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International Journal of Polymer Analysis and Characterization

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646643>

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Majda igon^a; Ema agar^a

^a National Institute of Chemistry, Ljubljana, Slovenia

To cite this Article igon, Majda and agar, Ema(2001) 'Association Behavior of Polyurethanes in Polar Solvents Studied by SEC Coupled with Light Scattering', *International Journal of Polymer Analysis and Characterization*, 6: 6, 521 – 532

To link to this Article: DOI: 10.1080/10236660108030867

URL: <http://dx.doi.org/10.1080/10236660108030867>

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Association Behavior of Polyurethanes in Polar Solvents Studied by SEC Coupled with Light Scattering

Majda Žigon and Ema Žagar

National Institute of Chemistry, Ljubljana, Slovenia

The solution behavior of non-carboxylated and carboxylated polyurethanes (PU) in THF, LiBr/DMF, and DMF was studied by size exclusion chromatography coupled with multiangle light scattering (SEC-MALS). This paper focuses on the association of PU macromolecules in DMF considering the influences of composition, solution concentration, and temperature. The degree of association increases with increasing amounts of polar urethane and carboxyl groups, with decreasing solution concentration, and by increasing the temperature of measurements or heat treatment—all of which demonstrate the role of impurities present in DMF on PU dilute solution behavior.

Keywords: Polyurethane; Size exclusion chromatography; Light scattering

INTRODUCTION

Polyurethanes (PU) are usually block copolymers composed of flexible soft polyester or polyether segments and hard segments, formed by diisocyanates and low molar mass diols. The hard segments tend to aggregate through hydrogen bonding of urethane groups to give ordered crystalline domains. The two kinds of segments differ in polarity and, consequently, are phase separated to a certain extent. Due to the polar hard

Received 9 November 1999; In final form 31 March 2000.

Address correspondence to Majda Žigon, National Institute of Chemistry, Hajdrihova 19, SI-1115 Ljubljana, Slovenia.

Presented at the 13th Bratislava International Conference on Polymers, "Separation and Characterization of Macromolecules," Bratislava, Slovakia, July 4–9, 1999.

segments, segmented PU are soluble mainly in polar solvents. PU solubility depends mainly on their composition, molar mass, and the type of the solvent used. For example, PU with high molar mass, high hard segment concentration, and bearing additional polar groups are soluble only in high polarity solvents like polar *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), or dimethyl sulfoxide (DMSO)^[1-7].

The specific properties of PU solutions are attributed to various molecular interactions. Specifically, macromolecules may interact with each other, with the solvent, or with solvent impurities. According to the choice of solvent, macromolecules can be molecularly dispersed; they may associate intramolecularly or intermolecularly forming physical bonds between attractive groups on the same chain or different chains. Intramolecular association leads to compact structures with small polymer coil size, while intermolecular association leads to supramolecular organization, e.g., to the formation of aggregates or even gels^[7-10].

Intramolecular and intermolecular interactions of polymer coils greatly affect the results of molar mass averages and distributions determined by conventional size exclusion chromatography (SEC). Since SEC gives relative results, which are related to the polymer standards used for column calibration, the intramolecular associates with compact chain conformations have large elution volumes and, consequently, small relative molar masses. However, supramolecular structures have small elution volumes and relative molar masses of a few orders of magnitude higher than the actual ones. Using size exclusion chromatography coupled with multiangle light scattering (SEC-MALS), absolute molar mass and size characteristics are obtained directly, without the need for column calibration^[11]. Therefore, SEC-MALS aids in the interpretation of SEC results^[6,7,12-15]. Moreover, it is among the most sensitive techniques for the detection of a small fraction of high-molar mass species and, as such, very suitable for studying the association of polymer chains in solution^[13,16].

