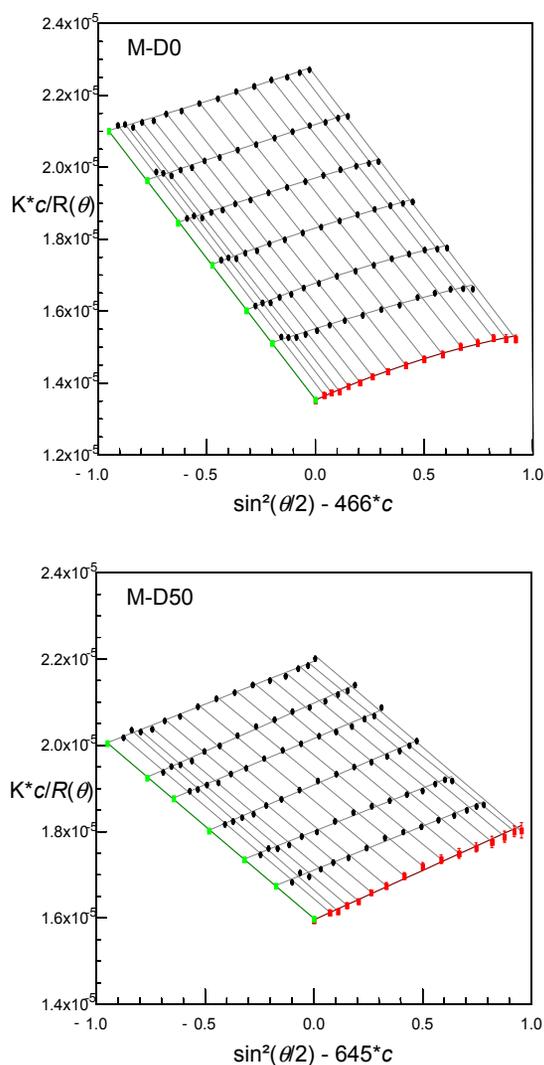


Figure 4. Zimm plots of non-carboxylated PU M-D0 and carboxylated PU M-D50 in THF. M-D0: $R_g = 28 \pm 2$ nm, $\overline{M}_w = (7.39 \pm 0.03) \cdot 10^4$ g mol $^{-1}$, $A_2 = (1.83 \pm 0.01) \cdot 10^{-3}$ mol mL g $^{-2}$. M-D50: $R_g = 23.5 \pm 0.4$ nm, $\overline{M}_w = (6.26 \pm 0.02) \cdot 10^4$ g mol $^{-1}$, $A_2 = (1.38 \pm 0.01) \cdot 10^{-3}$ mol mL g $^{-2}$.

The values of A_2 determined in THF are positive and increase in the order M-D50 < M-D0 < H-D0 < MDI-PTMO (Table 1). These results imply that low polarity THF is a good solvent for flexible soft segments (MDI-PTMO), but not as good a solvent for the hard segments. This is also evident from the only partial solubility of model compounds presenting hard segments (MDI-NPG, MDI-DMPA) in THF. Therefore, in very dilute solutions of PU in THF, PU chains might form intramolecular associates via intramolecular H-bond interactions between polar groups in hard segments. The degree of intramolecular interaction depends on the chemical composition of hard segments and their content within the macromolecular chains. Intramolecular interactions greatly influence the PU hydrodynamic volume.

Table 1. Results of static light scattering measurements for solutions of PU of different chemical composition in THF, LiBr/DMF, and DMF, together with PU dn/dc values.*

