Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Structure Determination of Complex Thermoset Networks: Polyflavonoid Tannin–Furanic Rigid Foams

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ABSTRACT: Polyflavonoid tannin–formaldehyde–furfuryl alcohol rigid foams yield hardened, rigid, tridimensional networks in which there are covalently linked structures derived from the reaction of their main components. Thus, polyflavonoid tannin structures, tannin–formaldehyde structures, furanic structures derived by the self-condensation of furfuryl alcohol, and mixed tannin–furane and tannin–furane–formaldehyde structures are all present in the continuous foam networks. Some complex, tridimensional structures involving tannin's flavonoid units, furan nuclei, and formaldehyde-derived methylene bridges appear to be formed too. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry has been used to determine the different segments contributing to forming the complex thermosetting networks of the hardened foams. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 1451–1456, 2008

Key words: MALDI; networks; resins; structure; thermosets

INTRODUCTION

Rigid foams based on phenol–formaldehyde (PF) resins have been known and used for a long time.[1] These rigid PF foams present the valuable characteristic of resistance to fire. Polyflavonoid tannins are natural oligomers of vegetable origin that present reactive phenolic nuclei. They can undergo the same reaction of phenol with formaldehyde and other aldehydes, their reactivity, however, being much greater than that of phenol. In mimosa (*Acacia mearnsii*, formerly *Acacia mollissima*) bark tannin extract, the flavan-3-ol repeating units (Fig. 1) are mostly 4,6-linked and sometimes 4,8-linked. Such flavonoid units are repeated 2–10 times[2] to produce a tannin with a number-average degree of polymerization of 4–5. The nucleophilic sites on the A-rings of the flavonoid repeating units are considerably more reactive toward aldehydes than those on the B-rings. For mimosa bark tannins, the reactivity of the flavonoid A-rings is comparable to, although slightly lower than, that of resorcinol. Tannin extracts are commercial materials that are 75–85% phenolic flavonoid material, the balance being mainly monomeric and oligomeric carbohydrates.

Chemically self-blowing rigid foam formulations based on tannin extract have been developed.[3] These foams, 95% composed of materials of natural origin, have mechanical and physical properties comparable to those of synthetic PF foams. The fluid phase before foaming is composed of a tannin–formaldehyde resin mixed with furfuryl alcohol, which is used as a heat-generating agent by both the self-polymerization reaction and by the reaction with tannin[3] under acidic conditions. The expansion of the fluid phase to a foam is brought about by a physical blowing agent with a low boiling point, whereas simultaneous crosslinking of the resin mix achieves dimensional stabilization at the desired low density.[3] The complex structures present in these foams, once they are hardened, have never been determined.

Since its introduction by Karas et al.[4] in 1987, matrix-assisted laser desorption/ionization (MALDI) mass spectrometry has greatly expanded the use of mass spectrometry toward large molecules and has been revealed to be a powerful method for the characterization of both synthetic and natural polymers.[5–10] Fragmentation of analyte molecules upon laser irradiation can be substantially reduced by them being embedded in a light-absorbing matrix. As a result, intact analyte molecules are desorbed
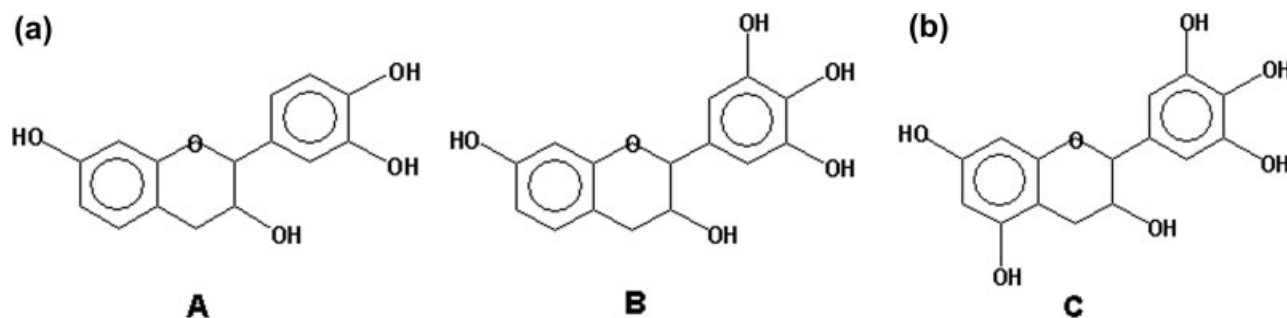
Figure 1 (a) Repeating units A and B with masses of 272.3 and 288.3 Da, respectively, and (b) repeating unit C with a mass of 306.3 Da.

