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Characterization of poly(naphthalenesulfonate) salts by ion-pair chromatography and ultrafiltration

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Abstract

The molecular mass distribution of naphthalenesulfonate condensation products (PNS) was investigated using ion-pair reversed-phase chromatography and ultrafiltration. The chromatograms obtained under an optimized solvent elution program yielded nearly 20 well resolved peaks corresponding to low and intermediate molecular mass species. A distinct broad peak was also resolved and attributed to polymeric species with relative molecular mass in excess of 5000. Under isocratic elution conditions, a linear relationship was obtained between the peak number and the log of the retention time for the first 17 peaks, thus indicating a homologous series of linear oligomers. The fractionation of the PNS mixtures by ultrafiltration enabled further resolution of the high molecular mass species; the latter also exhibited a broad distribution of molecular mass. Significant differences were also found amongst different commercial PNS products with similar average chemical composition.

1. Introduction

Poly(naphthalenesulfonic) acid is obtained by condensation of naphthalenesulfonic acid (α or β) with formaldehyde. A schematic representation of linear and singly-branched tetramers of poly(β-naphthalenesulfonate) (PNS) sodium salts is shown in Fig. 1. These polymers are broadly used as dispersants of organic or mineral colloids in aqueous systems. The ability of this type of products to fluidize fresh concretes at very low water/cement ratios makes them an essential component in the production of high performance concrete [1,2]. Other applications, such as "water reducer" in gypsum board fabrication, as dye dispersant in the textile industry [3] and as leather tanning additive [4] are also widely known.

The dispersing/fluidizing properties of PNS salts have been suggested, or shown, to be dependent on their molecular mass [5–10]. The suggested mode of action of these polymers involves adsorption on the dispersed particles and particle–particle repulsion through electrostatic or steric effects [5,7,8,11–13]. A more detailed understanding of these mechanisms clearly requires an accurate characterization of the molecular species (e.g. molecular mass, branching, crosslinking, degree of sulfonation).

The nature and distribution of the species present in PNS condensation products have been investigated using several chromatographic methods: paper [4,14], size-exclusion [6,15,16], salting-out [17,18], anion-exchange [19] and ion-pair [19] chromatography.

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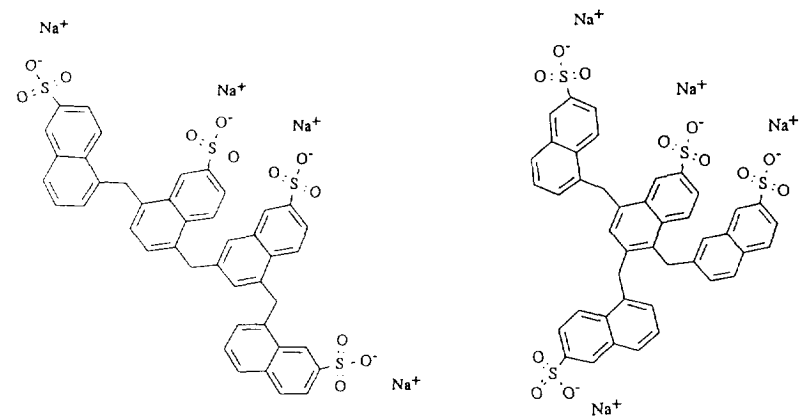

Fig. 1. Example of linear and branched tetramers of poly(β-naphthalenesulfonate) salts.

Fudano and Konishi [17] investigated various salting-out chromatographic columns and conditions and, under optimal conditions, resolved five distinct peaks; the first broad peak was further split up into five components by curve-shape analysis. The nine resulting peaks were compared with data from Hattori and Tanino [14], who had found nine spots in paper chromatographic analysis. Using size-exclusion chromatography (SEC), Garvey and Tadros [15] reported PNS oligomers with a degree of polymerization (P) between 1 and 9. Basile et al. [6] also used a SEC method to determine the number average $M_{r,n}$ of the fraction of PNS retained on an ultrafiltration membrane with a molecular mass cut-off (MWCO) of 1000. They obtained M_r values ranging from 435 ($P = 1.8$) to 735 ($P = 3$), depending on the reaction time.

More recently, Miller [19] investigated PNS separation using ion-pair chromatography and could resolve two peaks, respectively attributed to linear and branched polymers. A comparison with poly(styrenesulfonate) data suggests that the degree of polymerization of the high molecular mass fraction of PNS may be as high as 90 ($M_r = 21\,600$). With a similar method, Costa et al. [5] resolved the first peak into nearly ten peaks and identified ten additional peaks on the shoulder of the second broad peak.

