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Dilute solution behaviour of hexamethylene diisocyanate-based carboxylated polyurethanes and related ionomers in tetrahydrofuran

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Abstract

The mechanisms controlling the elution of carboxylated polyurethanes (CPUs) and polyurethane ionomers (PUIs) during the size exclusion chromatography (SEC) separation process in tetrahydrofuran (THF) were investigated. In order to elucidate the elution process, their dilute solution viscosity behaviour was studied as well. Sample molar mass averages were determined by SEC using polystyrene calibration (SEC-PS) and in the case of CPUs also by SEC coupled with a multi-angle light scattering detector (SEC-MALS). The molar mass averages and intrinsic viscosities of CPUs decrease with increasing degree of carboxylation as a consequence of side-reactions. The large difference in reduced viscosity between non-carboxylated PU and CPUs can be attributed to different macromolecular conformations in THF solution. The molar mass averages of PUIs determined by SEC-PS were much lower than those of the parent CPU and showed a slight dependence on the type of counterion used. In the selected series, the molar mass averages and intrinsic viscosities increased in the order $Ca^{2+} < Li^{+} < Na^{+} < K^{+}$. The addition of CF_3COONa had no influence on the solution viscosity of CPUs, while it prevented the association of PUIs.

Keywords: Carboxylated polyurethanes; Polyurethane ionomers; Size exclusion chromatography (SEC)

1. Introduction

Physical properties of polyurethanes (PUs) depend on the raw materials used for their synthesis, on the degree of phase separation between hard and soft segments, on the cohesion and interconnectivity of the hard domains and on average molar masses and molar mass distributions. Physical properties can be improved by incorporating hard segments with ionic groups, which tend to aggregate via coulombic interactions into so-called 'ionic domains' and thus promote phase separation and hard domain cohesion [1–3].

Generally, polymers containing small numbers of ionic groups, i.e. ionomers, are known to exhibit unusual solution properties (viscosity, conductivity, osmotic pressure, light scattering, etc.), which are influenced by several parameters: solvent polarity, temperature, polymer molar mass, the type, concentration and distribution of ionic groups in the polymer chain, the nature of the counterion, and the concentration of the polymer solution [4–6]. Depending primarily on the polarity of the solvent, the solution behaviour of ionomers can be described by two characteristic phenomena: (1) dissociation of ionic groups in polar solvents resulting in the expansion of the ionomer coil, the so-called polyelectrolyte effect, and (2) association of ionic groups which is described as aggregation behaviour due to the formation of ion pairs and even higher-order aggregates in low-polarity or non-polar solvents [4–6].

In low-polarity solvents (e.g. tetrahydrofuran (THF)), intramolecular association of ion pairs dominates at low ionomer concentrations and, consequently, ionomer chains contract. The reduced viscosity of the ionomer solution is lower than that of the parent polymer. At higher ionomer concentrations, intermolecular association prevails over intramolecular association and leads to the formation of intermolecular aggregates with a high molar mass and sometimes to gelation or insolubility. Thus, the reduced viscosity of the ionomer solution is higher than that of the parent polymer [4–6]. With increasing ion content, the reduced viscosity decreases at low ionomer concentrations and increases at higher concentrations. This effect was explained by the overall increase in attractive interactions between ion pairs [7]. The influence of the type of counterion on ionomer solution viscosity was explained by the difference in the desolvation of the counterion during

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the anion–cation interaction and association of ion pairs [4,8,9]. For the carboxylate system, (partial) desolvation of counterions occurs because of the large anionic field strength of the –COOH groups. The cation and anion can thus interact directly, and the unsolvated ion size (i.e. $Li^+ < Na^+ < K^+ < Cs^+$) becomes the determining factor for the solution properties [4]. The addition of simple salts to ionomer solutions suppresses the aggregation of ionomers; namely, interactions between ionic species are shielded by the ionic atmosphere of the added salt [10]. The majority of studies on dilute ionomer solution viscosity in low-polarity solvents have been made on poly(styrene-sulfonates) [7–12], the copolymers of methacrylic acid [8–10,12] and on polystyrene-based cationic ionomers [13]. To our knowledge, the viscosity behaviour of PU-ionomers in low-polarity solvents has been investigated only for PU-cationomers in methyl ethyl ketone (MEK) [14].

Molar mass averages and distributions are usually determined by size exclusion chromatography (SEC), where elution volume (V_e) relates to the hydrodynamic volume (V_h), i.e. to the size of a macromolecule in solution. By Einstein's equation, it is proportional to the product of intrinsic viscosity [η] and molar mass M [15]. The V_e of polymer species is thus dependent not only on M, but is also influenced by [η]. As discussed above, the [η] of ionomers in very dilute solutions of low-polarity solvents is strongly influenced by intramolecular association induced by electrostatic interactions, which markedly affects the SEC elution regime leading to anomalous molar mass distributions and incorrect molar mass averages.