and ionized along with the matrix and can be analyzed in a mass spectrometer. This soft ionization technique is mostly combined with time-of-flight (TOF) mass analyzers because TOF mass spectrometry presents the advantages of a complete mass spectrum per event, a virtually unlimited mass range, the need for only a small amount of analyte, and a relatively low equipment cost. The technique has been used to define many of the oligomer structures present in flavonoid tannins that could not be determined by other techniques.[2]

This articles deals with the MALDI-TOF mass spectrometry analysis of the structures present in tannin–formaldehyde–furfuryl alcohol foams.

EXPERIMENTAL

Samples

Commercial mimosa (*A. mearnsii*, formerly *Acacia mollissima*; de Wildt) (Tanac, Montenegro, Brazil) bark tannin extract from Brazil, containing 84% phenolic material, was used for the preparation of the foams. The samples that were analyzed by MALDI-TOF were (1) a tannin extract,[11] (2) a carbonized tannin extract,[11] (3) a carbonized pure furfuryl alcohol rigid foam, (4) an original tannin-based rigid foam that was not carbonized, and (5) a carbonized tannin-based rigid foam.[11]

Furfuryl alcohol (5.2 g), formaldehyde (37% water solution, 3.7 g), and water (3.0 g) were mixed with 15 g of mimosa tannin extract with strong stirring of the bulk. When agglomerate occurred, homogeneous diethyl ether (1.5 g) and then toluene-4-sulfonic acid 65% (6.0 g) were added and sufficiently mixed for 10 s before discharging into a lined box for foaming. The resin foam within 2 min of mixing, with the temperature rising to about 40°C, yielded a black foam with a density between 0.1 and 0.08 g/cm³. After the foam was left to harden and age for a few days, it was ground into a fine powder for MALDI-TOF analysis.

MALDI-TOF MS

The spectra were recorded on a Kratos Kompact MALDI 4 instrument (Shimadzu Europe, Duisbug, Germany). The irradiation source was a pulsed nitrogen laser with a wavelength of 337 nm. The length of one laser pulse was 3 ns. The measurements were carried out under the following conditions: positive polarity, a linear flight path, a high mass (20-kV acceleration voltage), and 100–150 pulses per spectrum. The delayed extraction technique was used with delay times of 200–800 ns.

MALDI-TOF sample preparation

The samples were dissolved in acetone (4 mg/mL). The sample solutions were mixed with an acetone solution (10 mg/mL of acetone) of the matrix. As the matrix, 2,5-dihydroxy benzoic acid was used. For the enhancement of ion formation, NaCl was added to the matrix. The solutions of the sample and matrix were mixed in equal amounts, and 0.5–1 μL of the resulting solution was placed on the MALDI target. After evaporation of the solvent, the MALDI target was introduced into the spectrometer. The mass peaks corresponded to M+Na (from natural abundance) and M+H attached cations.

RESULTS AND DISCUSSION

Tannin–formaldehyde–furfuryl alcohol foams give rise to complex, inter-reacted, mixed polymer networks. These networks can be determined by MALDI-TOF analysis. To understand what mixed networks are formed, it is necessary first to examine the components of these networks in more detail with the system method of analysis. This has been done and reported already for the same tannin used in this study.[2] This is reported in Table I.

The profisetinidin/prorobinetinidin types of polyflavonoid tannins are the most common ones extracted industrially.[11] Mimosa tannin is the main exponent of this class. It gives clear spectra showing