As is apparent from the above overview, the polymeric species present in PNS mixtures are difficult to separate and identify. In view of the importance of the species distribution on the functional properties of the polymers, the present study was undertaken to reexamine some previously used analytical separation methods, and to further explore their potential for deriving information on the size and structure of PNS polymers.

2. Experimental

2.1. Material

Water was distilled and deionized with a Milli-Q (Millipore, Saint-Quentin-en-Yvelines, France) system (resistivity $> 17\ M\Omega\ cm^{-1}$) and then filtered over 0.22 μm filter. The acetonitrile used was of HPLC grade; glacial acetic acid and tetrabutylammonium bromide (TBAB) were ACS reagent grade. All other chemicals used were laboratory reagent grade. PNS compounds labelled A, B, C, D are all commercial preparations of sodium salts of PNS intended for fluidization of concrete or gypsum pastes, or for dispersion in other industrial applications.

2.2. Methods

Partisil 5 ODS-3 (Whatman, Clifton, NJ, USA) and Bondclone 10C18 (Phenomenex, Torrance, CA, USA) HPLC columns, 300 × 3.9 mm I.D., were used; the chromatographic ma-

terial consisted of C_{18}-grafted silica particles of 5 μm and 10 μm diameter, respectively. Detection was performed by measuring absorbance at 280 nm. Injections were made through a 50-μl or a 100-μl loop loaded with 10–50 μg of PNS (dry basis) in water. Integration was made using the area normalization method.

The eluent was a mixture of two solvents prepared as described by Miller [19]. Solvent A was 0.01 *M* TBAB in 99% water and 1% glacial acetic acid; solvent B was 0.01 *M* TBAB in 99% acetonitrile and 1% glacial acetic acid. The elution programs were executed by a gradient pump module (Dionex, Sunnyvale, CA, USA). The flow-rate of the eluent was maintained constant within ± 0.05 ml/min during each run; for any given run, it was adjusted at a value between 1.0 and 1.5 ml/min.

Ultrafiltration experiments were carried out in stirred cells (Amicon, Beverly, CA, USA) using the following series of membranes: YC05, YM2, YM5, PM10 (Amicon). The membrane specifications are given in Table 1. In the procedure followed here, a 10% solution of crude PNS was first filtered on the membrane with MWCO 500. The retained fraction was then diluted with water and filtered again on the same membrane; these operations were repeated for a total of at least five times. The membrane with the smaller pore size was used first in order to eliminate most of the electrolytes, thereby ensuring that the subsequent filtrations are performed at minimal ionic strength. The filtrates were combined and analyzed, while the final retained fraction was used as starting material for ultrafiltration on the membrane with the next larger pore size. The complete ultrafiltration procedure is illustrated schematically in Fig. 2.

Table 1
Ultrafiltration membrane specifications (Amicon)

Membrane	Approximate pore diameter (Å)	Nominal M_r cut-off
YC05	10.5	500
YM2	12	1000
YM5	13.5	5000
PM10	15	10 000
XM50	32	50 000
YM100	51	100 000

Nominal cut-off and pore diameter are established with globular proteins 95% retained on the membrane.

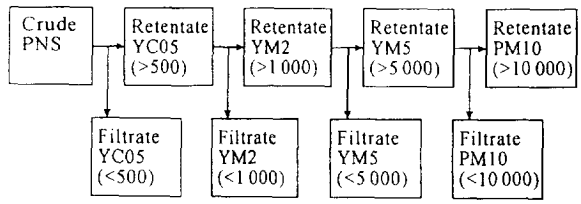

Fig. 2. Ultrafiltration procedure.

