

# Solution properties of carboxylated polyurethanes and related ionomers in polar solvents (DMF and LiBr/DMF)

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## Abstract

Solution properties of carboxylated polyurethanes (CPUs) and related ionomers (PUIs) in *N,N*-dimethylformamide (DMF) and DMF with added LiBr of different concentrations were investigated by size exclusion chromatography (SEC), viscometry and in the case of CPUs also by SEC coupled with a multi-angle light scattering detector (SEC–MALS). In DMF, both kinds of PUs have multimodal molar mass distributions, while the reduced viscosity–concentration profiles indicate an upturn in very dilute regions usually related to the polyelectrolyte effect. However, SEC–MALS measurements of non-carboxylated PU (NPU) and CPUs indicate that these PUs aggregate in DMF. After the addition of LiBr to DMF unimodal molar mass distributions with much larger elution volumes ( $V_e$ ) and linear concentration dependences of reduced viscosity are obtained for both kinds of PUs. LiBr in DMF not only screens the ionic groups of carboxylated PUIs but also specifically interacts with the polar groups of PUs. Thus, LiBr suppresses any electrostatic and/or molecular interactions and consequently eliminates all the peculiarities encountered in SEC characterization of both kinds of PUs in DMF. © 2000 Elsevier Science Ltd. All rights reserved.

**Keywords:** Carboxylated polyurethanes; Polyurethane ionomers; Size exclusion chromatography

## 1. Introduction

Polyurethanes (PUs) are an important class of block copolymers used in a variety of fields. The incorporation of functional groups (i.e. carboxylic, sulfonic, phosphonic groups) in the PU backbone, able to react further covalently or non-covalently, leads to PU-ionomers with the improved characteristics (adhesion, dyeability, ionic conductivity, etc.) or polymers with special properties (haemocompatibility, polymers with shape memory effects and non-linear optic properties). This kind of PUs are utilized mainly as water dispersions (coatings, adhesives) and also as biomedical devices, temperature-sensing elements, polymer electrolytes, etc.

The molar masses of PUs are usually determined by size exclusion chromatography (SEC), which separates macromolecules according to their hydrodynamic volume ( $V_h$ ) [1]. SEC molar masses are relative values related to the polymer standards used for the column calibration. Hydrodynamic volume is, particularly in the case of PUs and PU-ionomers, beside molar mass, strongly influenced by various

interactions between PU polar groups and/or charged sites located along the macromolecular backbone, as well as between macromolecules and the solvent [2–7]. Therefore, the evaluation and comparison of the relative molar masses of different PU samples is difficult.

Electrostatic interactions have a large influence on the elution process of ionomers and result in peculiar SEC curves [8]. Namely, in non-polar or low-polarity solvents such as THF, PU-ionomers have unexpectedly large elution volumes as a consequence of intramolecular dipolar attractions between ion pairs [3]. In high polarity solvents (DMF, *N,N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidinone (NMP) etc.), SEC curves show multiple peaks with abnormally small elution volumes due to repulsive electrostatic interactions between like charges on the same chain that lead to chain expansion, also known as the polyelectrolyte effect [4]. Such behavior was reported for SEC analysis of PU-anionomers in DMF by George et al. [5] and Radhakrishnan et al. [6]. The addition of LiBr to DMF resulted in unimodal distribution curves with larger elution volumes. Namely, LiBr acts as a screening electrolyte that suppresses the polyelectrolyte effect and thus leads to contraction of the ionomer chain [4]. Hann [7] reported another anomalous SEC behavior of PU-ionomers in DMF: PU-cationomer with quaternary amine groups was found to strongly interact

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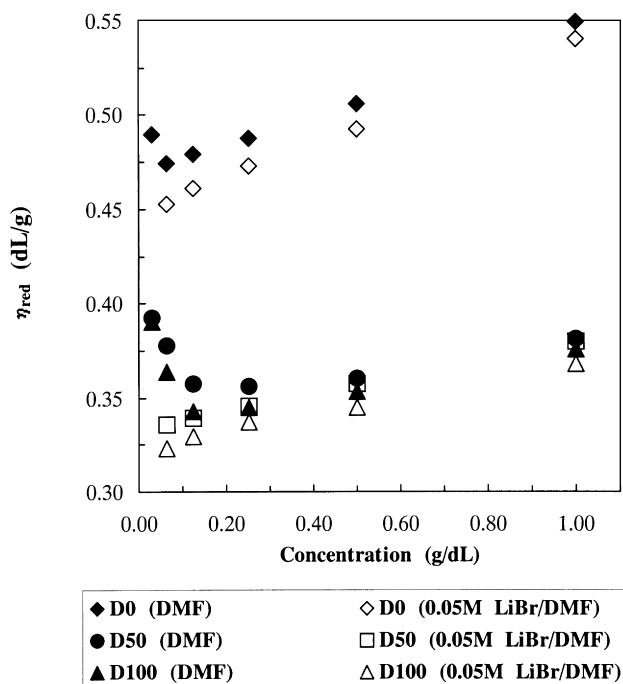


Fig. 1. Reduced viscosity ( $\eta_{red}$ ) vs. concentration for non-carboxylated and carboxylated PUs (DX; X = 0, 50, 100) in DMF and 0.05 M LiBr/DMF.

with the column packing and thus eluted at unexpectedly large elution volume. The polymer-column interaction was prevented by the addition of LiBr to DMF. Other electrolytes, like  $Bu_4NBr$  [9] and  $LiNO_3$  [10], have also been used in the place of LiBr for SEC of PU-ionomers in DMAc.