Ionomers are highly polar in nature and therefore poorly soluble in low-polarity solvents. This is the reason why SEC literature on ionomers in low-polarity solvents is scarce. Siebourg et al. [16] studied the molar mass distribution of sulfonated polystyrenes in solvents of varying polarity using non-polar polystyrene gel as the packing material. SEC curves in THF indicated very broad multiple-peak distributions. In a THF–$LiNO_3$ system, SEC curves had a narrow single-peak distribution with smaller V_e values. The results in THF were explained by poor solute–solvent interactions causing adsorption of ionomers on column packing, which resulted in a delayed elution. Intramolecular association was suggested as a less probable explanation. After the addition of $LiNO_3$ to THF the ionomers eluted according to their hydrodynamic volumes.

The relative molar mass averages of ionomers obtained by SEC and polystyrene calibration (SEC-PS) are strongly influenced by the choice of the eluent. In SEC analysis of polyurethane ionomers (PUIs), the situation may be even more complicated due to the chemical composition distribution along the chain originating from three or four components used in the synthesis and due to polar groups present in the backbone. Carboxylated PUIs beside carboxylate ionic groups also contain urethane, ether or ester, and terminal hydroxyl groups. Due to the above-mentioned electrostatic interactions between ion pairs in low-polarity solvents and the possible interactions of polar groups with the solvent and column packing, the PUI molar mass averages and distributions determined by SEC are likely to be anomalous.

The aim of the present work was to investigate the interactions controlling the elution of carboxylated PUIs and their parent carboxylated polyurethanes (CPUs) on a crosslinked polystyrene gel in THF during the SEC separation process. For this purpose, non-carboxylated polyurethane (NPU), CPUs with different amounts of carboxylic groups, and related ionomers were synthesized and characterized by SEC-PS and in the case of NPU and CPUs also by SEC coupled with a multi-angle light scattering detector (SEC-MALS). The dilute solution properties of the synthesized samples were studied by viscometry.

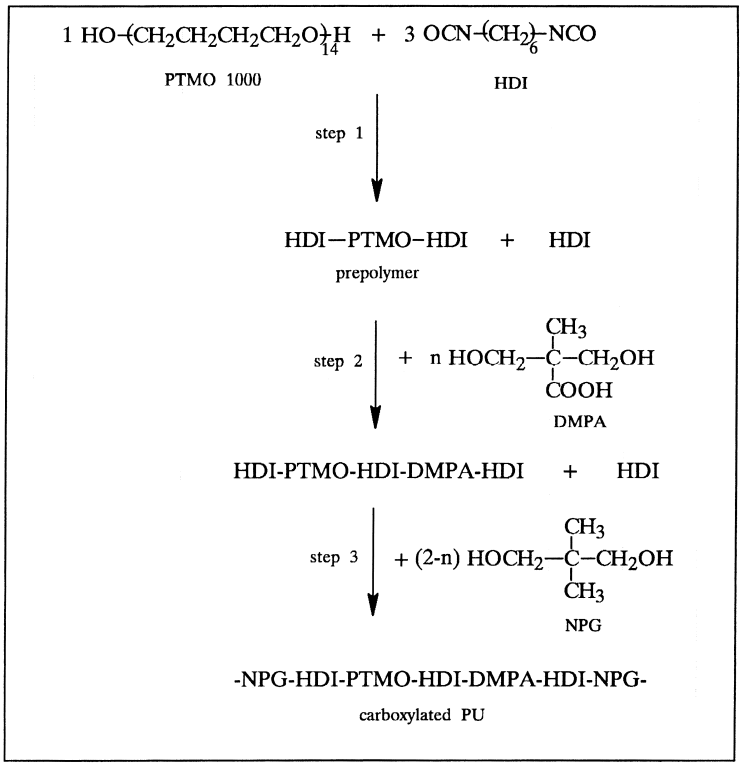
2. Experimental

2.1. Materials

Poly(tetramethyleneoxide) (PTMO, BASF) with $M_n = 1000$ was dried under vacuum at 60–65°C for 9 h before use. Hexamethylene diisocyanate extra-pure grade (HDI, Fluka), 2,2-dimethyl-1,3-propanediol (synonym neopentyl glycol, NPG, Fluka), sodium trifluoroacetate (CF_3COONa, Fluka), triethylamine (TEA, Aldrich), tetrahydrofuran (THF, water content $< 0.05\%$, Fluka), *N*,*N*-dimethylformamide (DMF, water content $< 0.005\%$, Aldrich) were used as received and stored in a dry box with a relative humidity of approx. 1%. 2,2-Bis(hydroxymethyl)propionic acid (synonym dimethylolpropionic acid, DMPA, Jansen) was dried in a vacuum oven at 90°C for 6 h and stored in a dry box. Methyl ethyl ketone (MEK), $LiOH \cdot H_2O$, KOH, $Ca(OH)_2$ (Kemika) and dibutyltin dilaurate (DBTDL, Acima) were used as received.