3. Results and discussion

3.1. Ion-pair chromatography

Isocratic elution

Although isocratic elution rarely represents the optimum condition to achieve separation of a complex mixture, it can nevertheless give valuable information on the partitioning between the static and the mobile phases. When pure water was used as the eluent, there was no retention and a single peak was detected. Conversely, when solvent A (water + TBAB) was used, no PNS was eluted. This stresses the critical role of ion-pairing on the retention mechanism. Using only solvent B, we detected a single peak at minimum retention time. Following various attempts with different A/B mixing ratios, a mixture containing 35% A and 65% B yielded the PNS chromatogram shown in Fig. 3. Because of considerable overlap, the precise integration of each of the twenty peaks observed can not be achieved, but their retention times yield valuable information. A plot of log (t_R) against the peak number is found to be linear (slope = 0.0615, R.S.D. = 0.6%, r = 0.9996); this relationship strongly indicates the presence of linear PNS oligomers and polymers [20–22] with a degree of polymerization as high as 17. Although the procedures used differ, the chromatogram shown in Fig. 3 is similar to that reported by Miller [19]; from NMR data, Miller attributed the first peak

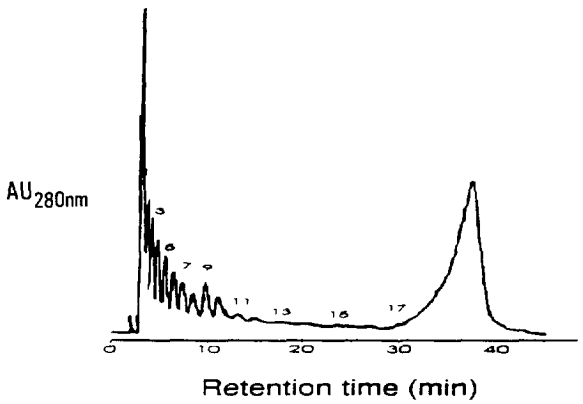

Fig. 3. Chromatogram of PNS-A with isocratic elution (35% A; 65% B).

(which corresponds to the group of 17 peaks found here) to linear PNS polymers.

Programmed solvent elution

Upon varying the A/B ratio, it was noticed that with 40% B, only the first four peaks of the PNS sample injected were eluted; with a higher content of solvent B (60%), the mid peaks were eluted, but the final broad peak was not. These experiments led to the conclusion that the resolution of either the first four peaks, or the mid peaks, was optimum when the eluent contained the minimum proportion of solvent B which achieved elution. All attempts to resolve the final peak into distinct components were unsuccessful. After numerous runs under varying conditions, the solvent elution program reported in Table 2 was adopted. It should be noted that the analytical separation is completed after the first 50 min of the elution program. The dual purpose of the rest of the elution program is first to prevent any micro-bubble formation and, second to ensure a regular purge of the column; in the absence of the latter procedure, the complex solubility behavior of PNS [10], can sharply reduce the column's life-time. Using this program, chromatograms were obtained for various naphthalenesulfonates; the t_R values for these compounds are reported in Table 3. α-Naphthalenesulfonate and β-naphthalenesulfonate exhibit the same retention time as the first peak of the chromatogram obtained for PNS (Figs. 4b, 5); naphthalene di- and tri-sulfonates were eluted in the mid peak region of the chromatogram.

Table 2
Elution program

Time (min)	Solvent A (%)	Solvent B (%)
0	60	40
10	35	65
25	35	65
35	20	80
45	20	80
47	0	100
50	0	100
52	20	80
54	20	80
55	60	40
60	60	40

Solvent A: TBAB 0.01 *M* in 99% water, 1% acetic acid.
Solvent B: TBAB 0.01 *M* in 99% acetonitrile, 1% acetic acid.

For PNS, the expected first and second peaks were only weakly resolved by this solvent elution program; however the mid peaks were well resolved. The chromatograms of Fig. 4b, 5 and 6 show that the first twenty peaks previously observed under isocratic elution are slightly asymmetric. Hence, while the maximum of each peak may correspond to a linear polymer, the area under the peaks cannot be exclusively attributed to linear polymer populations. The

Table 3
Retention time and peak area from chromatograms of various naphthalenesulfonate salts

Compound	Retention time (min)	Relative peak area (%)
α-Naphthalenesulfonate	5.3	100.0
β-Naphthalenesulfonate	5.3	100.0
2,7-Naphthalenedisulfonate	6.3	100.0
2,6-Naphthalenedisulfonate	6.1	100.0
Naphthalenetrisulfonate	6.4	2.7
	7.0	1.6
	8.8	92.3
	12.7	3.3