Regarding PU dilute solution properties, tetrahydrofuran (THF), a low-polarity solvent, is a good solvent for flexible soft segments, but not as good a solvent for hard segments^[3,5,6]. PU chains in THF might form intramolecular associates having a more or less compact structure depending on the polarity of hard segments^[6]. However, DMF, a high polarity solvent, is a good solvent for soft, as well as hard segments, and various polar groups of PU. (In addition to urethane groups, there are hydroxyl end-groups, urea and amide groups.) One should expect good solubility and almost no interactions in DMF. However, the experimental SEC results show the presence of polydisperse PU associates^[1,7-10]. Similar observations were reported for other polar polymers like polyacrylonitrile and acrylic polymers in polar amide solvents^[12,13,17-24]. Their elution peculiarities were ascribed to the formation of polymer complexes involving interactions with impurities present in DMF^[24].

As shown by many authors, the addition of a small amount of LiBr to DMF inhibits these interactions completely.

In our laboratory, determination of molar mass averages and distributions of various types of polyurethanes (PU), such as segmented non-carboxylated and carboxylated PU or ionomers (PUI), have been performed by SEC using the eluent THF^[6,25]. In cases where the solubility in THF was low, DMF was used^[7]. However, some peculiarities were observed in DMF. First, the SEC curves of segmented PU showed additional peaks, while reproducibility of the measurements of carboxylated PU and related PUI was poor. Second, multimodal molar mass distributions with high relative molar masses were obtained. The addition of a small amount of LiBr to DMF resulted in unimodal molar mass distributions.

The aim of this paper is to show PU dilute solution behavior in THF, DMF, and DMF with added electrolyte LiBr, and to focus particularly on the association of PU macromolecules in DMF. The influences of composition, solution concentration, and temperature on the degree of PU association were studied using SEC-MALS. We determined the distributions and apparent averages of molar mass and radius of gyration R_g of segmented non-carboxylated and carboxylated PU of medium molar masses ($M_w = 30,000 - 70,000$). For this study we also utilized other complementary techniques, namely viscometry, static light scattering (LS), and NMR, the results of which will be reported on in forthcoming papers.

EXPERIMENTAL

Synthesis

Segmented non-carboxylated and carboxylated PU were prepared as 40% solutions in DMF (water content < 0.005%, Aldrich) by a two-step procedure described in our previous paper^[6]. For their synthesis we used aliphatic (hexamethylene diisocyanate, HDI, Fluka) or aromatic diisocyanates (methylene bis(*p*-phenylene isocyanate), MDI, Aldrich), a polyether diol (poly(tetramethyleneoxide), PTMO, $M_n = 1000$, BASF), and two low molar mass diols: 2,2-bis(hydroxymethyl)propionic acid (synonym dimethylolpropionic acid, DMPA, Jansen) and 2,2-dimethyl-1,3-propanediol (synonym neopentylglycol, NPG, Fluka). The molar ratio of MDI to PTMO to chain extenders (molar ratio DMPA: NMP = 1:1) was 3:1:2. The chain extension reaction was catalyzed with dibutyltin dilaurate (DBTDL, Acima). Polymers were precipitated by pouring DMF solutions into distilled water and drying them under vacuum at 50°C until ¹H signals of water and DMF in ¹H NMR spectra disappeared.

Non-carboxylated PU are designated as H-D0 (prepared with HDI) and M-D0 (prepared with MDI), while carboxylated PU are designated

as M-D50, where "50" stands for the molar percentage of DMPA in the chain extender mixture.