2.2. Synthesis

NPU and CPUs were synthesized by a two-step procedure in DMF as 40% solutions (Scheme 1, Table 1). NCO-terminated prepolymers were prepared by reacting PTMO with HDI dissolved in DMF at 75°C for approximately 4 h. The chain extension reaction was catalysed with DBTDL (0.03 wt% based on prepolymer) and carried out at 95°C with DMPA and at 80°C with NPG. The course of the reaction was followed by infrared absorption of the isocyanate stretching band at 2200–2300 cm^{-1} and the reaction was considered to be complete when this band disappeared. When both chain extenders were used, DMPA was added first and the reaction ran for 48 h, then NPG was added and the reaction ran until completion. The molar ratio of HDI:PTMO:chain extender(s) was 3:1:2. Polymers were precipitated by pouring DMF solutions into distilled water and were dried under vacuum at 50°C



Scheme 1. Synthetic route to carboxylated PU DX.

until ^{1}H signals of water and DMF in ^{1}H NMR spectra disappeared.

PUIs were prepared by neutralization of carboxylic groups with a metal hydroxide (LiOH, NaOH, KOH, $Ca(OH)_2$) or TEA. The dried CPUs were dissolved in MEK and mixed with a stoichiometric amount of a neutralizing agent dissolved in methanol. The neutralization was carried out at 60°C for 4 h. The solvents were evaporated at 50°C to give films which were further dried under vacuum at the same temperature, until ^{1}H signals of solvents in ^{1}H NMR spectra disappeared.

The non-carboxylated PU (NPU), carboxylated PUs (CPUs) and PU-ionomers (PUIs) are designated as follows:

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

2.3. Characterization methods

The content of carboxylic groups in CPUs was determined by acid–base titration [17].

SEC-PS measurements were performed at room temperature on a Perkin-Elmer liquid chromatograph equipped with an LC-30 differential refractometer (DRI). A PLgel 5 μm column Mixed D of length 30 cm with a precolumn and THF as eluent with a flow rate of 1.0 ml min^{-1} were used. The sample concentration was 1% (w/v) and the injection volume 20 μl. The calibration was made with PS standards.

The SEC-MALS measurements of NPU and CPUs were performed at 25°C on a Wyatt Technology Dawn-DSP instrument equipped with an He–Ne laser ($\lambda_0 = 633$ nm) and an Optilab-DSP differential refractometer. Typically, the injected amounts of the samples were approximately 1.5×10^{-3} g (solution concentration 1.5%, w/v). The refractive index increments (dn/dc) were measured by an

Table 1
Parameters for the synthesis of non-carboxylated and carboxylated PU DX (X = 0, 25, 50, 100)

PU	Molar ratio PTMO:HDI:NPG:DMPA	Mol% DMPA in (DMPA + NPG)	Mol% –COOH in PU	Mmol –COOH per 100g PU		
				Calc.	Exp. (titration)	Exp./calc. (%)
D0	1:3:2:0	0	0.00	0.00	0.00	
D25	1:3:1.5:0.5	25	8.33	28.95	27.87	96.3 ± 0.1
D50	1:3:1:1	50	16.67	57.41	55.21	96.2 ± 0.5
D100	1:3:0:2	100	33.33	112.87	109.60	97.1 ± 0.1

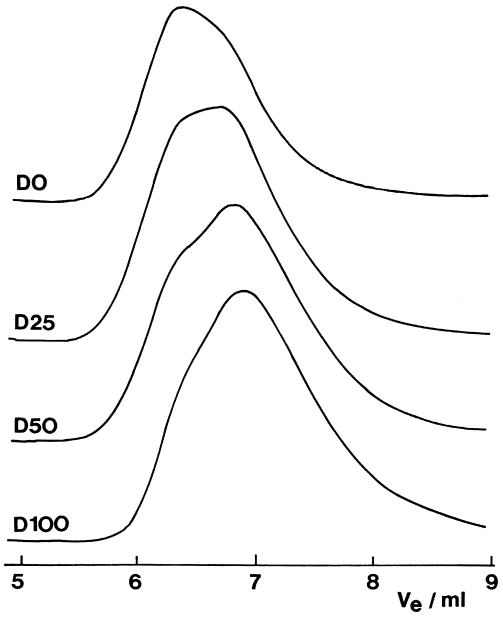


Fig. 1. SEC curves of non-carboxylated and carboxylated PU DX (X = 0, 25, 50, 100) in THF.