Sample	Parameters	THF	LiBr/DMF	DMF
H-D0	dn/dc (mL g $^{-1}$)	0.083	0.048	0.045
	$\overline{M}_w \cdot 10^{-4}$ (g mol $^{-1}$)	3.2	3.2	9.2
	R_g (nm)	11	10	65
	$A_2 \cdot 10^3$ (mol mL g $^{-2}$)	1.87	0.91	1.46
M-D	dn/dc (mL g $^{-1}$)	0.143	0.105	0.101
	$\overline{M}_w \cdot 10^{-4}$ (g mol $^{-1}$)	7.4	7.35	8.8
	R_g (nm)	28	23	37
	$A_2 \cdot 10^3$ (mol mL g $^{-2}$)	1.83	1.06	1.35
M-D50	dn/dc (mL g $^{-1}$)	0.140	0.104	0.099
	$\overline{M}_w \cdot 10^{-4}$ (g mol $^{-1}$)	6.3	6.2	–
	R_g (nm)	23	22	–
	$A_2 \cdot 10^3$ (mol mL g $^{-2}$)	1.38	1.19	–
MDI-PTMO	dn/dc (mL g $^{-1}$)	0.108	0.072	0.068
	$\overline{M}_w \cdot 10^{-4}$ (g mol $^{-1}$)	3.1	3.0	6.9
	R_g (nm)	14	12	51
	$A_2 \cdot 10^3$ (mol mL g $^{-2}$)	1.95	0.33	0.68

* The model compounds representing hard segments (MDI-NPG, MDI-DMPA) were only partially soluble in all the solvents used.

Table 2. Results of SEC-MALS measurements for solutions of PU of different chemical composition in THF, LiBr/DMF, and DMF.*

Sample	Parameters	THF	LiBr/DMF	DMF***
H-D0	$\overline{M}_w \cdot 10^{-4}$ (g mol $^{-1}$)	3.2	3.2	10^4 – 10^5
	$\overline{M}_n \cdot 10^{-4}$ (g mol $^{-1}$)	2.5	2.5	
	$\overline{M}_w / \overline{M}_n$	1.3	1.3	
	R_g (nm)	12**	10**	>100
M-D0	$\overline{M}_w \cdot 10^{-4}$ (g mol $^{-1}$)	7.3	7.4	10^4 – 10^5
	$\overline{M}_n \cdot 10^{-4}$ (g mol $^{-1}$)	5.2	5.3	
	$\overline{M}_w / \overline{M}_n$	1.4	1.4	
	R_g (nm)	23	19	>100
M-D50	$\overline{M}_w \cdot 10^{-4}$ (g mol $^{-1}$)	6.2	6.3	10^4 – 10^6
	$\overline{M}_n \cdot 10^{-4}$ (g mol $^{-1}$)	4.4	4.2	
	$\overline{M}_w / \overline{M}_n$	1.4	1.5	
	R_g (nm)	20	16	>100
MDI-PTMO	$\overline{M}_w \cdot 10^{-4}$ (g mol $^{-1}$)	3.1	3.0	10^4 – 10^5
	$\overline{M}_n \cdot 10^{-4}$ (g mol $^{-1}$)	2.6	2.3	
	$\overline{M}_w / \overline{M}_n$	1.2	1.3	
	R_g (nm)	15	below 10**	>100

* The model compounds representing hard segments (MDI-NPG, MDI-DMPA) were only partially soluble in all the solvents used. ** unreliable R_g determination since the values are at the lower limit of the photometer sensitivity. *** MMA and MMD values depend on solution concentration and temperature.¹³

The conformational plots, representing the dependence of $\log R$ on $\log M$, reveal that all investigated PU samples, except carboxylated PU M-D50, have random coil conformation in THF (the slope of the

line around 0.5, Figure 5). From the comparison of the molar mass distributions of H-D0 with slightly higher MMA and lower A_2 than corresponding values for MDI-PTMO (Tables 1, 2), we can see that at a particular elution volume ($V_{e,i}$; i representing a particular slice in the chromatogram) where the macromolecules with the same hydrodynamic volume elute from the column, the M_i of H-D0 is slightly higher than that of MDI-PTMO (Figure 6). This means that the conformation of H-D0 coils is more compact than that of MDI-PTMO coils. These results can be explained by the higher content of urethane groups in the chains of H-D0 leading to a greater number of intramolecular interactions. This is also confirmed by the differences between H-D0 and MDI-PTMO in term of R_g and $[\eta]$ (Tables 1, 2). The intermolecular interactions are most pronounced in the case of carboxylated PU M-D50 containing hard segments bearing two kinds of polar groups, urethane and carboxyl groups, which are able to form H-bonds. Therefore, M-D50 has the lowest A_2 value (Table 1) and the most compact sphere conformation in THF (slope of the line is approx. 0.33, Figure 5).