This work focuses on dilute solution properties of PUs in DMF and LiBr/DMF depending on their chemical composition, i.e. a carboxylic group content, ionic group concentration and kind of counterion and on the LiBr concentration in DMF. Non-carboxylated PU (NPU), carboxylated PUs (CPUs) with different contents of carboxylic groups and related PU-ionomers (PUIs) with different counterions were characterized by SEC and viscosity measurements. Molar mass averages of NPU and CPUs were also determined by SEC coupled with a MALS photometer (SEC-MALS). Dilute solution behavior of the same PUs in THF has previously been reported [3].

## 2. Experimental

### 2.1. Materials and synthesis

Non-carboxylated PU (NPU) was synthesized from hexamethylene diisocyanate (HDI, Fluka), poly(tetramethyleneoxide) (PTMO,  $M_n = 1000$ , BASF) and 2,2-dimethyl-1,3-propanediol (synonym neopentyl glycol, NPG, Fluka) in *N,N*-dimethylformamide (DMF, water content <0.005%, Aldrich) as a 40% solution. Carboxylated PUs (CPUs) were prepared in a similar way, only that 25, 50 and

100% of NPG were replaced with an ionic chain extender 2,2-bis(hydroxymethyl)propionic acid (synonym dimethylolpropionic acid, DMPA, Jansen). The molar ratio of MDI to PTMO to chain extender(s) was 3:1:2. The chain extension reaction was catalyzed with dibutyltin dilaurate (DBTDL, Acima). Polymers were precipitated by pouring their DMF solutions into distilled water and dried under a vacuum at 50°C, until  $^1H$  signals of water and DMF in the NMR spectra disappeared.

PU-ionomers (PUIs) were prepared by neutralization of carboxylic groups with a metal hydroxide ( $LiOH \cdot H_2O$ ,  $KOH$ ,  $Ca(OH)_2$ , Kemika and  $NaOH$ , Chemapol) in methyl ethyl ketone (MEK, Merck Alkaloid).

The detailed preparation of the samples was described in our previous paper [3]. The following designation of non-carboxylated PU (NPU), carboxylated PUs (CPUs) and PU-ionomers (PUIs) is used throughout this paper:

DX...NPU and CPUs; X is the molar percentage (mol%) of DMPA in the chain extender mixture.  
DX-M...PUIs; M is the counterion.

### 2.2. Characterization methods

SEC measurements were performed at room temperature on a Perkin-Elmer liquid chromatograph equipped with an LC-30 differential refractometer (DRI). A PLgel 5  $\mu m$  column Mixed D of 30 cm length with a precolumn and eluents DMF or DMF with added LiBr (Aldrich) at a flow rate of 0.8 ml/min were used. The sample concentration was 1% (w/v) and the injection volume 20  $\mu l$ . We report only elution volumes ( $V_e$ ) of PUs as the calculation of the relative molar mass averages based on polystyrene (PS) calibration curve in this highly polar solvents gives meaningless values. Namely, strong interactions of PS standards with column packing move the calibration curve toward higher elution volumes resulting in excessively high molar mass values of PUs [11].

The SEC-MALS measurements of NPU and CPUs were performed at room temperature on a Wyatt Technology Dawn-DSP instrument equipped with an He-Ne laser ( $\lambda_0 = 633$  nm) and an Optilab-DSP interferometric refractometer operating at the same wavelength as the DOWN. The injected amounts of the samples were approximately  $3 \times 10^{-3}$  g (solution concentration  $\sim 3\%$ , (w/v)). The refractive index increments ( $dn/dc$ ) were measured by an Optilab DSP. Data acquisition and evaluation were carried out using Astra 4.50 and DNDC 5.00 software.

Solution viscosity was measured in DMF and LiBr/DMF using an Ubbelohde capillary viscometer, whose size was selected to be appropriate to the viscosity range of the samples under study. In all cases, the flow times at  $25 \pm 0.05^\circ C$  were more than 171.47 s for PU solutions in DMF and more than 186.12 s for PU solutions in 0.10 M LiBr/DMF. The flow times of PU solutions and both solvents were corrected for the kinetic energy effects. The measurements were performed at concentrations ranging from 0.03 to

Table 1

Elution volumes ( $V_e$ ) of non-carboxylated and carboxylated PUs DX ( $X = 0, 25, 50, 100$ ), and PU-ionomers DX-M ( $M = \text{Li, Na, K, Ca}$ ) in DMF and 0.05 M LiBr/DMF.  $V_e$  is given for the apex of the peak. For comparison the  $V_e$  values determined in THF [3] are also presented