Optilab DSP. Data acquisition and evaluation utilized Astra 4.20 and DNDC 5.00 software. Owing to the fluctuations in the chemical composition and in molar mass of NPU and CPUs and due to the fact that only an average d*n*/d*c* of the sample and not d*n*/d*c* of the individual fractions could be used, SEC-MALS measurements gave an apparent weight-average molar mass (M_w^{app}) [18].

Dilute solution viscosity was determined using an Ubbelohde viscometer 0c at 25 ± 0.05°C in a thermostated water bath. Dried samples were dissolved in THF at room temperature under stirring. The solutions were filtered through a 0.2 mm PTFE filter (Sartorius) directly into the viscometer. The viscometer was equipped with a $CaCl_2$ tube and prior to each flow-time measurement the temperature was equilibrated for approx. 15 min. For each concentration, the measurements were repeated until the relative error of five successive measurements was less than 0.1% and an average value of flow times was recorded. The specific (η_{sp}) and reduced (η_{red}) viscosities were calculated at six different concentrations and converted to intrinsic viscosity ([η]) by extrapolation to infinite dilution [19]:

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c \quad (1)$$

where k' is the Huggins coefficient and c the concentration of the polymer solution.

Infrared (IR) spectra were recorded using an FTIR spectrophotometer, Perkin-Elmer, Model 1725X, at 2 cm^{-1} resolution.

The ^{1}H NMR measurements were carried out by using a VARIAN VXR 300 NMR spectrometer at 25°C. The samples were dissolved in DMSO-d_6 and TMS was used as an internal reference.

3. Results and discussion

3.1. Non-carboxylated polyurethane (NPU) and carboxylated polyurethanes (CPUs)

The SEC curves of NPU and CPUs with different contents of carboxylic groups are shown in Fig. 1. The molar mass averages of CPUs calculated by using PS calibration (SEC-PS) are lower than those of NPU and decrease with

Table 2
SEC-PS molar mass averages ($\bar{M}_w$, $\bar{M}_n$), polydispersity index ($\bar{M}_w/\bar{M}_n$), and elution volumes (V_e) of non-carboxylated and carboxylated PU DX (X = 0, 25, 50, 100) and PU-ionomers DX-M (M = Li, Na, K, Ca, TEA) in THF; V_e is given for the apex of the peak

PU	V_e (ml)	$\bar{M}_w$ (g mol^{-1})	$\bar{M}_n$ (g mol^{-1})	$\bar{M}_w/\bar{M}_n$
D0	6.44	58000	29000	2.0
D25	6.74	46000	22000	2.1
D25-Li	6.88	34000	17000	2.0
D25-Na	6.86	36000	16000	2.2
D25-K	6.80	42000	19000	2.2
D25-Ca	7.36	15000	5000	2.3
D25-TEA	6.76	47000	20000	2.3
D50	6.89	32000	14000	2.2
D50-Li	*	*	*	*
D50-Na	7.16	19000	10000	2.0
D50-K	7.01	25000	12000	2.1
D50-Ca	*	*	*	*
D50-TEA	6.89	35000	15000	2.4
D100	7.04	22000	10000	2.2
D100-Li	*	*	*	*
D100-Na	*	*	*	*
D100-K	*	*	*	*
D100-Ca	*	*	*	*
D100-TEA	7.07	24000	10000	2.4

*Insoluble.

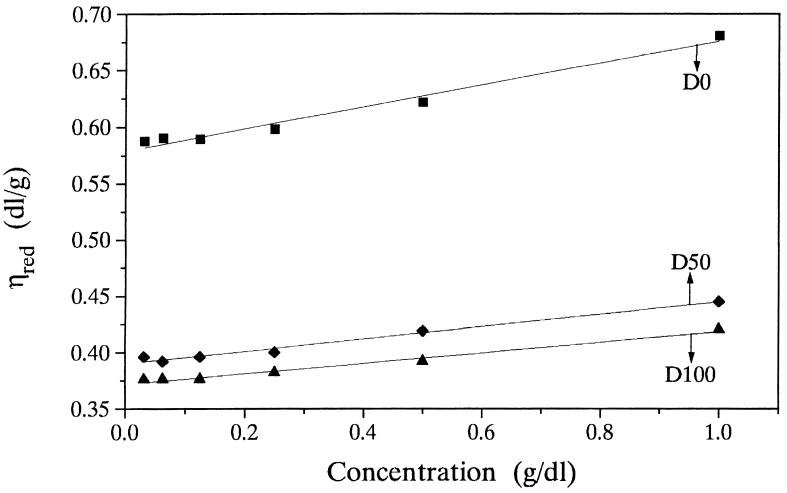


Fig. 2. Reduced viscosity (η_{red}) vs. concentration for non-carboxylated and carboxylated PU DX (X = 0, 50, 100) in THF.

the increasing content of carboxylic groups in the polymer chains (Table 2).