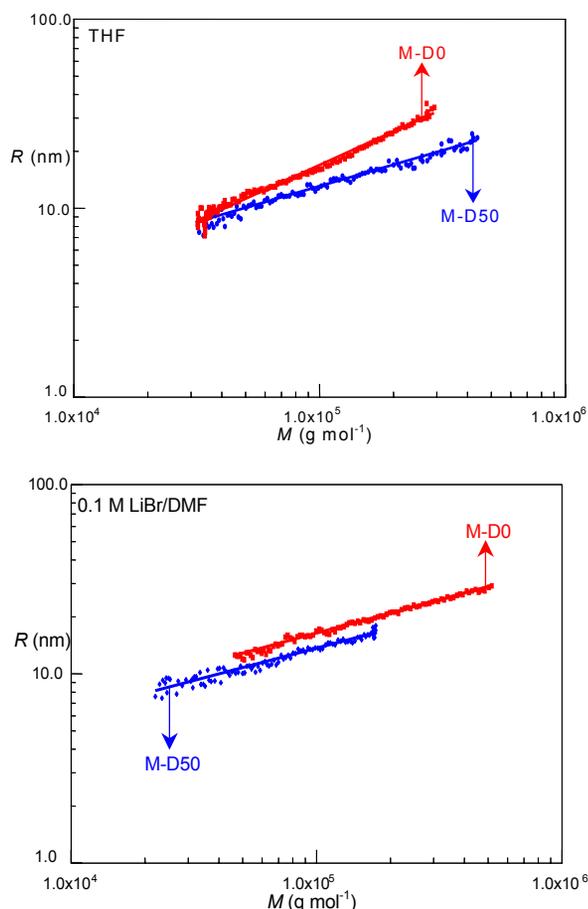


Figure 5. Conformation plots ($\log R$ as a function of $\log M$) for non-carboxylated PU M-D0 and carboxylated PU M-D50 in THF (line slope: 0.53 for M-D0 and 0.33 for M-D50), and LiBr/DMF (line slope: 0.35 for M-D0 and 0.34 for M-D50).

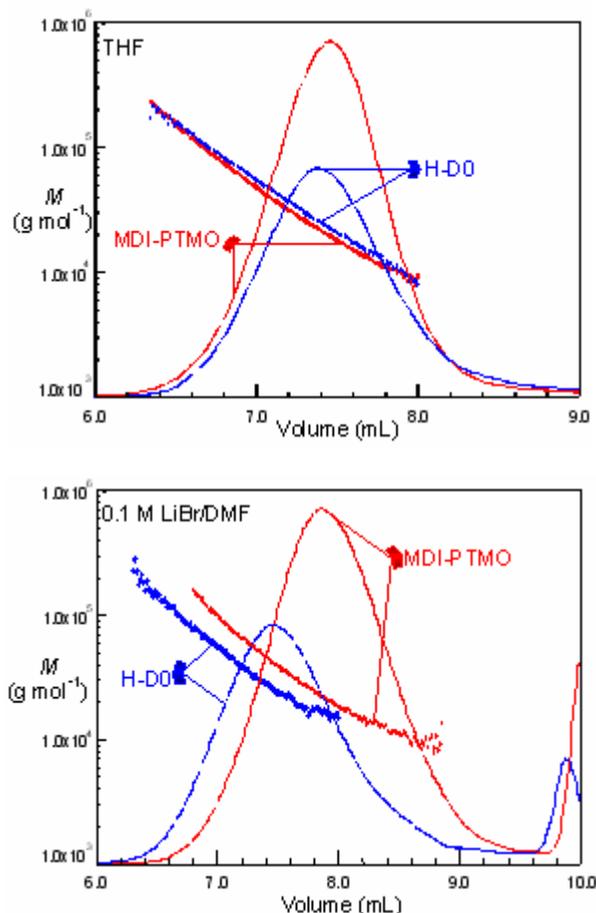


Figure 6. Molar mass (M) as a function of elution volume together with RI chromatograms for non-carboxylated PU H-D0 and model PU MDI-PTMO in THF and LiBr/DMF.