Characterization Methods

The SEC-MALS measurements were performed at 25°C and 75°C using a Hewlett-Packard pump series 1100 coupled to a Wyatt Technology Dawn-DSP laser photometer equipped with an He-Ne laser ($\lambda_0 = 633$ nm) and to an Optilab-DSP differential refractometer (DR). A PLgel 5- μ m column Mixed D of 30-cm length with a precolumn with the eluents THF ($\epsilon_{25} = 7.6$, water content $< 0.05\%$, Fluka), DMF ($\epsilon_{25} = 36.7$, water content $< 0.01\%$, Aldrich, used as received) or DMF with added LiBr (0.1 M) at a flow rate of 0.8 mL/min was used. The typical amount of each sample injected was approximately $1.5\text{--}3.0 \cdot 10^{-3}$ g (solution concentration 1.5–3.0%, w/v, injection volume 100 μ L). The refractive index increments (dn/dc) were measured using an Optilab DSP at $\lambda_0 = 633$ nm. Data acquisition and evaluation utilized Astra 4.50 and DNDC 5.00 software. Due to the fluctuations in the chemical composition and molar mass of PU, as well as to the fact that only an average dn/dc of the sample and not dn/dc of the individual fractions could be used, SEC-MALS measurements gave an apparent weight-average molar mass (M_w^{app}).

RESULTS AND DISCUSSION

PU Dilute Solution Behavior in THF and LiBr/DMF

Figure 1 shows a representative SEC-MALS chromatogram of a carboxylated PU M-D50 with a broad molar mass distribution in THF where the responses of the differential refractometer (DR) and 90° light scattering (LS) photometer are drawn as a function of the elution time t_e , which is proportional to the elution volume V_e by a factor of 0.8. As characteristic of broad distribution polymers, the light scattering response is skewed toward the high molar mass at smaller V_e , since scattering intensity is proportional to the product of the concentration c of a polymer solution and its molar mass M . The molar mass and radius of gyration R_g were calculated for each slice i of the peak by extrapolation of the reciprocal intensities of the scattered light to a zero scattering angle, and the corresponding averages were obtained using the usual summation expressions. R_g values below 15 nm were not reliable since the results for molecules below this size could not be determined precisely.

The application of an LS photometer enabled us to monitor the intensity of the scattered light at multiple angles (Figure 2). The

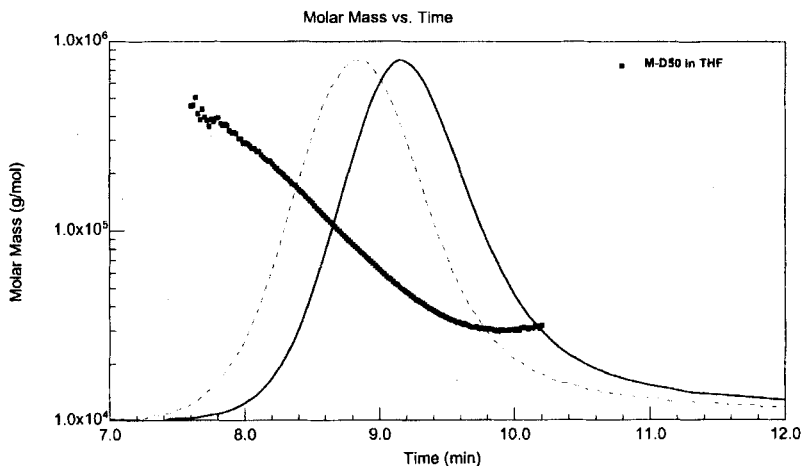


FIGURE 1 Molar mass as a function of elution time and the SEC-MALS chromatogram of carboxylated polyurethane M-D50 in THF; --- LS response at angle 90° , — DR response.

three-dimensional (3D) plots of both types of PU in THF and LiBr/DMF show that LS intensity does not change as a function of scattering angle, which is typical of small particles. From Table I it can be seen that the $\langle M_w \rangle$ of non-carboxylated and carboxylated PU range from 3.1×10^4 to 7.1×10^4 g/mol.