The concentration dependence of reduced viscosity for NPU and CPUs in THF is linear (Fig. 2). However, the reduced and intrinsic viscosities of CPUs are smaller than those of NPU (Table 3). They decrease with the increasing content of carboxylic groups indicating the decrease in molar mass, which is consistent with SEC-PS measurements.

Since the observed decrease in viscosity and molar mass could be a consequence of interactions of carboxylic groups, the viscosity of CPU D50 was measured in THF with added CF_3COONa, which is known to effectively prevent such interactions [9]. Fig. 7 shows that the addition of CF_3COONa had no influence on the concentration dependence of the reduced viscosity of CPU D50. This means that neither intra- nor intermolecular interactions induced by carboxylic groups participate in CPUs' solution behaviour. This has also been confirmed by absolute SEC-MALS results, which are not influenced by intramolecular interactions [20] (Table 4).

The decrease in molar mass and intrinsic viscosity of CPUs with increasing degree of carboxylation can be attributed to side-reactions of the isocyanate with carboxylic groups of DMPA and water present as an impurity. Namely, the degree of DMPA hydration during weighing in a dry box with 1% humidity could be higher than that of NPG. In addition, the titration results (Table 1) show that CPUs contain 3–4 mmol% fewer carboxylic groups per 100 g PU than initially added. Additional consumption of isocyanate groups in side-reactions leads to a non-stoichiometric ratio of functional groups and, consequently, the number average degree of polymerization is lower [21]. The average composition of CPUs is therefore influenced by the content of DMPA in the chain extender mixture.

Table 3
Intrinsic viscosities ([η]) and Huggins coefficients (k') of non-ionic and carboxylated PU DX (X = 0, 50, 100), and PU-ionomers D50-M (M = Na, K, TEA) determined by viscosity measurements in THF

PU	[η] (dl g^{-1})	k'
D0	0.579	0.289
D50	0.390	0.333
D100	0.372	0.337
D50-Na	0.184	*
D50-K	0.192	*
D50-TEA	0.394	*

*Linear fit for the Huggins equation (Eq. (1)) cannot be applied.

The presence of side-products was inferred from titration results (Table 1) and the NH region of the ^{1}H NMR spectra of reaction products. Namely, the intensity of the peak at 5.7 ppm, assigned to urea groups [22–24], is higher in the CPUs' spectra than in the NPU spectrum and slightly increases with the degree of carboxylation. In the ^{1}H NMR spectra of CPUs there is an additional signal of very low intensity at around 6.2 ppm, which is also present in a spectrum of the model compound prepared from HDI and DMPA. The reaction of isocyanate with carboxylic groups leads to a urea or an amide side-product. In the latter case a branched macromolecular structure is formed [1]. The same urea side-product can also be formed by the reaction of isocyanate groups with water [1]. Hence ^{1}H NMR spectra cannot infer which of these side reaction is favoured in the preparation of CPUs.

SEC-MALS measurements also confirm the decrease in molar mass of CPUs with increasing degree of carboxylation (Table 4, Fig. 3). However, the difference between SEC-PS and SEC-MALS molar mass averages of CPUs diminishes with higher degrees of carboxylation (Table 4). This can be explained by the fact that the polymer hydrodynamic volume is determined by the conformation occupied by its macromolecular chain, which in a given solvent depends on its chemical composition [25]. For this reason changes in hydrodynamic volume greatly affect

Table 4
SEC-PS and SEC-MALS molar mass averages of non-ionic and carboxylated PU DX (X = 0, 25, 50, 100)

PU	dn/dc(ml g^{-1})	$\bar{M}_w$ (g mol^{-1})		$\bar{M}_n$ (g mol^{-1})		$\bar{M}_w/\bar{M}_n$	
		SEC-PS	SEC-MALS	SEC-PS	SEC-MALS	SEC-PS	SEC-MALS
D0	0.083	58 000	28 100	29 000	19 900	2.0	1.4
D25	0.084	46 000	26 300	22 000	16 000	2.1	1.6
D50	0.085	32 000	22 900	14 000	13 400	2.2	1.7
D100	0.088	22 000	20 000	10 000	12 100	2.2	1.7

SEC-PS results of CPUs. Much lower molar mass averages of NPU determined by SEC-MALS (Table 4), as compared to those determined by SEC-PS (Table 3), are due to the higher hydrodynamic volume of the PU chain in comparison with the hydrodynamic volume of the PS chain of the same molar mass. Similar observations have been reported for the intrinsic viscosities of PUs and PS [26,27].