PU	$V_e$ (ml)		
	DMF	0.05 M LiBr/DMF	THF
D0	4.68 and 6.82 <sup>a</sup>	6.88	6.44
D25	5.16 <sup>b</sup>	7.08	6.74
D25-Li	<sup>b</sup>	7.23	6.88
D25-Na	<sup>b</sup>	7.13	6.86
D25-K	<sup>b</sup>	7.09	6.80
D25-Ca	<sup>b</sup>	8.13	7.36
D50	5.25 <sup>b</sup>	7.41	6.89
D50-Li	<sup>b</sup>	7.62	<sup>c</sup>
D50-Na	<sup>b</sup>	7.61	7.16
D50-K	<sup>b</sup>	7.57	7.01
D50-Ca	<sup>c</sup>	<sup>c</sup>	<sup>c</sup>
D100	5.36 <sup>b</sup>	7.84	7.04
D100-Li	<sup>b</sup>	8.19	<sup>c</sup>
D100-Na	<sup>b</sup>	8.17	<sup>c</sup>
D100-K	<sup>b</sup>	8.01	<sup>c</sup>
D100-Ca	<sup>c</sup>	<sup>c</sup>	<sup>c</sup>

<sup>a</sup> Major RI peak of NPU.

<sup>b</sup> Multimodal molar mass distribution;  $V_e$  are presented only for CPUs for the most intense peak.

<sup>c</sup> Insoluble.

1 g/dl. The preparation of the samples and detailed measurement procedure are described in our previous paper [3].

The  $^1\text{H}$  NMR measurements were carried out by a Varian VXR 300 NMR spectrometer. The samples were dissolved

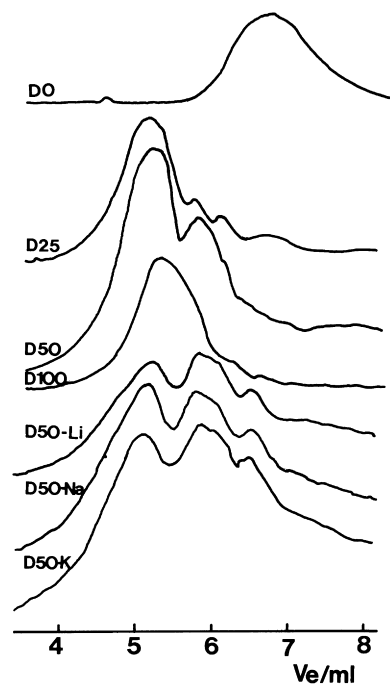


Fig. 2. SEC curves of non-carboxylated, carboxylated PUs (DX;  $X = 0, 25, 50, 100$ ) and PU-ionomers (D-50-M;  $M = \text{Li, Na, K}$ ) in DMF.

in DMF- $d_7$  and LiBr/DMF- $d_7$  (0.1 M solution) to a concentration of 20 wt%. TMS was used as an internal reference.

### 3. Results and discussion

#### 3.1. Non-carboxylated and carboxylated polyurethanes in DMF

The concentration dependence of reduced viscosity for NPU in DMF is linear with only one small deviation of the point at the lowest solution concentration,  $\sim 0.03$  g/dl (Fig. 1). The NPU Huggins coefficient ( $k'$ ) [12] characterizing polymer–polymer interaction is somewhat higher in DMF ( $k'_{\text{DMF}, 25^\circ\text{C}} = 0.34$ ) than in THF ( $k'_{\text{THF}, 25^\circ\text{C}} = 0.29$ ) [3] reflecting the lower solvent power of DMF for the dissolution of NPU. The determined NPU intrinsic and reduced viscosities in DMF ( $[\eta]_{\text{DMF}, 25^\circ\text{C}} = 0.47$  dl/g) are lower than those in THF solution ( $[\eta]_{\text{THF}, 25^\circ\text{C}} = 0.58$  dl/g) [3]. This is in accordance with SEC results, where the major part of the sample elutes in DMF at larger elution volume than in THF (Table 1, Fig. 2). These results can be ascribed to different conformations of NPU macromolecular chains in THF and DMF solutions. The NPU molar mass distribution in DMF shows two separated peaks (Fig. 2), the minor one at smaller and the major one at a larger elution volume.

The CPUs' SEC curves exhibit broad molar mass distributions with smaller elution volumes than that of NPU (Fig. 2). However, the reduced viscosities of CPUs solutions are lower than that of NPU. Their concentration dependences cannot be expressed by the Huggins equation [12], as significant upward discrepancies from the straight lines were observed in a very dilute region below  $\sim 0.2$  g/dl (Fig. 1).

The observed molar mass distributions of NPU and CPUs in DMF are in contradiction with the previously reported SEC results in THF, which show unimodal molar mass distributions and an increase of elution volume with the degree of carboxylation [3]. Additionally, they are not in agreement with the viscosity results. To elucidate such solution behavior a molar mass sensitive laser photometer (MALS) was used as a SEC detector. For NPU (Fig. 3a), a  $90^\circ$  light scattering curve shows an intense signal of the peak barely detected by the RI-detector. At the far left of the  $90^\circ$  LS chromatogram additional intense signals appear, which were not detected even by the RI-detector. The intensity of all these signals increase with lowering the scattering angle (Fig. 4), indicating a minute amount (below 0.8 wt%) of high molar mass species [13]. On the contrary, the LS intensity of the major peak with the largest elution volume is independent of the angle of observation indicating small particles [13]. The calculated  $\bar{M}_w^{\text{app}}$  of the first small peak in RI chromatogram is about 2–3 orders of magnitude higher ( $10^7$ ) than that of the second peak ( $10^4$ ). The latter  $\bar{M}_w^{\text{app}}$  is of the same order of magnitude as the value determined by SEC–MALS in THF [3], although the elution volumes are different (Table 1).