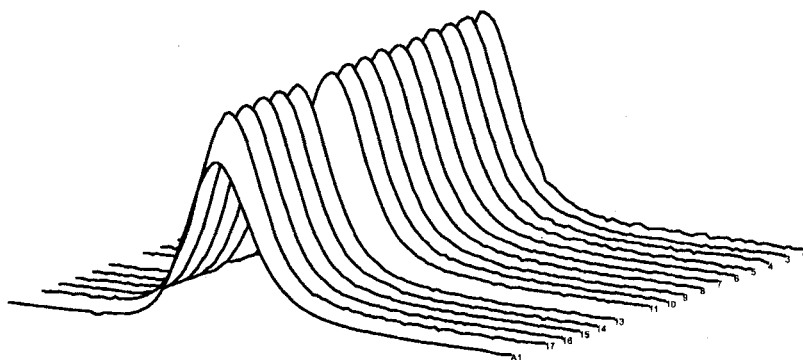


FIGURE 2 3D plot of carboxylated polyurethane M-D50 in THF, --- LS responses at different scattering angles (marked as 2-17), — DR response (marked as A1).

TABLE I SEC-MALS Results for Polyurethanes with Different Chemical Compositions in Solvents THF, 0.1 M LiBr/DMF, and DMF

PU Sample	THF			0.1 M LiBr/DMF			DMF		
	dn/dc mL/g	$\langle M_w \rangle$ g mol ⁻¹	$\langle R_g \rangle_z$ nm	dn/dc mL/g	$\langle M_w \rangle$ g mol ⁻¹	$\langle R_g \rangle_z$ nm	dn/dc mL/g	$\langle M_w \rangle$ g mol ⁻¹	$\langle R_g \rangle_z$ nm
H-D0	0.083	3.1·10 ⁴	12 ^a	0.048	3.1·10 ⁴	12 ^a	0.045	10 ⁴ –10 ⁵	> 100
M-D0	0.143	6.9·10 ⁴	23	0.105	7.1·10 ⁴	19	0.101	10 ⁴ –10 ⁵	> 100
M-D50	0.140	6.0·10 ⁴	20	0.104	6.1·10 ⁴	16	0.099	10 ⁵ –10 ⁶	> 100

^a unreliable values.

For a dilute solution of a polydisperse polymer, the conformation of macromolecules in the selected solvent can be estimated from the bi-logarithmic plot of R_g vs. molar mass considering the scaling relationship $R_g \sim M^\alpha$. The power law exponent may extend from about 0.3 for spheres to about 1 for rigid rods. The slope of non-carboxylated PU H-D0 is 0.50 and of M-D0 is 0.56, which is indicative of a random coil conformation, while the slope of carboxylated PU M-D50 is 0.34, indicative of a globular conformation, which may be due to intramolecular interactions of poorly solvated carboxyl groups. In LiBr/DMF, the power law exponent is 0.32 for both types of PU, which indicates a globular conformation for the non-carboxylated PU as well. Intramolecular interaction of both kinds of PU in a high polarity solvent LiBr/DMF, which otherwise effectively prevents intermolecular interactions of polar and ionic groups, can be explained by its somewhat lower solvent power for low polarity soft segments compared to THF. This is also reflected in the smaller R_g in LiBr/DMF than in THF (Table I), indicating stronger intramolecular interactions and, consequently, more compact chain structures. However, the PU weight-average molar masses are the same in both solvents.

PU Dilute Solution Behavior in DMF

The Influence of Composition on the Degree of PU Association

In the chromatogram of non-carboxylated PU, new small peaks appear at small V_e and are detected by both the DR and LS photometer (Figure 3). The molar mass of the small peaks is a few orders of magnitude higher than the main peak (e.g., 10⁶ vs. 10⁴); it is also higher for aliphatic H-D0, compared to aromatic M-D0, due to the higher amount of urethane groups per gram of PU. 3D plots show a pronounced angular