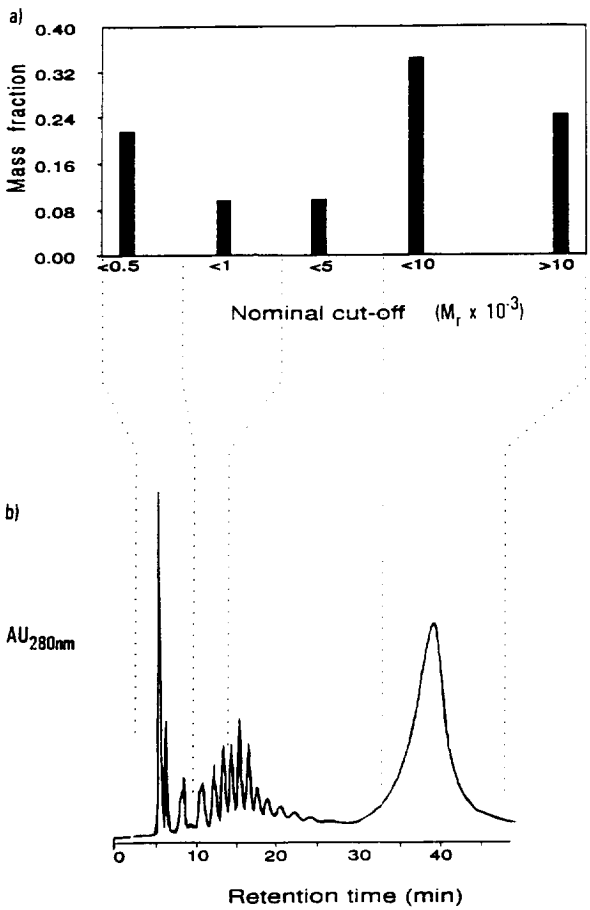

Fig. 4. (a) Size distribution of PNS-A obtained from successive ultrafiltrations; (b) Chromatogram of PNS-A using the elution program from Table 2.

relative areas computed from Fig. 4b gave about 7% for the first peak (which includes monomers and dimers), about 4% for the two following peaks (corresponding to oligomers with $P = 3,4$), about 25% for the rest of the mid peak region, and finally about 65% for the last broad peak (attributed to polymer with higher molecular mass). Since the extinction coefficient at 280 nm varies with the molecular mass of the polymer [10], the peak areas correspond only roughly to the relative populations; the smaller molecules have a lower specific absorbance, therefore their populations are underestimated. Nevertheless, the chromatograms provide a highly convenient relative basis for both qualitative and quantitative characterization of PNS mixtures as usually found in commercial preparations.

Fig. 5 shows chromatograms for three commercial PNS mixtures (B, C, D) and Table 4 lists the relative area under the peaks for all PNS samples investigated. Comparing the peak intensities for PNS-A (Fig. 4b) and PNS-B, it is readily seen that a higher proportion of PNS-A is eluted in the last peak; however, the overall patterns of polymer distribution, as reflected by the chromatographic peak intensities, are similar. The molecular mass distribution (intensities) of PNS-C and PNS-D are strikingly different from those of the A or B samples.

Number and mass average molecular mass values ($M_{r,n}$ and $M_{r,m}$) have been computed from the chromatograms and the results are collected in Table 5. For these calculations, it was assumed that the peaks numbered 1 to 20 are oligomers having the corresponding degree

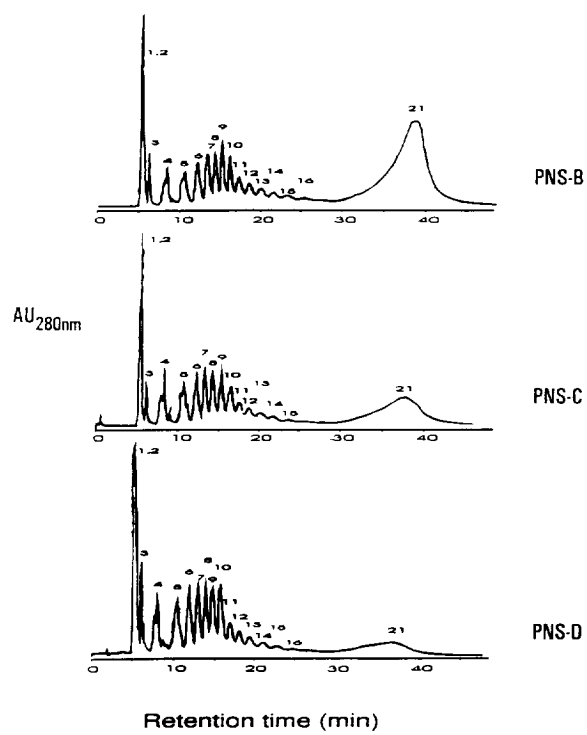

Fig. 5. Chromatograms of several commercial PNS preparations (B, C, D).