TABLE I
MALDI Fragmentation Peaks for the Industrial Mimosa Tannin Extract

Oligomer Type	M + Na$^+$		Unit type			Remarks
	Experimental	Calculated	A	B	C	
Dimers						
	602	601	—	2	—	
Trimers						
	858	857	2	1	—	
	874	873	1	2	—	
		or	2	—	1	Angular tannin
	890[a]	889	1	1	1	
		or	—	3	—	
	906[a]	905	—	2	1	Angular tannin
		or	1	—	2	Angular tannin
	922	921	—	1	2	Diangular structure
Tetramers						
	1147	1145	2	2	—	
		or	3	—	1	
	1163	1161	1	3	—	
		or	2	1	1	
	1179[a]	1177	—	4	—	
		or	1	2	1	
		or	2	—	2	
	1195	1193	—	3	1	Angular tannin
		or	1	1	2	
	1211	1209	—	2	2	Angular tannin
		or	1	—	3	Diangular structure
Pentamers						
	1467	1465				
Hexamers						
	1756	1753				
Heptamers						
	2045	2041				
Octamers						
	2333	2329				

The predominant repeat unit in this tannin is 288 Da, and this indicates that the tannin is predominantly a prorobinetinidin.[2]
[a] Dominant fragment.

the degree of polymerization of the building units and oligomer series with repeat unit masses of 272.3, 288.3, and 304.3 (Table I).[2] The masses of units A and B [Fig. 1(a)] and unit C [Fig. 1(b)] are 274.3, 290.3, and 306.3 Da, respectively. The correct equation for calculating the different possibilities is then $M+Na^+ = 23(Na) + 2(End\ groups,\ 2 \times H) + 272.3A + 288.3B + 304.3C$ (Table I). Table I indicates the many valid combinations of different repeating units that are possible.[2]

A, B, and C repeating units are 4,6- or 4,8-linked to form tannin oligomers, with units A and B being almost always 4,6-linked, whereas both of them are 4,6- and 4,8-linked to the rarer C-type units to form a so-called angular tannin (Fig. 2). The possible combinations are shown in Table I.

In Table II are reported the mixed oligomer species that can be observed by MALDI-TOF on the tannin–formaldehyde–furfuryl alcohol hardened foam in Figure 3. It must be kept in mind that unlike the
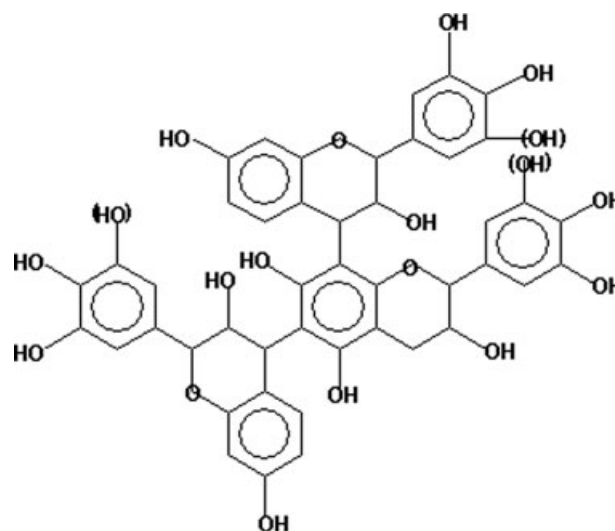

Figure 2 Units A and B are linked both 4,6 and 4,8 to the rarer C-type units to form a so-called angular tannin.