The SEC curves of NPU and CPUs have broad molar mass distributions with asymmetrical shapes (Fig. 1). Two fractions (the higher and the lower molar mass parts of the peak) of the sample D50 were collected at the column outlet and characterized by ^{1}H NMR. Fig. 4 shows that the lower molar mass fraction (B) contains considerably more hard segments originating from the chain extender NPG than does the higher molar mass fraction (A). Fraction B also contains a higher number of NPG hydroxyl terminal groups.

Considering the ^{1}H NMR results as well as the exclusion limit and molar mass working range of the column, we can conclude that the size exclusion mechanism is predominant in the elution processes. However, non-size exclusion effects might also take place, particularly in the elution of low molar mass species with a high concentration of terminal hydroxyl groups.

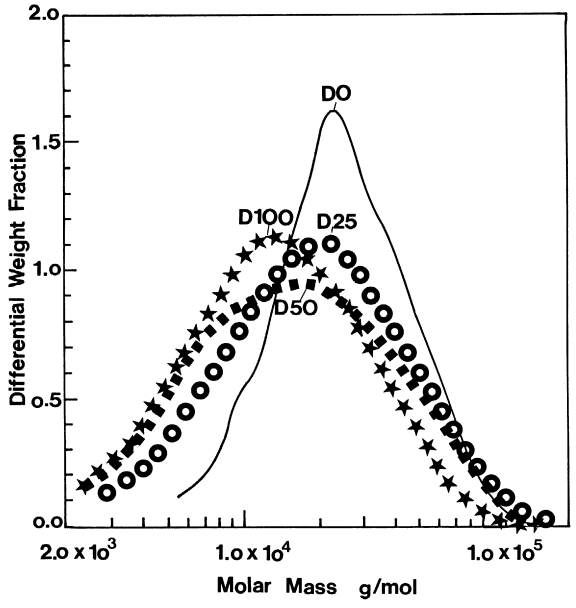


Fig. 3. Differential weight fractions of non-carboxylated and carboxylated PU DX (X = 0, 25, 50, 100) in THF as determined by SEC-MALS.

3.2. Polyurethane ionomers (PUIs)

PUIs differ in the concentration of ionic groups (approximately 8, 16 and 32 mol% of COO^-M^+) and in the type of counterion (Li^+, Na^+, K^+, Ca^{2+}, TEA). PUIs with TEA have a similar molar mass distribution and concentration dependence of reduced viscosity as the parent CPUs (Figs 5 and 6). This can be explained by the fact that the majority of TEA (approximately 85%) evaporated during vacuum drying of the samples. Consequently, the degree of neutralization of carboxylic groups and the concentration of ionic groups, respectively, are much lower than in other PUIs. Since the overall attractive interactions between ion pairs in dilute solutions are low [7], PUIs with TEA elute at smaller V_e than other PUIs and at similar V_e to the corresponding CPUs (Table 2).

In the case of D50-Li, D50-Ca and the D100-M series, intermolecular association at the concentration of 1.0 g dl^{-1} leads to strong interchain ionic crosslinks [11] that prevent dissolution of these ionomers in low-polarity THF; i.e. THF cannot solvate polar ionic groups and is therefore thermodynamically incompatible with highly polar ionic associates.

In the selected series, the SEC-PS molar mass averages of PUIs with mono- and divalent metal counterions are much lower than those of the parent CPU and depend on the valence and the type of counterion, showing an increase in molar mass in the order $Ca^{2+} < Li^+ < Na^+ < K^+$ (Table 2, Fig. 5). The lowest molar mass averages of D25-Ca in the D25-M series and the fact that D50-Ca was almost completely insoluble in THF at a concentration of 1.0 g dl^{-1} confirm that Ca^{2+} as counterion has the largest effect on the aggregation behaviour of PUIs.

Considerably lower SEC-PS molar mass averages of PUIs in comparison with the parent CPUs indicate that the hydrodynamic volume of contracted PUI coils is smaller than that of CPU coils. The difference in molar mass averages between the individual PUI and the corresponding CPU increases with the increasing content of carboxylate groups. This can be ascribed to the overall increase in attractive intramolecular interactions between ion pairs [7]. The SEC curves of PUIs have symmetrical molar mass distributions, which can be attributed to the formation of compact intramolecular associates with non-solvated ionic groups.