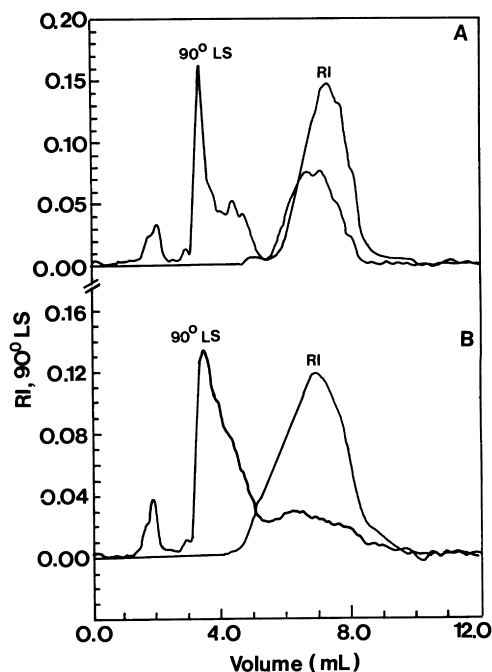


Fig. 3. 90° LS and RI curves of PUs in DMF: (a) non-carboxylated PU (D0), (b) carboxylated PU (D50).

Regarding the viscosity results in DMF (Fig. 1), the early elution of CPUs could be due to the expansion of the macromolecular chains as a consequence of a polyelectrolyte effect operating at higher dilutions, which are also

encountered in the SEC measurements. However, SEC–MALS results of CPUs are not consistent with the above explanation. Namely, partially charged species are known to cause a decrease in the scattered light intensity [5,13–15], whereas, the LS chromatograms of CPUs show the opposite effect (Fig. 3b). The LS signal of the polymer fractions that elute from the column first (5–10 wt%), exhibits the characteristics of light scattering by large particles, i.e. very large LS intensity and pronounced angular dependence of the scattered light (Fig. 5). The LS response of the polymer fractions with larger elution volumes is much less intense and independent of the angle of observation. Its  $\bar{M}_w^{\text{app}}$  is of the same order of magnitude ( $10^4$ ) as that determined by SEC–MALS in THF [3]. At the extreme left of the chromatogram at very small elution volumes, the light scattering indicates even higher molar mass species not detected by the RI-detector.

The above SEC–MALS results show that NPU and CPUs aggregate in DMF. The degree of aggregation is much higher for CPUs than for NPU. The presence of the aggregated species in solutions of non-ionic PUs was also observed for polyester PU in DMF [7] and for polyurethaneurea in DMAc [16,17].

### 3.2. Non-carboxylated and carboxylated polyurethanes in LiBr/DMF

The addition of LiBr to DMF eliminates the NPU minor peak, while the elution volume of the major peak slightly

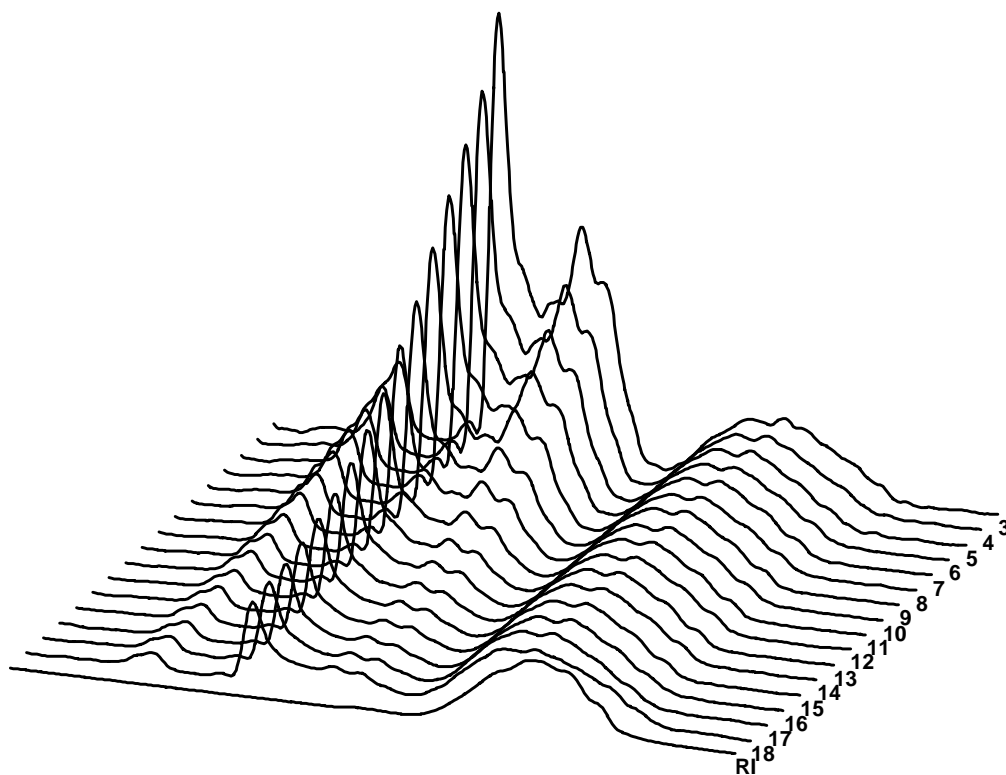


Fig. 4. LS curves of non-carboxylated PU (D0) at different scattering angles together with RI curve in DMF.