TABLE II
MALDI Fragmentation Peaks for the Mimosa Tannin Extract Rigid Foam

M + Na⁺		Peak intensity (%)	Unit type						Oligomer type
Experimental	Calculated		A	B	C	CH$_2$	+OH	FA	
327.5	327.3	10	—	—	1	—	—	—	T$_C$
357.3	357.3	11	—	—	1	1	1	—	T$_C$—CH$_2$OH
370.6	370.3	7	—	—	1	2	1	—	CH$_2$—T$_C$—CH$_2$OH
371.8	23								
403.4	405.3	19	1	—	—	2	1	1	T$_A$—CH$_2$—FA—CH$_2$OH or FA—CH$_2$—T$_A$—CH$_2$OH
431.6	433.4	19	1	—	—	3	2	1	HOCH$_2$—T$_A$—CH$_2$—FA—CH$_2$OH
502.0	503.0	12	—	—	—	—	—	6	FA$_6$
564.4	565.6	10	2	—	—	—	—	—	T$_A$—T$_A$
579	579.5	8	2	—	—	1	—	—	T$_A$—CH$_2$—T$_A$
608.9	609.3	14	—	—	1	2	1	3	(FA)$_3$—T$_C$—CH$_2$OH
631.6	631.6	6	—	—	2	—	—	—	T$_C$—T$_C$
642.0	641.6	22	—	2	—	2	1	—	T$_B$—CH$_2$—T$_B$—CH$_2$OH
664.5	664.0	100	—	—	—	—	—	8	FA$_8$
670.3	671.3	16	—	2	—	3	2	—	HOCH$_2$—T$_B$—CH$_2$—T$_B$—CH$_2$OH
	or 671.6 (703.6−32)		2	—	—	2	—	1	T$_A$—CH$_2$—T$_A$—CH$_2$—FA—CH$_2$
686.9	686.9 (703.6−16)	52	1	1	—	2	—	1	T$_A$—CH$_2$—T$_B$—CH$_2$—FA—CH$_2$
702.9	703.6	38	—	2	—	2	—	1	T$_B$—CH$_2$—T$_B$—CH$_2$—FA—CH$_2$ or CH$_2$—T$_B$T$_B$—CH$_2$—FA—CH$_2$ or T$_B$—CH$_2$—FA—CH$_2$—T$_B$—CH$_2$
843.2	841.9	7	3	—	—	—	—	—	T$_A$—T$_A$—T$_A$
857.6	857.9	16	2	1	—	—	—	—	T$_A$—T$_A$—T$_B$
873.0	873.9	8	1	2	—	—	—	—	T$_A$—T$_B$—T$_B$
908.9	905.9	15	—	2	1	—	—	—	T$_B$—T$_C$—T$_B$ angular tannin
1201.9	1200.2	22	—	4	—	2	—	—	T$_B$—CH$_2$—T$_B$T$_B$—CH$_2$—T$_B$
	or 1203.9		—	1	—	1	—	11	CH$_2$—T$_B$—CH$_2$—FA$_{11}$
1217.9	1217.9	13	—	3	1	2	—	—	T$_C$—CH$_2$—T$_B$T$_B$—CH$_2$—T$_B$
			—	1	—	1	1	11	HOCH$_2$—T$_B$—CH$_2$—FA$_{11}$
			—	—	1	1	—	11	CH$_2$—T$_C$—CH$_2$—FA$_{11}$

FA, furfuryl alcohol; T$_A$, tannin repeating unit A; T$_B$, tannin repeating unit B; T$_C$, tannin repeating unit C.

tannin in Table I, the hardened foam is a continuous network, and the oligomers that are observed are then smaller or bigger oligomer fragments constituting and derived from this network. The oligomers that can be observed are of different kinds. They comprise short tannin chains composed of 1, 2, or 3 tannin repeating units of types A, B, and C, such as the peaks at 564.4, 631.6, 843.2, 857.6, 873.0, and
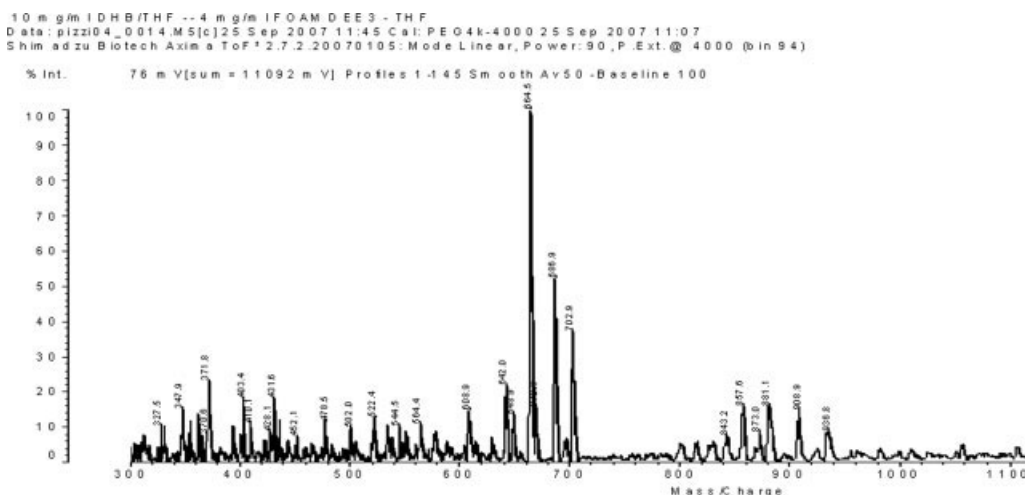

Figure 3 MALDI-TOF mass spectrum for the mimosa tannin extract–formaldehyde–furfuryl alcohol rigid foam.
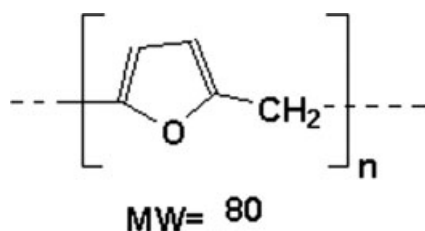
Figure 4 Long linear furanic oligomers derived by the self-condensation of furfuryl alcohol (indicated by FA_n in the tables; MW = molecular weight).