The concentration dependence of the reduced viscosity for the soluble PUI series D50-M is characteristic of

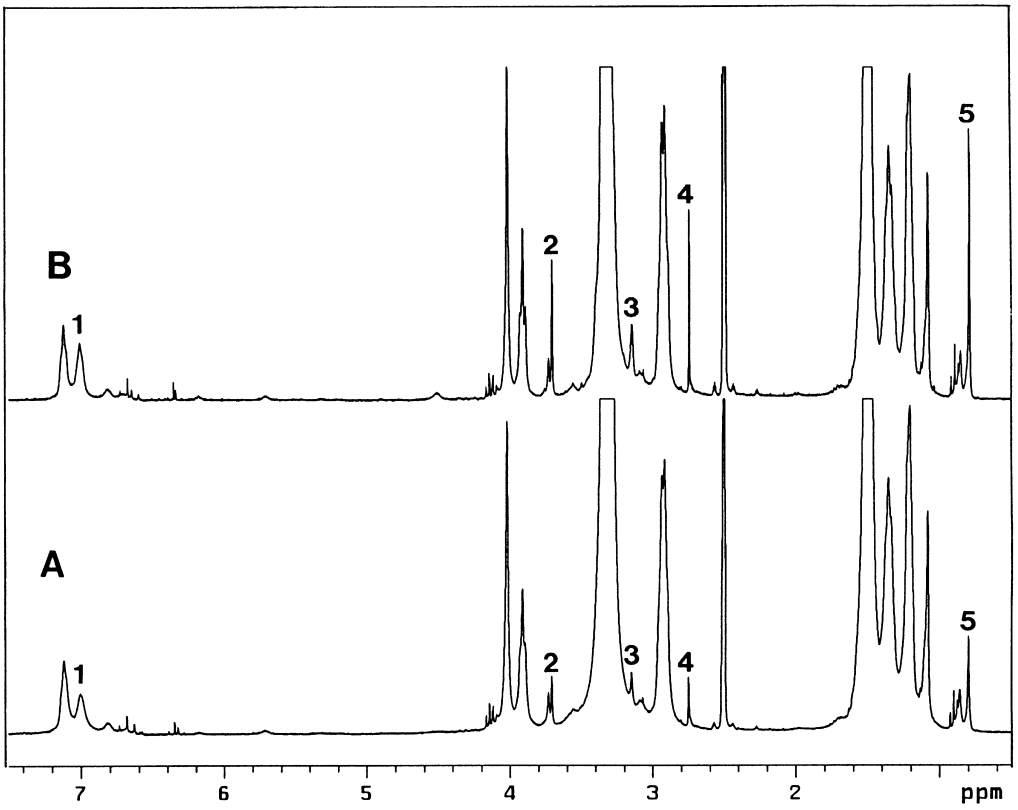


Fig. 4. ^{1}H NMR spectra of the higher (A) and lower molar mass (B) fractions of the carboxylated PU D50. Numbers 1, 2, 3 and 5 designate NPG proton resonances (1, –NHCOO–; 2, $-CH_2O-$; 3, $-CH_2OH$; 5, $-CH_3$) and number 4 ($-CH_2-$ of HDI), a signal of a branched structure.

aggregation behaviour [4–6]. At low concentrations of ionomer solutions, the reduced and intrinsic viscosities are much lower than those of the parent CPU D50, while at higher ionomer concentrations, the reduced viscosities approach or even exceed that of CPU (Fig. 6, Table 3). Namely, in the low concentration region, ionomer coils contract and become more compact due to the intramolecular dipolar interactions between ion pairs; at higher concentrations, ionic associates of different composition and of high molar masses are formed via interchain cross-links, which is reflected in higher reduced viscosity.

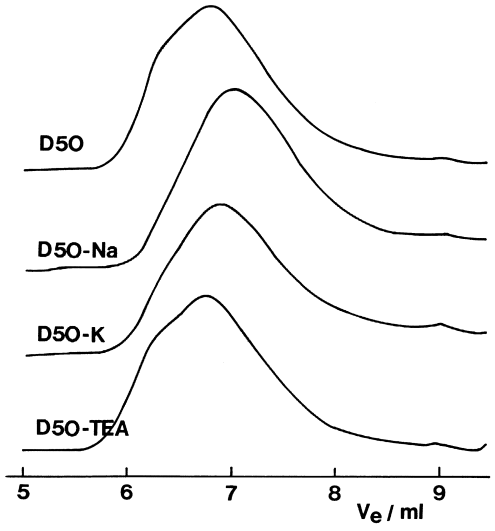


Fig. 5. SEC curves of carboxylated PU D50 and PU-ionomers D50-M (M = Na, K, TEA) in THF.

Comparing the viscosity curves of CPU D50 and related D50-M PUIs (Fig. 6), it can be seen that the intermolecular aggregation, indicated by the intersection of the viscosity curves [11], becomes dominant for D50-Na at lower concentration than for D50-K. The intrinsic viscosity of D50-Na is also lower (Table 3). Within the series of PUIs with monovalent counterions, the viscosity and SEC measurements (Figs 5 and 6) show that the intramolecular association in dilute solutions increases in the order $K^+ < Na^+ < Li^+$. Our findings are in agreement with the results reported on other carboxylated ionomers in low-polarity solvents [8–10,12].