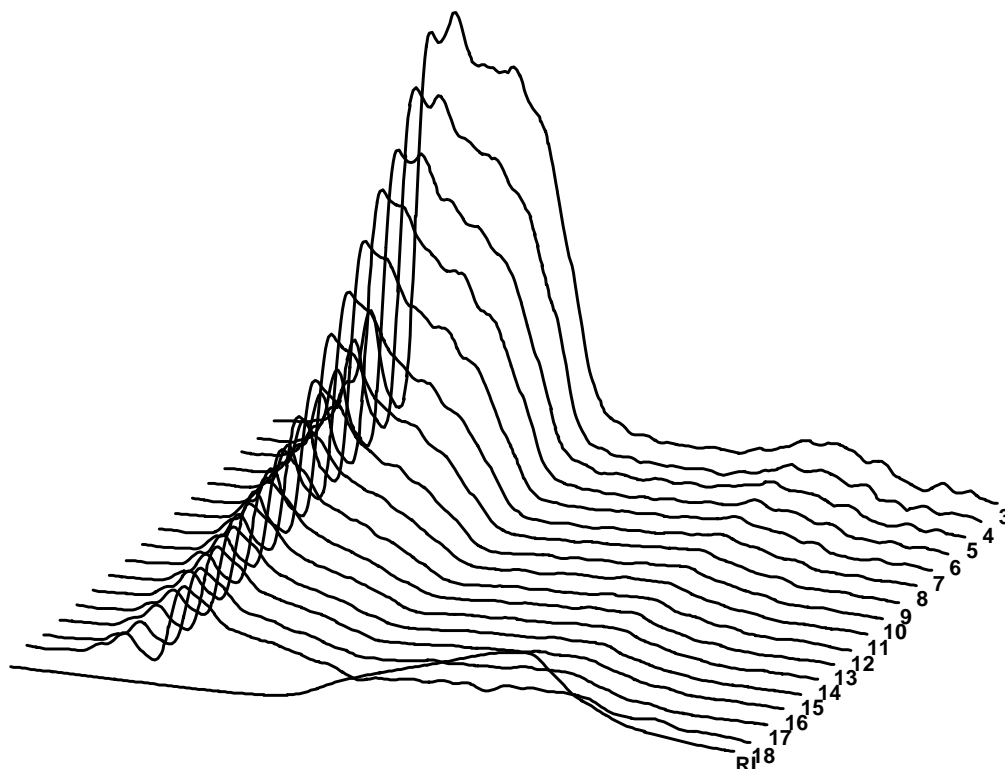


Fig. 5. LS curves of carboxylated PU (D50) at different scattering angles together with RI curve in DMF.

increases (Fig. 6, Table 1). The salt effect on NPU hydrodynamic volume changes was also studied using viscosity measurements. In the presence of LiBr, the reduced and intrinsic viscosities of NPU somewhat decrease (Fig. 1), which is in agreement with the SEC results.

In the case of CPUs, LiBr has a pronounced effect on their elution from the column and their solution viscosity behavior (Figs. 6 and 1). Namely, CPUs have unimodal molar

mass distributions with much larger elution volumes than those found in pure DMF (Fig. 6). The elution volume increases with the degree of carboxylation (Table 1) indicating a decrease in molar mass, which corresponds to the results obtained in THF [3], and is also confirmed by SEC–MALS results (Tables 1 and 2). The NPU and CPUs  $\bar{M}_w^{\text{app}}$  values determined in this solvent are comparable to the values found in THF (Table 2) irrespective of the differences in elution volumes (Table 1). A large decrease in the reduced viscosity of CPUs solutions was observed especially in a very dilute region (Fig. 1), which is in agreement with the SEC results.

In order to explain the aggregation behavior of NPU and CPUs in DMF,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in solvent DMF- $d_7$  with and without LiBr. The addition of LiBr to DMF shifts the  $^1\text{H}$  signals of urethane and urea (formed in side reactions) [3] groups significantly toward the lower magnetic field (higher ppm) (Fig. 7), while the  $^{13}\text{C}$  chemical shifts of urethane and urea  $-\text{C}=\text{O}$  groups do not change significantly. Based on these results, we have hypothesized a solution structure of PUs in LiBr/DMF solutions: bromide ions strongly interact with the  $-\text{NH}-$  groups, while lithium ions are probably located adjacent to the carbonyl oxygen of DMF forming bulky cations  $[\text{Li}\cdot x\text{DMF}]^+$  [18–20]. These positively charged species solvate the negatively charged sites on PU macromolecules, which originate from the interaction of  $\text{Br}^-$  ions with  $-\text{NH}-$  groups. Thus, the intermolecular H-bonding between PU macromolecules in DMF is disrupted and the possibility

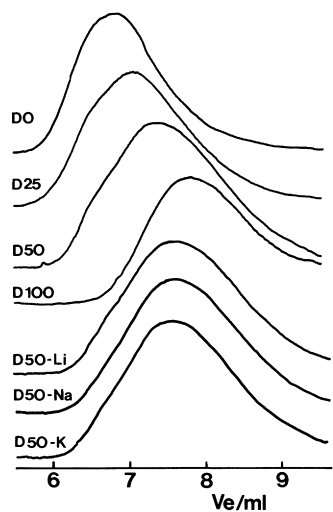


Fig. 6. SEC curves of non-carboxylated, carboxylated PUs (DX;  $X = 0, 25, 50, 100$ ) and PU-ionomers (D50-M;  $M = \text{Li, Na, K}$ ) in 0.05 M LiBr/DMF.