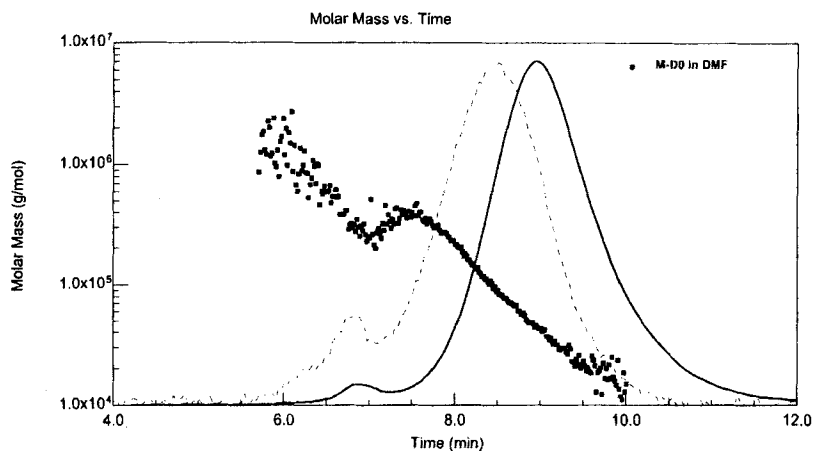


FIGURE 3 Molar mass as a function of elution time and the SEC-MALS chromatogram of non-carboxylated polyurethane M-D0 in DMF; --- LS response at angle 90° , — DR response.

dependence of the light scattering intensity for the small peaks, indicating high molar mass species, and almost no angular dependence for the main peak of low molar mass species.

The 90° LS response of carboxylated PU M-D50 is very intense in a small V_e region (Figure 4), and the 3D plot is characteristic of large

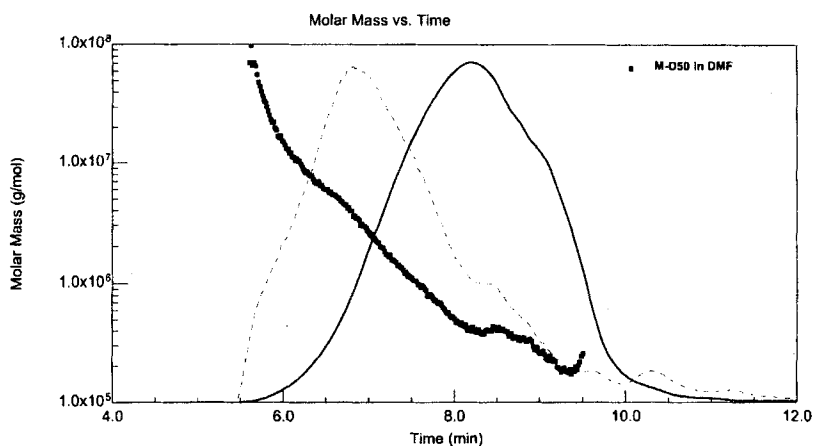


FIGURE 4 Molar mass as a function of elution time and the SEC-MALS chromatogram of carboxylated polyurethane M-D50 in DMF; --- LS response at angle 90° , — DR response.

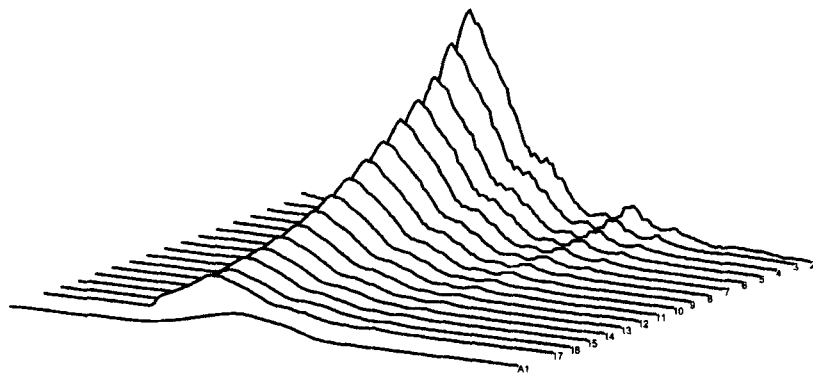


FIGURE 5 3D plot of carboxylated polyurethane M-D50 in DMF, — LS responses at different scattering angles (marked as 2-17), — DR response (marked as A1).

particles (Figure 5). The molar masses of the individual slices of chromatographic peaks are much higher than those of the non-carboxylated M-D0. A high degree of association of carboxylated PU is also confirmed by a large R_g , over 100 nm (Table I).