The effect of the addition of a simple salt (CF_3COONa) on dilute viscosity behaviour of ionomers is shown for the PUI D50-Na sample (Fig. 7). Both intra- and intermolecular interactions between ion pairs decrease with the increasing concentration of CF_3COONa. In a 0.1 M CF_3COONa solution, the association of ion pairs is reduced to such a degree that the concentration dependence of the reduced viscosity approaches linearity as in the case of CPU D50 (Fig. 7).

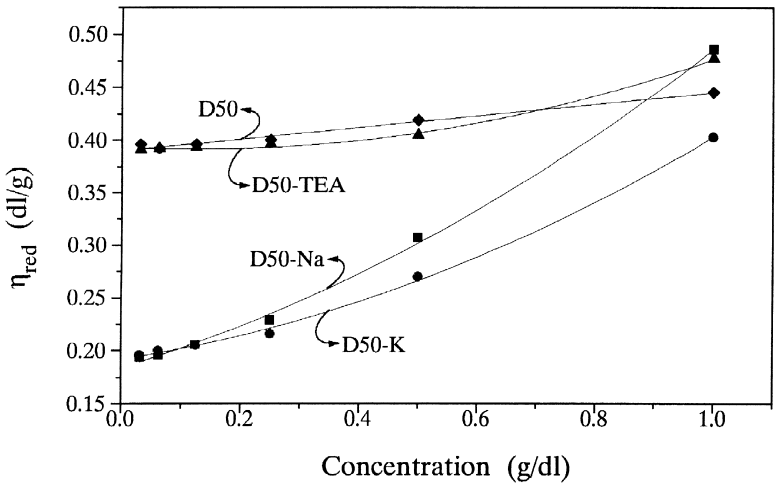


Fig. 6. Reduced viscosity (η_{red}) vs. concentration for carboxylated PU D50 and PU-ionomers D50-M (M = Na, K, TEA) in THF.

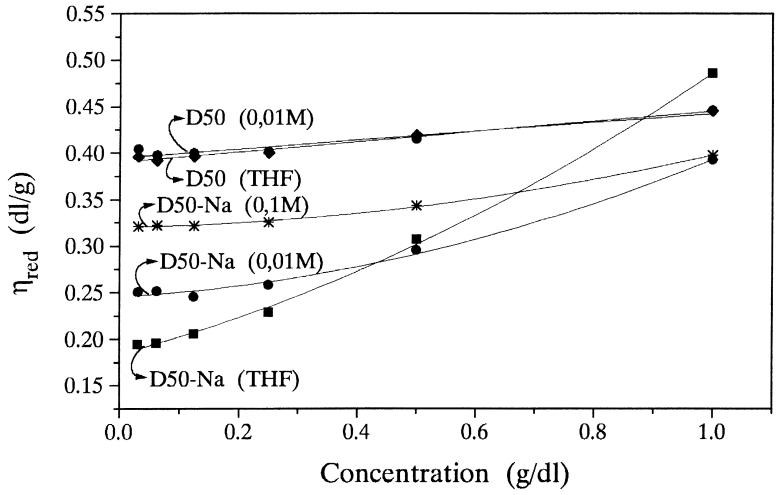


Fig. 7. Reduced viscosity (η_{red}) vs. concentration for carboxylated PU D50 and PU-ionomer D50-Na in THF with various CF_3COONa concentrations.

4. Conclusion

To explain the unusual SEC-PS results of the molar mass determination of a non-carboxylated polyurethane (NPU), carboxylated polyurethanes (CPUs) and related ionomers (PUIs) in THF, their dilute solution behaviour was investigated by viscometry, and for CPUs also by SEC-MALS. Viscometric results of CPUs were in agreement with SEC results. The SEC-PS and SEC-MALS molar mass averages and intrinsic viscosities of CPUs decrease with the increasing content of carboxylic groups, as a consequence of side-reactions. To a certain extent the isocyanate groups react with carboxylic groups, as well as with water present as an impurity. These side-reactions significantly lower the CPU molar masses and viscosities as compared to NPU.

The SEC-PS molar mass averages and intrinsic viscosities [η] of the selected series of PUIs are much lower than those of the parent CPUs. The large difference is ascribed to intramolecular association of carboxylate groups in dilute solutions, which increases with the increasing content of carboxylate groups. Molar mass and [η] depend on the type of counterion used in the following order: $Ca^{2+} < Li^{+} < Na^{+} < K^{+}$. The addition of CF_3COONa to THF prevents intra- and intermolecular association of PUIs.

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