In LiBr/DMF the determined molar mass averages of PUs are comparable to those determined in THF, although the A_2 values are lower (Tables 1, 2). Since LiBr/DMF is a worse solvent for PU than THF, the PU hydrodynamic volumes are smaller, as indicated by smaller values of R_g and $[\eta]$ (Tables 1, 2 and Figure 2). A_2 increases such that MDI-PTMO < H-D0 < M-D0 < M-D50; the opposite of the results in THF (Table 1). These results indicate that LiBr/DMF is a good solvent for hard segments, but not as good a solvent for soft segments. Since soft segments are poorly solvated, M-D0 and M-D50 have compact sphere conformation (Figure 5). The values of R_g for H-D0 and MDI-PTMO are at the lower limit of the sensitivity of the photometer and have a high error of determination (Tables 1, 2). Therefore, in this solvent it was not possible to determine their conformation. Nevertheless, the comparison of molar mass distribution of these two kinds of PU indicates that the conformation of MDI-PTMO is more compact than that of H-D0 (Figure 6). Good solvation of hard segments by LiBr/DMF is also evident from the chemical shifts of protons of urethane and urea groups

in PU ^1H NMR spectra. The chemical shifts of these groups in LiBr/DMF- d_7 are in a lower magnetic field (higher ppm) than in THF- d_4 .

Conclusions

The investigation of dilute solution behavior of PUs by LS, SEC-MALS and viscometry indicated that PU hydrodynamic volume depends not only on macromolecular size, but also on a kind of the solvent and PU chemical composition. Solvent polarity and chemical composition of PU chains determine the kind and intensity of interactions between the segments in PU, which is reflected in R_g and $[\eta]$ of individual PU sample. The A_2 parameter, which was determined by static light scattering measurements, depends on the PU chemical composition and has a positive value in all the solvents studied. The values of A_2 indicate that THF is a better solvent for the soft segments, whereas LiBr/DMF and DMF are better for the hard segments in PU chains. The weight average molar masses of a particular PU determined by LS or SEC-MALS in THF or LiBr/DMF are comparable and independent on solution concentration indicating that PUs are dissolved on the molecular level. Molar mass averages and R_g determined in DMF were due to association higher than those determined in THF or LiBr/DMF. The association of PUs in DMF was prevented by the addition of LiBr to DMF.

Dedication

The authors wish to dedicate this contribution to the memory of Prof. Tatjana Malavašič in appreciation for her professional contribution to the development of polymer science in Slovenia, as well as her personal influence on generations of students and coworkers.