Table 4
Retention time and peak area of various PNS mixtures

Peak	Retention time (min)	Relative area			
		PNS-A (%)	PNS-B (%)	PNS-C (%)	PNS-D (%)
1	5.4	7.4	8.4	17.8	21.0
2	5.7	–	–	–	–
3	6.2	1.9	1.9	2.7	5.7
4	8.3	2.2	3.2	7.7	8.6
5	10.7	2.6	3.7	7.9	8.3
6	12.2	2.8	3.6	7.3	8.1
7	13.3	3.0	3.7	7.0	7.4
8	14.2	2.9	3.6	6.4	6.4
9	15.3	3.7	4.2	6.6	7.4
10	16.3	3.2	3.7	5.7	8.0
11	17.4	2.0	2.6	3.9	3.8
12	18.7	1.6	2.1	3.0	2.8
13	20.1	1.2	1.7	2.2	1.9
14	21.9	0.7	1.2	1.2	1.1
15	23.0		0.7		0.6
16	25.0		0.3		
21	36–38	64.8	55.4	20.6	8.8

of polymerization. The M_r value of the polymers under the last broad peak was taken as either 25 000 or 100 000. $M_{r,n}$ were found to be insensitive (within 5%) to the latter assumption; as expected, $M_{r,m}$ depended strongly on the assumed molecular mass of the larger polymers. The different PNS samples exhibit $M_{r,n}$ values between 700 and 2100, the lower value being in good agreement with earlier reports [6,14,15,17]. The polydispersity given by $M_{r,m}/M_{r,n}$ is very high, ranging between ~5 and ~30.

3.2. Fractionation through ultrafiltration

The ultrafiltration procedure described in Section 2.2 was used to separate a sample of the PNS-A into five fractions. Typical results are illustrated as a bar chart in Fig. 4a. This molecu-

Table 5
Molecular mass averages of PNS calculated from HPLC and ultrafiltration

	HPLC			Ultrafiltration		
	$M_{r,m}$		$M_{r,n}$	$M_{r,m}$		$M_{r,n}$
	A[a]	B[b]		A[a]	B[b]	
PNS-A	17 000	65 000	2100	11 000	35 000	2200
PNS-B	15 000	56 000	1800			
PNS-C	6000	22 000	910			
PNS-D	3500	10 000	770			

[a] Assumption A: M_r of last peak is 25 000.
[b] Assumption B: M_r of last peak is 100 000.

lar size distribution is very similar to the one found by ion-pair chromatography. As in the latter, a first peak is found corresponding to very low molecular mass species, followed by a minimum at the oligomer position. The "high molecular mass" region ($M_r > 5000$) is again found to represent about 60% of the total. It was also noticed that a large proportion of these high molecular mass species (retained on MWCO = 5000) was found in the lowest molecular mass side (passed MWCO = 10 000) of the band. Further ultrafiltration experiments using membranes having larger pore size indicated that substantial fractions of the polymers retained on the MWCO = 10 000 membrane were also retained on membranes with MWCO values of 50 000 and 100 000 (data not shown).

As with the HPLC data, the ultrafiltration results were used to derive average molecular mass values ($M_{r,n}$, $M_{r,m}$) under various assumption (Table 5). M_r values of respectively 300, 750, 2500 and 7500 were assigned to the four passing fractions. For the retained fraction, M_r values of either 25 000 or 100 000 were used, as in the treatment of the HPLC data. Comparison of the M_r values obtained from the two techniques shows a rather good agreement.

3.3. Correlation between HPLC and ultrafiltration results

To evaluate the effectiveness of the membrane fractionation process, the different fractions were analyzed by the chromatographic method described above and the results are illustrated in Fig. 6. Monomers up to tetramers apparently passed through the YC05 membrane, indicating that the membrane has an actual MWCO for PNS of about 1000 (compared to the nominal MWCO of 500, Table 1). The chromatograms of the ultrafiltration fractions also show that pentamers, hexamers and heptamers were retained on the YC05 membrane and passed the YM2 membrane, along with some octamers to decamers; the effective MWCO of the YM2 membrane for PNS would thus be about 2000 (compared to the nominal MWCO of 1000). With the next membrane (YM5), PNS oligomers of P up to 20 were