908.9 Da. Equally present are segments derived from the reaction of the tannin with formaldehyde. These are characterized by the presence of (1) methylene ($-CH_2-$) bridges between tannins (e.g., 579.0 and 1201.9 Da), (2) methylene bridges that have been detached from other parts of the network (e.g., 370.6 Da), or (3) still reactive methylol groups ($-CH_2OH$; e.g., 357 Da) and by the joint presence of both methylene bridges and methylol groups (e.g., 670 Da). These show the extent of the reaction of tannin with formaldehyde. Furthermore, there are long linear furanic oligomers derived by the self-condensation of furfuryl alcohol (e.g., 502 Da and the main peak at 664.5 Da; see Fig. 1), these linear oligomers being indicated by FA_n in the tables (Fig. 4).

There are mixed oligomers in which furanic rings and tannin units are linked to one another by the reaction of furfuryl alcohol with tannin or of furfuryl alcohol self-condensation oligomers with tannin or in which furfuryl residues and oligomers are linked to tannin units through formaldehyde-derived methylene bridges (or both). Examples of this type abound, as shown in Table II and Figure 1 (e.g., the peaks at 403.4, 608.9, 686.9, 702.9, and even 1201.9 Da). These mixed peaks comprise some of the most
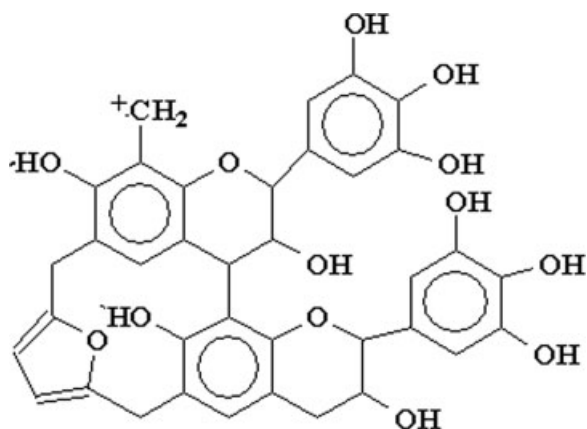

Figure 6 Structure of higher probability for the same condensation oligomer described in Figure 5.

abundant fragments, such as 686.9 and 702.9 Da. The clear indication then is that tannin–formaldehyde–furfuryl alcohol rigid foams are formed by a covalent network in which the three main components are covalently and randomly linked to one another, all effectively participating in and being structural constituents of the network.

A few features present in all the materials are of particular interest. Of these, the existence of the peak at 701–703 Da is the most interesting one. This reaction product is a mixed tannin–formaldehyde–furfuryl alcohol species arranged in such a way as to be particularly stable.[12–16]

Several structures could correspond to this molecular weight. The structure is composed of two flavonoid units and one furfuryl alcohol unit, which has reacted with them through the formation of a methylene bridge from furfuryl alcohol, plus two methylene bridges produced by a reaction with formaldehyde of either (or both) of the tannin units (most likely) and/or with the furanic ring, as shown in principle in Figure 5.

In reality, the particularly marked heat resistance of the structure[12–14] indicates a very well intrabonded structure. Several possibilities exist, the most likely being the one shown in Figure 6. The two flavonoid units are linked through a formaldehyde-generated methylene bridge, and the furanic ring is linked to the two flavonoids both by a furfuryl