Considering the presence of the PU associated species in dilute DMF solutions determined by SEC-MALS, the increase in reduced viscosity in a very dilute region (below ~ 0.2 g/dL), known as the polyelectrolyte effect^[26], should be interpreted as occurring not only by expansion of macromolecules but also by association phenomenon, which has already been cited^[8,13].

The Influence of Solution Concentration on the Degree of PU Association

The DR responses of both non-carboxylated and carboxylated PU follow the expected relationship between elution volume and solution concentration (Figure 6): the apex of the main peak shifts to smaller V_e and higher molar masses with decreasing concentration^[27-29]. The same also holds for the 90° LS curves of the main peak. However, the apexes of the peaks at small V_e in the early portion of molar mass distribution shift to smaller V_e and the intensity of the peaks increases with decreasing concentration. As a consequence, the increase in overall weight-average molar mass with decreasing concentration is considerable. When 0.0001 and 0.0002 g of non-carboxylated PU M-D0 were injected, the $\langle M_w \rangle$ were 1.6×10^5 and 1.1×10^5 , respectively, while at 0.0002 and 0.0006 g of carboxylated PU M-D50 the $\langle M_w \rangle$ were 2.5×10^6 and 5.3×10^5 , respectively.

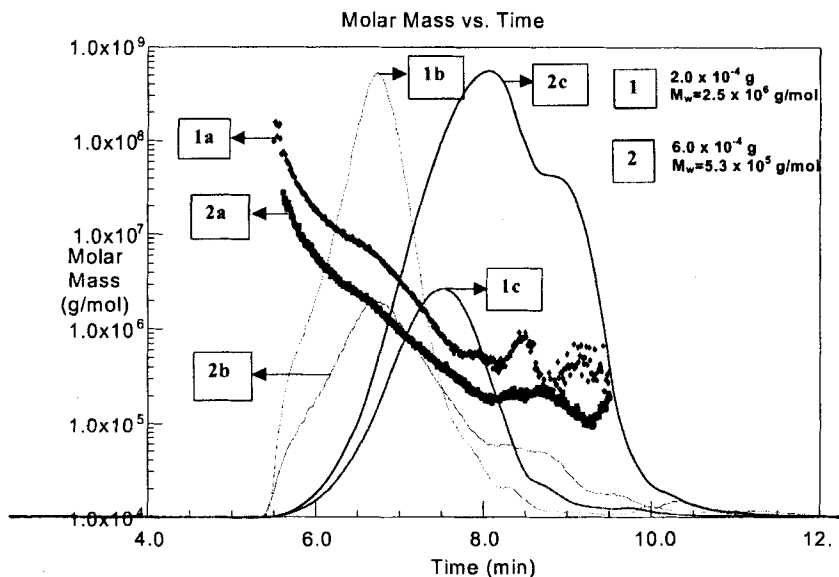


FIGURE 6 Molar mass as a function of elution time (1a, 2a) and the SEC-MALS chromatograms of carboxylated polyurethane M-D50 in DMF at two injected amounts: (1) 0.0002g, and (2) 0.0006g; --- LS response at angle 90° (1b, 2b), — DR response (1c, 2c).

The Influence of Temperature on the Degree of PU Association

The SEC-MALS measurements were regularly performed at 25°C . To observe the influence of temperature on the degree of association, the measurements were run at 75°C . The PU samples were also held at 75°C for 14h and measured at 75°C . The 90° LS intensity of the peaks at small V_e increases at 75°C and especially after heat treatment (Figure 7) thus showing the pronounced temperature effect on the formation of associates. It is worth noting that the differences in V_e of the main peak are also detected by a differential refractometer, meaning that temperature effects should be taken into account with the conventional SEC.