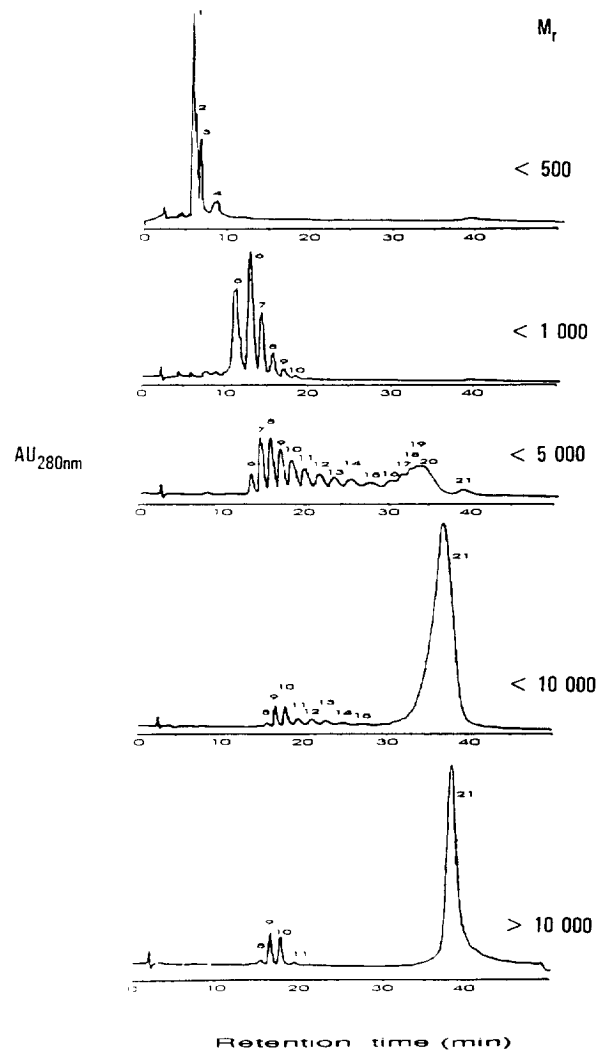

Fig. 6. Chromatograms of the fractions obtained by ultrafiltration.

allowed through; the effective PNS MWCO of this membrane would thus be of about 5000 (same as the nominal MWCO). Unfortunately, the resolution of the ion-pair chromatographic method does not provide further information on fractions that are retained on the YM5 membrane. All of those fractions showed small peaks in the region corresponding to $P \sim 10$ (≈ 15 min) and a large peak at around 38 min. As can be seen from Fig. 4, ion-pair chromatography yields

more detail in the low and intermediate molecular mass region, while ultrafiltration provides more information on the high molecular mass fractions of PNS.

4. Conclusions

The results presented above confirm the potential of ion-pair HPLC and ultrafiltration for the characterization of poly(naphthalenesulfonate) mixtures.

The HPLC technique, as used here, enables a separation of the monomers and oligomers with $P \approx 20$ (or M_r up to ~ 5000) from mixed PNS condensation products. The method involves a relatively complex solvent elution program but, compared to other characterization methods (e.g. GPC), it is relatively rapid (~ 1 h).

The ultrafiltration technique also enables an adequate separation of PNS polymers by M_r classes; the technique is relatively long (many hours) and is particularly well-suited for high M_r values, typically in the range 10^3–10^6.

Overall, the results show that the PNS dispersant polymers exhibit a high degree of polydispersity. A similar trend, or shape, of the PNS species distribution was observed with both techniques. A typical mixture of PNS condensation products used as dispersant/fluidizer consists of a fairly high proportion of oligomers (about 10% of $P = 1$–4) in which the monomers are the more abundant species. Linear polymers can be found in the mixtures, with M_r values as high as 5000 ($D \sim 20$), the maximum of this population being near 2500 ($P = 10$). The high molecular mass fraction contains $\sim 35\%$ of intermediate species ($M_r = 5000$ to 10 000; $P = 20$–40) and $\sim 25\%$ of species with M_r values much higher. The presence of branched PNS polymers was not directly evidenced, but the high proportion of monomer, combined with the high polydispesity, strengthens the suggestion of chain branching proposed from considerations on the reaction path [10] and from NMR data [20].

Finally, calculations of average M_r values show an excellent agreement between the ultrafiltration and HPLC data. The number average values ($M_{r,n}$) of PNS condensation products are usually low due to the presence of a high proportion of monomers. Hence, in order to adequately define the speciation of a PNS mixture, mass average molecular mass ($M_{r,m}$), or polydispersity values, must also be provided.

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