Figure 5 Possible structure formed by two flavonoid units and one furfuryl alcohol unit, which reacted with them through the formation of a methylene bridge from furfuryl alcohol, plus two methylene bridges produced by the reaction with formaldehyde of either or both of the tannin units and/or the furanic ring.
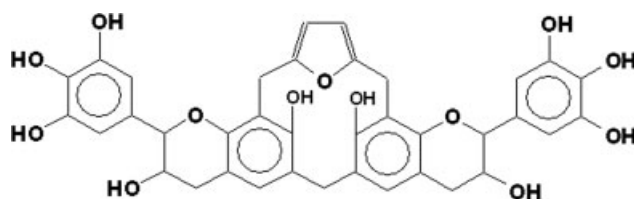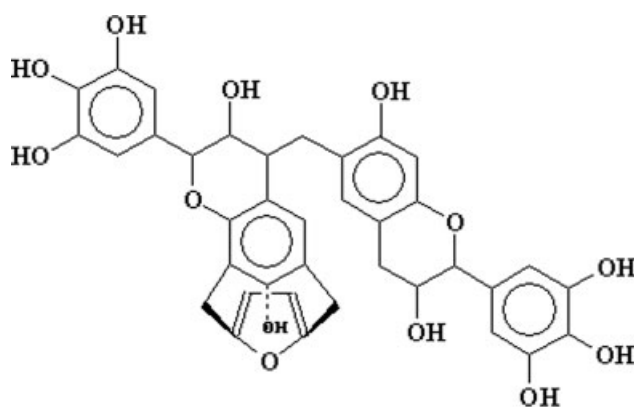

Figure 7 Different, also possible spatial arrangement for the structural combination in Figures 5 and 6. The furanic nuclei are linked here through two methylene bridges to a single flavonoid unit.
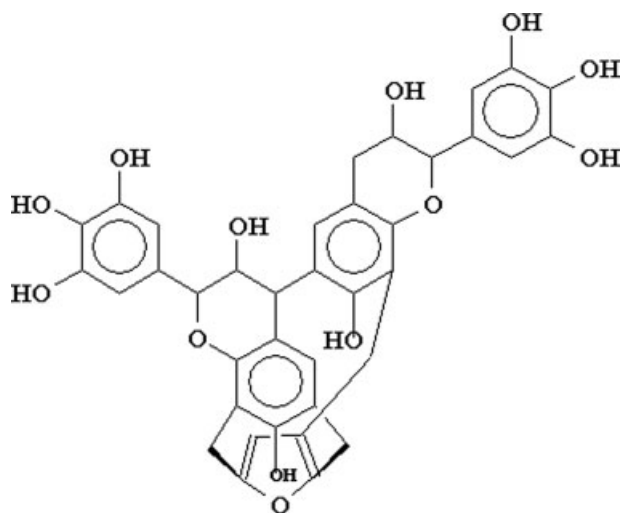
Figure 8 Different spatial arrangement of the structural combination in Figures 5 and 6. Structures in which the two flavonoids and the furan nuclei are linked to form a tridimensionally tight structure are also possible.

alcohol generated methylene bridge and by a formaldehyde-generated methylene bridge. This generates a particularly stable 12-bond ring.

Different spatial arrangements are also possible, such as one in which the furanic nuclei are linked through two methylene bridges to a single flavonoid unit, as shown in Figure 7.

The evidence does not support the existence of such a structure, first of all because of a peak at 379 Da due to a single flavonoid linked in this way to furan nuclei, which should also be rather intense. Instead, it does not occur in the MALDI-TOF spectrum.

Lastly, structures in which the two flavonoids and the furan nuclei are linked to form tridimensionally tight structures are also possible (Fig. 8).

A simple molecular mechanics modeling trial[17] of such a molecule indicated that it could exist, but only with a rather severe, possibly too severe, strain on parts of the structure and thus with too much potential energy for the system. Its existence can then be discarded.

CONCLUSIONS

Polyflavonoid tannin–formaldehyde–furfuryl alcohol rigid foams yield a tridimensional network in which several different structures present in the network are covalently linked in consistently high proportions. Such structures include polyflavonoid tannin structures, tannin–formaldehyde structures, furanic structures derived from the self-condensation of furfuryl alcohol, and mixed tannin–furane and tannin–furane–formaldehyde structures, all being present in the foam network. The structural determination of segments belonging to a hardened thermosetting network in which there is random crosslinking without continuously repeating features is then possible by MALDI-TOF analysis. In conclusion, MALDI-TOF appears to be a suitable method for examining oligomer residues present in complex polymer cross-linked networks, and it appears capable of determining aspects of the structure and characteristics of these solids that are too difficult to determine by other techniques.

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