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References

- G. Oertel, "Polyurethane Handbook", Hanser Publishers, New York, 1985.
- J. Moacanin, *J. Appl. Polym. Sci.* **1959**, *1*, 272–282.
- H. C. Beachell, J. C. Peterson, *J. Polym. Sci.: Part A-1* **1969**, *7*, 2021–2029.
- Z. Tuzar, H. C. Beachell, *J. Polym. Sci.: Polym. Lett. Ed.* **1971**, *9*, 37–41.
- L. Šimek, Z. Tuzar, M. Bogdanecky, *Makromol. Chem.: Rapid Commun.* **1980**, *1*, 215–220.
- S. I. Ali, S. Ali, *Acta Polym.* **1991**, *42*, 597–599.
- K. Kamide, A. Kiguchi, Y. Miyazaki, *Polym. J.* **1986**, *18*, 919–925.
- V. Kašparkova, L. Šimek, *Macromol. Chem. Phys.* **1996**, *197*, 3757–3772.
- D. C. Lee, T. A. Speckhard, A. D. Sorensen, S. L. Cooper, *Macromolecules* **1986**, *19*, 2383–2390.
- M. Žigon, A. Mirčeva, T. Malavašič, Z. Grubišič – Gallot, *J. Chromatogr.* **1993**, *16*, 3813–3825.
- M. Žigon, E. Žagar, *Polymer* **1999**, *40*, 2727–2735.
- M. Žigon, E. Žagar, *Polymer* **2000**, *41*, 3513–3521.
- M. Žigon, E. Žagar, *Int. J. Polym. Anal. Charact.* **2001**, *6*, 521–532.
- F. Prochazka, T. Nicolai, D. Durand, *Macromolecules* **2000**, *33*, 1703–1709.
- R. Murgasova, E. L. Brantley, D. M. Hercules, *Macromolecules* **2002**, *35*, 8338–8345.
- W. W. Yau, J. J. Kirkland, D. D. Bly, "Size Exclusion Liquid Chromatography" in "High Performance Liquid Chromatography", Ed. P. R. Brown, R. A. Hartwick, John Wiley & Sons, New York, **1988**, 277–317.
- M. G. Styring, A. E. Hamielec, "Determination of Molecular Weight Distribution by Gel permeation Chromatography" in "Determination of Molecular Weight", Ed. A. R. Cooper, John Wiley & Sons, New York, **1989**, 263–301.
- S. T. Balke, "Characterization of Complex Polymers by Size Exclusion Chromatography and High Performance Liquid Chromatography" and G. R. Meira, "Data Reduction in Size Exclusion Chromatography of Polymers" in "Modern Methods of Polymer Characterization", Ed. H. G. Barth, J. W. Mays, John Wiley & Sons, New York, **1991**, 1–103.
- J. W. Dawkins, "Size Exclusion Chromatography", in "Comprehensive Polymer Science; Polymer Characterization", Ed. G. Allen, J. C. Bevington, Vol.1, Pergamon Press, New York, **1989**, 231–328.
- P. Kratochvíl, "Classical Light Scattering from Polymer Solutions", Elsevier, Amsterdam, **1987**.
- M. B. Huglin, "Light Scattering from Polymer Solutions", Academic Press, London, **1972**.
- P. J. Flory, "Statistical Mechanics of Chain Molecules", Interscience Publishers (a Division of John Wiley & Sons), New York, **1969**.
- B. Chu, "Laser Light Scattering; Basic Principles and Practise", Academic Press, London, **1991**.
- W. Burchard, G. D. Patterson "Light Scattering from Polymers", Springer-Verlag, Berlin, **1983**.
- H. Zimm, *J. Chem. Phys.* **1948**, *16*, 1099–1108.
- Y. Itoh, R. Aoki, S. Matsuda, *Sen-I-Gakkai Shi* **1996**, *52*, 339–347.
- H. G. Barth, F. E. Regnier, *J. Chromatogr.* **1980**, *192*, 275–293.
- N. Hann, *J. Polym. Sci.: Polym. Chem.* **1977**, *15*, 1331–1339.
- Y. Nakano, A. Nakashima, H. Hanahata, K. Okajima, *Polymer* **1997**, *38*, 817–825.
- I. A. Kovaleva, N. I. Morozova, P. I. Zubov, *Vysokomol. Soedin A+* **1986**, *28*, 753–757.

Povzetek

Raziskali smo lastnosti razredčenih raztopin PU različne kemijske sestave v THF, LiBr/DMF in DMF s statičnimi meritvami sipanja svetlobe (LS), izključitveno kromatografijo v povezavi s sipanjem svetlobe (SEC-MALS) in merjenjem koncentracijske odvisnosti viskoznosti raztopin. Ugotovili smo, da so povprečja molskih mas, ki smo jih določili z LS ali SEC-MALS metodo v THF (LiBr/DMF) za vse raziskane PU primerljiva, poleg tega pa tudi neodvisna od koncentracije raztopin, kar kaže, da so bili PU v omenjenih topilih raztopljeni na molekularnem nivoju. Iz vrednosti drugega virialnega koeficienta PU, ki smo jih določili z LS metodo, so pokazale, da je THF boljše topilo za PU kot LiBr/DMF, in da je THF predvsem dobro topilo za mehke segmente, LiBr/DMF pa za trde segmente v PU. Iz omenjenega razloga ima posamezen PU v LiBr/DMF manjši hidrodinamski volumen kot v THF, kar dokazujejo manjše vrednosti R_g in $[\eta]$ kot v THF. PU v DMF so kazali neobičajne lastnosti; zelo visoka povprečja molskih mas, R_g in $[\eta]$ v primerjavi z vrednostmi, ki smo jih določili v LiBr/DMF ali THF. Zato smo sklepali, da PU v DMF asociirajo, stopnja asociacije pa je odvisna od kemijske sestave PU.