Table 2

Apparent molar mass averages of non-carboxylated and carboxylated PUs DX ( $X = 0, 25, 50, 100$ ) determined by SEC–MALS in 0.05 M LiBr/DMF. For the comparison the corresponding values determined in THF [3] are also presented

PU	$\bar{M}_w^{\text{app}}$ (g/mol)		$\bar{M}_n^{\text{app}}$ (g/mol)		$\bar{M}_w^{\text{app}}/\bar{M}_n^{\text{app}}$	
	LiBr/DMF	THF	LiBr/DMF	THF	LiBr/DMF	THF
D0	29 600	28 100	22 100	19 900	1.3	1.4
D25	27 300	26 300	19 100	16 000	1.4	1.6
D50	25 600	22 900	17 500	13 400	1.4	1.7
D100	18 800	20 000	11 500	12 100	1.6	1.7

of aggregation is minimized. LiBr can also neutralize any column charge characteristics and consequently any possible polymer–column interaction. The specific interaction of simple salts (LiCl) with urethane and especially urea groups of PUs in DMAc solutions has already been reported [17,21].

### 3.3. Polyurethane ionomers in DMF

PUIs differ in the concentration of ionic groups (approximately 8, 16 and 32 mol%) and kind of counterion ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ). All PUIs were soluble in DMF, except D50-Ca and D100-Ca, which were only partially soluble due to strong interchain ionic crosslinks [22].

PUIs in DMF show similar anomalous SEC behavior like CPUs (Fig. 2), i.e. early elution and broad molar mass distributions. Their molar mass distributions depend mainly on the concentration of ionic groups and only slightly on the kind of counterion. PUIs synthesized from both chain extenders (DMPA + NPG) show broader molar mass distributions than PUIs synthesized solely with the ionic chain extender (DMPA).

The concentration dependences of reduced viscosity of PUIs series D50-M (Fig. 8), show that at higher concentrations the reduced viscosities are lower than that of the parent CPU. Similar results were obtained by George et al. [5] for

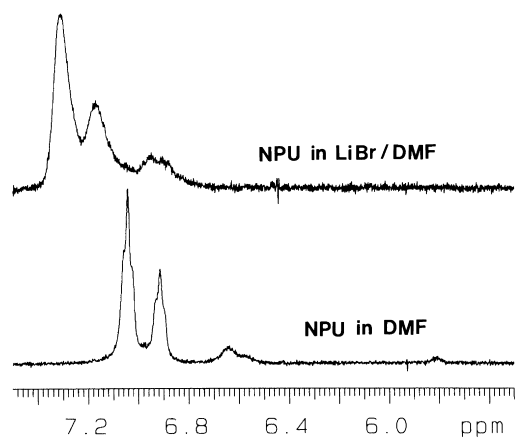


Fig. 7.  $^1\text{H}$  NMR spectra of non-carboxylated PU (D0) in DMF- $d_7$  and LiBr/DMF- $d_7$  (urethane  $-\text{NH}-$ : 6.5–7.1 ppm, urea  $-\text{NH}-$ : 5.8 ppm).

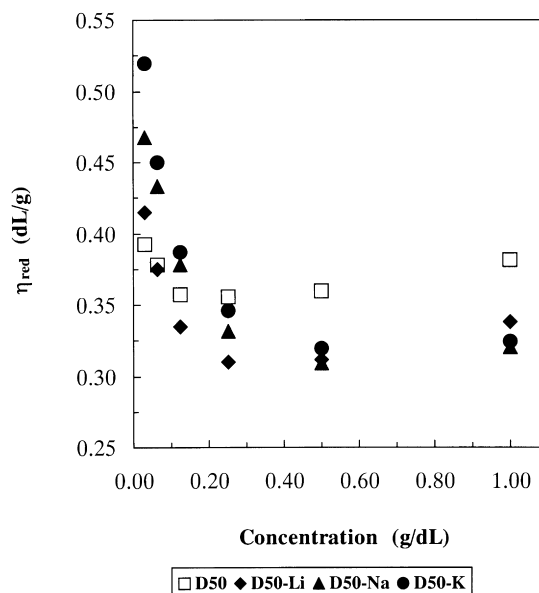


Fig. 8. Reduced viscosity ( $\eta_{\text{red}}$ ) vs. concentration for carboxylated PU (D50) and PU-ionomers (D50-M; M = Li, Na, K) in DMF.