In order to find out which polar groups are responsible for the pronounced intermolecular interaction, we recorded ^1H NMR spectra at various temperatures. Surprisingly, at 75°C the signals of the NH urethane group shifted to a higher field, indicating the weakening or disruption of hydrogen bonds, which should lower the degree of association. However, the solution concentration for ^1H NMR measurements was much higher than the concentrations of individual fractions of the chromatographic peaks. This means that the intermolecular interaction be-

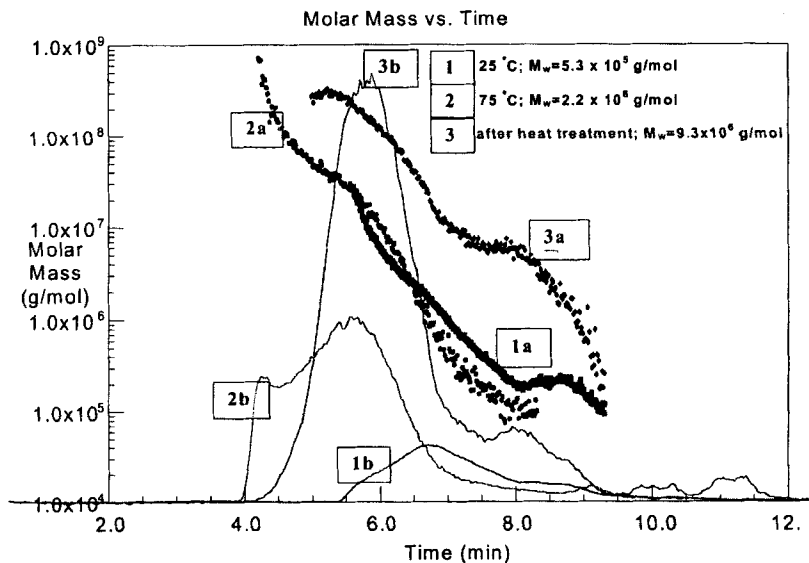


FIGURE 7 Molar mass as a function of elution time (1a, 2a, 3a) and the SEC-MALS chromatograms of carboxylated polyurethane in DMF as a function of temperature: (1) measurements at 25°C, (2) measurements at 75°C, and (3) measurements at 25°C after heat treatment at 75°C for 14h; — LS response at angle 90° (1b, 2b, 3b).

comes very important at very high dilutions; this has also been demonstrated by the increase in $\langle M_w \rangle$ with decreasing concentration (Figure 6).

A possible explanation for the peculiar behavior of PU solutions in DMF was proposed by Dias et al.^[24] stressing the role of the impurities present in this solvent. Specifically, DMF is known to degrade over time to form polar amines and oxalic acid. According to Dias, the source of the intermolecular interaction is presumed to be ionic species generated from dissociated amines and oxalic acid. Even a very small quantity of these species has a dramatic effect on the dilute solution properties of polar polymers. If we assume an approximately constant amount of impurities in the solvent, their influence on dilute solution behavior is far more pronounced at the high dilutions (≤ 0.01 mg/mL) encountered in the SEC measurements. Similarly, at elevated temperatures the degradation is accelerated and, consequently, the degree of association increases.

CONCLUSION

SEC-MALS has proved to be a very sensitive tool for the study of intramolecular and, especially, intermolecular interactions of polar polymers in very dilute solutions. The determination of molar mass distributions, averages, and radius of gyration of non-carboxylated and carboxylated polyurethanes in THF and LiBr/DMF indicates only intramolecular interactions. In DMF, the presence of associates gives evidence of a significant intermolecular interaction being influenced by composition, solution concentration, and temperature. The relationships between these parameters and the degree of association demonstrate the influence of impurities present in DMF on the extent of intermolecular interaction.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the Ministry of Science and Technology of the Republic of Slovenia for their financial support of research program No. P1-514. The authors also thank Mrs. Mira Mikuž for her valuable technical assistance.

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