PU sulphonate anionomers and by Chen et al. [23] and Chan et al. [24] for PU cationomers. Such viscosity results in moderately concentrated solutions of PUIs were interpreted by aggregation as a consequence of the high content of ionic groups [23,24]. The existence of the aggregated species together with free polyions in dilute solutions of PUIs in polar solvents has already been assumed by others [5–7] and recently proved by Cooper et al. [25] using dynamic light scattering measurements. Aggregation behavior of ionomers in polar *N*-methylformamide at dilute solution concentration was also observed for poly(styrene-sodium 2-(acrylamido)-2-methylpropanesulfonate) [26].

In a very dilute region (below  $\sim 0.2$  g/dl), PUIs' reduced viscosities increase sharply with dilution and thus become larger than that of the parent CPU indicating a prevailing electrostatic repulsive interaction (polyelectrolyte effect) [4]. In a selected PUIs series D50-M (Fig. 8), the type of counterion also influences the solution properties of the PUIs. This is due to the differing degrees of ionization of ionic groups, which is, in turn, directly related to the strength of counterion binding to the carboxylate group [5]. Viscosity results indicate an increase in counterion binding such that  $\text{K} < \text{Na} < \text{Li} < \text{Ca}$ , which is the same as in THF solutions [3] and is in agreement with the results for 4,4'-diphenylmethane diisocyanate based PU carboxylated ionomers [27] and ionomers based on styrene/methacrylic acid [28,29].

### 3.4. Polyurethane ionomers in LiBr/DMF

As in the case of CPUs, all the peculiarities encountered in SEC characterization of PUIs in DMF were eliminated by the addition of LiBr to DMF (Fig. 6, Table 1). In the

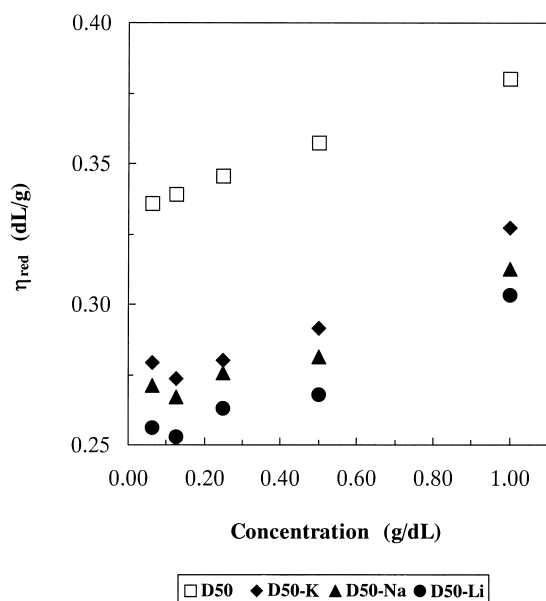


Fig. 9. Reduced viscosity ( $\eta_{red}$ ) vs. concentration for carboxylated PU (D50) and PU-ionomers (D50-M; M = Li, Na, K) in 0.05 M LiBr/DMF.

presence of the electrolyte, PUIs show unimodal molar mass distributions with much larger elution volumes than were found in pure DMF. Elution volumes are larger than those of the parent CPUs and in the selected series slightly increase in the same order as previously reported for PUIs solutions in THF ( $K < Na < Li < Ca$ ) [3]. The influence of Ca counterion could only be determined for the series D25-M, as the ionomers with higher concentration of ionic groups (D50-Ca, D100-Ca) were not completely soluble.

The effect of LiBr on solution viscosity behavior of PUIs series D50-M is illustrated in Fig. 9. There we see that the PUIs reduced viscosities are lower than those in pure DMF,

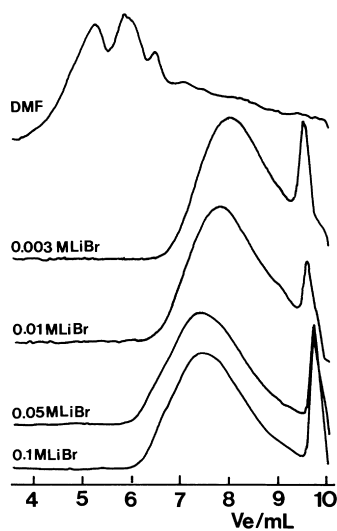


Fig. 10. SEC curves of PU-ionomer D50-Na in DMF and DMF with various concentrations of LiBr (0.003, 0.01, 0.05 and 0.10 M).

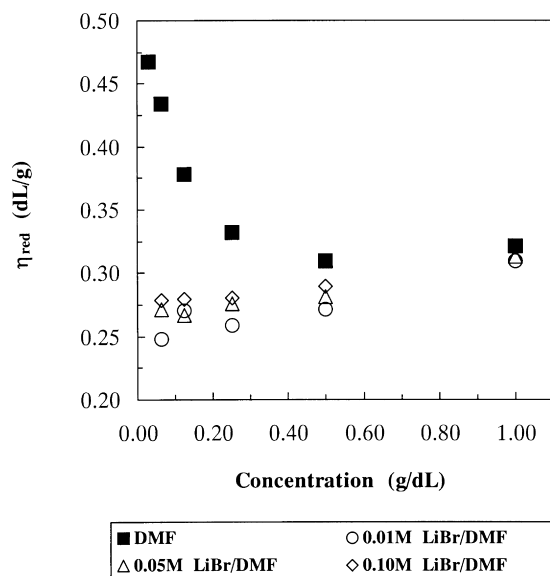


Fig. 11. Reduced viscosity ( $\eta_{red}$ ) vs. concentration for PU-ionomer D50-Na in DMF and DMF with various concentrations of LiBr (0.01, 0.05 and 0.10 M).

especially in the very dilute region. Screening of carboxylate ionic groups by LiBr prevents the ion–ion electrostatic repulsive interaction, which results in a smaller hydrodynamic volume of PUIs. The PUIs solution viscosities in LiBr/DMF are also lower than that of the parent CPU and, like the elution volume in SEC, depend slightly on the kind of counterion. These results may be due to attraction between ion pairs causing contraction of the macromolecular chains [4].

As in 0.05 M LiBr/DMF some of the PUIs show a deviation from the linear concentration dependence of reduced viscosity, we performed SEC and viscosity measurements in DMF with different concentrations of LiBr (Figs. 10 and 11). With increasing LiBr concentration elution volumes of PUIs decrease (Fig. 10, Table 3) until they become constant at about 0.05 M.

The concentration dependences of reduced viscosity of ionomer D50-Na (Fig. 11) in LiBr/DMF show a broad maximum at the low LiBr concentrations (0.01, 0.05 M), while at higher LiBr concentration linear relationship was obtained (0.10 M). The same influence of the external salts on solution viscosity behavior was reported for polyelectrolytes in aqueous solutions [30–32] and ionomer solutions in polar organic solvents [4,33]. However, in contrast to the usual decrease in reduced viscosity of the polyelectrolyte or ionomer solutions [4,30–33], the reduced viscosity of PUI increases with increasing concentration of the external salt (LiBr). This reflects an increase in the PUI hydrodynamic volume, which corresponds to the decreasing elution volume obtained by SEC measurements. One of the reasons for this phenomenon could be a specific interaction of the complex  $[Li \cdot xDMF]^+ Br^-$  with urethane and urea groups. This interaction, as has been already suggested, prevents

Table 3

Elution volumes ( $V_e$ ) of some PU-ionomers DX-M in DMF and LiBr/DMF of different concentrations (0.003; 0.011; 0.05; 0.1 M LiBr)

PU	DMF	$V_e$ (ml)			
		0.003 M LiBr	0.011 M LiBr	0.05 M LiBr	0.1 M LiBr
D25-Na	<sup>a</sup>	7.38	7.27	7.13	7.13
D50-Na	<sup>a</sup>	8.11	7.92	7.61	7.58
D100-Na	5.73 <sup>a</sup>	8.74	8.67	8.17	<sup>b</sup>
D100-Li	5.76 <sup>a</sup>	8.97	8.66	8.19	<sup>b</sup>

<sup>a</sup> Multimodal molar mass distribution;  $V_e$  in DMF are presented for the most intense peak.<sup>b</sup> Insoluble.

inter-molecular H-bonding and consequently the aggregation of PUs in DMF. The chains become less entangled and even better solvated by the complex than in pure DMF. Additionally, any intra-molecular H-bonding can be disrupted through the above-mentioned interaction. By these means the increasing concentration of LiBr can induce conformational change of the macromolecules so that the chains are more expanded. Specific interactions of simple salts with certain polar non-ionic polymers, which induce changes in polymer hydrodynamic volume and their solution viscosity behavior, were also reported for polyamides in LiCl/DMAc [34,35] and for polyaniline in LiCl/NMP solutions [36–38].

#### 4. Conclusion

This paper focuses on the influence of various interactions (between PU polar groups and/or charged sites located along the macromolecular backbone and also between macromolecules and solvent) on dilute solution properties of carboxylated polyurethanes (CPUs) and related polyurethane ionomers (PUIs) in DMF and LiBr/DMF. For this purpose, CPUs were characterized by SEC, viscometry and SEC–MALS technique, while PUIs were only characterized by SEC and viscometry.

In DMF, both kinds of PUs show multimodal molar mass distributions and non-linear concentration dependences of reduced viscosity, which are usually correlated to the expansion of macromolecular chains due to the polyelectrolyte effect operating in dilute solutions. However, the SEC–MALS results of NPU and CPU show that they aggregate in DMF. Aggregation behavior is a consequence of the strong tendency of the urethane and urea groups of PUs for H-bond formation, which can be prevented by the addition of LiBr to DMF. In particular, the complex  $[\text{Li}\cdot x\text{DMF}]^+\text{Br}^-$  interacts with the  $-\text{NH}-$  groups of PUs and thus prevents the aggregation induced by H-bonding.

Viscosity behavior of PUI solutions in DMF shows a typical polyelectrolyte effect at very low concentrations. In a selected PUI series with different counterions, the increase in counterion binding such that  $\text{K} < \text{Na} < \text{Li} < \text{Ca}$  is observed as in THF solutions. LiBr

added to DMF suppresses the polyelectrolyte effect of PUIs by screening the ionic groups on macromolecular chains. This is reflected in linear concentration dependences of reduced viscosity and unimodal molar mass distributions. At the same time, LiBr also interacts with the urethane and urea groups of PUs. This interaction appears to be responsible for the increasing hydrodynamic volume of PUIs with increasing LiBr concentration, resulting in a decreasing elution volume and increasing reduced viscosity.

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