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Thermospray Ionization Mass Spectrometry of Polydimethylsiloxane Antifoams

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Mass Spectrometric characterization of several polydimethylsiloxane (PDSI) antifoams has been studied using a thermospray (TSP) ionization technique. The PDSI antifoams dissolved into an eluent were flow-injected to a TSP interface without column separation. A selective formation of PDSI ammonium adduct ions directly reflecting their molecular weight distributions was observed in the mass region up to 3500 daltons. Both cyclic PDSIs and fatty acid esters were detected for a water-dilutable antifoam and their relative abundances and species were characteristic to a particular formulation of antifoam emulsion. Thus TSP mass spectrometric technique seems suitable and useful for analysis of an aqueous antifoam sample to identify both its molecular weight distribution of PDSIs and a type of antifoam formulations used in various fields such as food and pharmaceutical industries.

Since silicone oils are offen used to eliminate foam that has already formed (defoam) and to prevent the formation of foam (antifoam). There are mainly two types of silicone antifoams: One is the antifoam emulsion which is a water-dilutable formulation containing fatty acid esters as emulsifiers, and another is so called the antifoam oil which is a formulation without a water-dilutable emulsifier.

Very few mass spectrometric studies of PDSI polymers have been reported so far. Appeared in the literature were the electron ionization (EI)[1] and fast atom bombardment (FAB)[2] techniques which provided mass spectra covering only the range less than 500 daltons, and their interpretations were limited to fragment ions because of such a hard ionization. Mass spectra reported, therefore, suffer from lack of PDSI molecular weight distribution which is highly important to characterize and/or to identify a formulation of antifoam in a sample to be analyzed.

Field desorption and laser desorption mass spectrometries may be applicable to measure molecular weight distributions of PDSI polymers. There has been a recent publication of mass spectra of quasi-molecular ions obtained by a laser microprobe.[3] However, thermospray (TSP) ionization mass spectrometry[4] is another soft ionization technique to produce mainly quasi-molecular ions, and is directly applicable to an aqueous sample. Here reported is a study on measurement of PDSI molecular weight distributions over a high mass range up to 3500 daltons using TSP ionization mass spectrometry.

Experimental

Instruments. TSP mass spectra were obtained on a Finnigan MAT-90 double-focusing magnetic sector mass spectrometer equipped with a TSP interface and a DEC PDP 11/73 data primary processor system. Voltages applied to an ion source and extraction lens were adjusted to optimize both the intensity and peak shape of *m*/*z* 141 ions which are the acetonitrile cluster ions, $(CH_3CN)_3NH_4^+$. All experiments were carried out under mass resolution of ca. 5500 (at 10% valley) at this mass and with the vaporizer and ion source temperatures of about 160 and 230 °C, respectively. The eluents for antifoam emulsions and antifoam oils were a mixture of 30% acetonitrile and 70% reagent water containing 0.1 M (M=mol dm^{-3}) ammonium acetate and that of 30% acetone and 70% 0.1 M ammonium acetate, respectively. The former eluent was chosen since emulsion antifoams are soluble to an aqueous solution but oil antifoams are not. The latter eluent was used for oil antifoams since those such as the KF-96 series partially dissolve into acetone and also acetone itself has a good solubility to water. The eluents were degassed by a continuous purge with helium at about 30 ml min^{-1} to maintain very low levels of dissolved air. The eluents were introduced into a thermospray vaporizer at a flow rate of 1.2 ml min^{-1} using a Waters MS-600 HPLC pump and were effectively pumped out from the ion source by a Bulzers UNO-016B rotary pump with volume flow rate of 16 m^3 h^{-1}. PDSI samples were prepared to be in a concentration of 100—1000 ppm level by an eluent, and were flow-injected directly to a TSP interface by a 100 μl Rheodyne 7125 loop injector without column separation.

Materials. Anti-foaming silicone oils were obtained commercially: Two typical oil antifoams, KF-96-10CS (lot 908646) and KF-96-100CS (lot 906524), and two typical water-dilutable emulsions, KM-72A (lot 909609) and KM-82F (lot 904228). These were all obtained from the Shin Etsu Silicone Corp. Acetonitrile and acetone were of the super special grade (Wako Pure Chemical Industries, LTD.), and reagent water was obtained from a Milli-Q (Millipore Corp.) water purification system. Ammonium acetate was of the JIS super grade (Wako Pure Chemical Industries, LTD.).

Results and Discussion

Molecular Weight Distribution of Polydimethylsiloxanes. TSP ionization of a molecule (A) using ammonium acetate solution results mainly in formation of both molecular protonated ions (AH^+) (Reaction 1) and ammonium adduct ions (ANH_4^+) (Reaction 2), although generally other ions (Reaction 3—5) could be produced. A schematic picture of ion formation could be given briefly as follows:

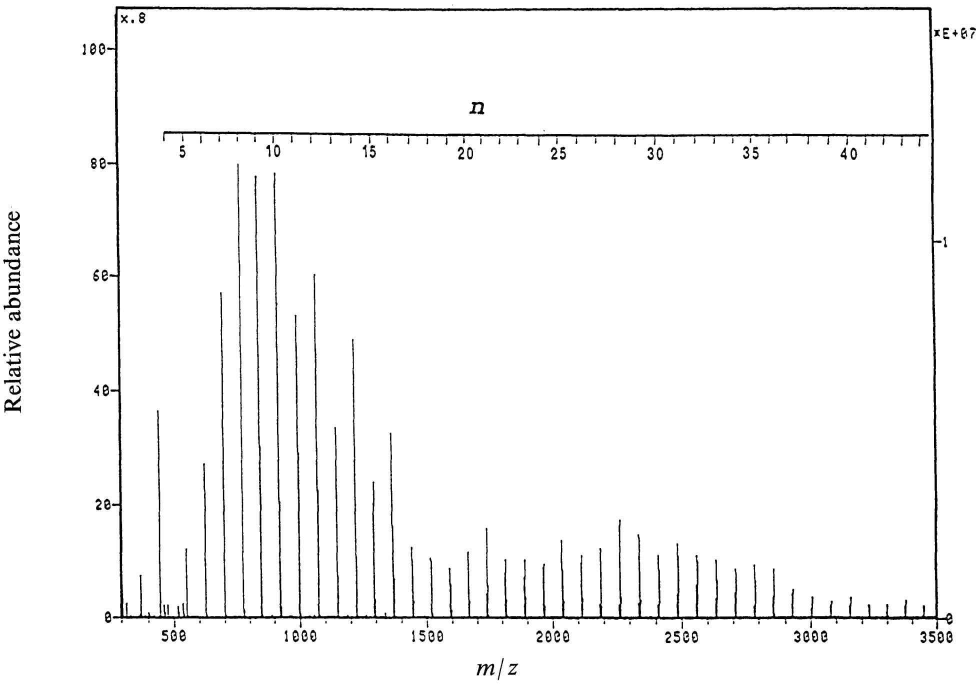

Fig. 1. A TSP mass spectrum of a medium size silicone oil antifoam (Shin Etsu KF-96-10CS).

$$A + (CH_3CN)_3NH_4^+ \longrightarrow AH^+ + 3\ CH_3CN + NH_3 \quad (1)$$

$$\longrightarrow ANH_4^+ + 3\ CH_3CN \quad (2)$$

$$\longrightarrow A(CH_3CN)NH_4^+ + 2\ CH_3CN \quad (3)$$

$$\longrightarrow A(CH_3CN)_2NH_4^+ + CH_3CN \quad (4)$$

$$\longrightarrow A(CH_3CN)_3NH_4^+ \quad (5)$$

when $(CH_3CN)_3NH_4^+$ is a reactant ion, which is one of reagent ions observed commonly in TSP mass spectra obtained using the eluent of ammonium acetate-acetonitrile, while their exact mechanisms of formation have not been known. Abundances of product ions may depend entirely on chemical nature such as proton affinities etc. of both a sample molecule A and a conjugate base of reactant ion. The formation of PDSIs ammonium adduct ions (Reaction 2) took place selectively. The chemical formula of both linear and cyclic PDSIs are respectively:

$$[(CH_3)_3Si\text{-}O\text{-}\{(CH_3)_2Si\text{-}O\text{-}\}_n\ Si(CH_3)_3 + NH_4^+] \quad (6)$$

$$[\{\text{-}(CH_3)_2Si\text{-}O\text{-}\}_{l+2} + NH_4^+] \quad (7)$$

Herein n and l correspond to the size of linear and cyclic PDSIs. Figire 1 shows a typical TSP mass spectrum obtained for the linear silicones (KF-96-10CS) in which individual peaks correspond to quasi-molecular ions formed via ammonium addition to PDSIs of their different sizes. This silicone oil has two maxima in its molecular weight distribution: One is located around n=9 and another is around n=27.

A high natural abundances of Si isotopes results in broad isotope distributions which vary drastically with increasing the size of PDSI, n (Fig. 2). The isotope ratio of $[P_{M+1}]/[P_M]$ for the linear silicones can be

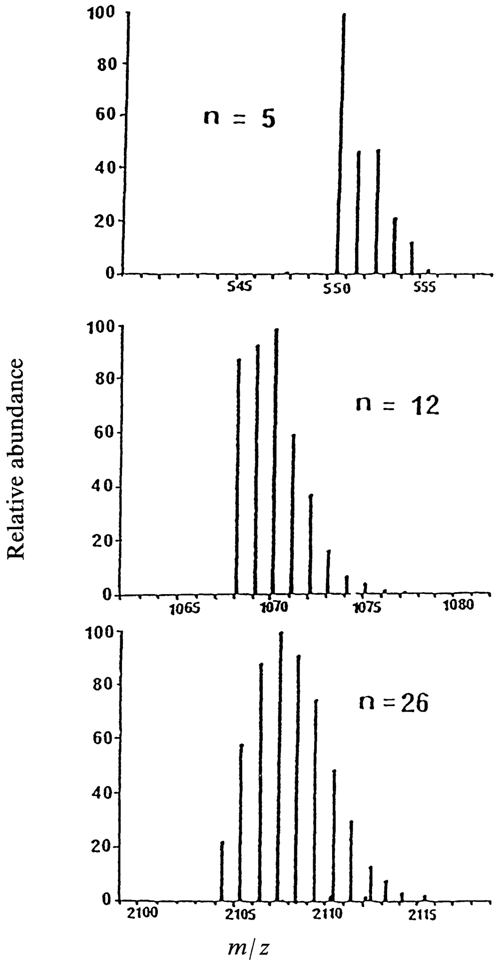

Fig. 2. Typical isotope distributions of several large linear PDSIs (Shin Etsu KF-96-10CS).

approximately expressed by[5]

$$[P_{M+1}]/[P_M]=0.07438n+0.17593 \qquad (8)$$

using both the chemical formula of $M=C_{2n+6}H_{6n+22}O_{n+1}Si_{n+2}N_1$, which is the ammonium adduct quasi-molecular ions of linear PDSIs, and the natural isotope abundances for the individual component atoms known in the literature.[6]

Experimental ratios of $[P_{M+1}]/[P_M]$ observed were compared to those calculated by Eq. 8 in Fig. 3, and showed a reasonably good agreement with the calculation. Scattered points for $n>20$ in the figure may be due to low signal-to-noise ratio of the [M] and [M+1] signals observed for a large size silicone. This result may support validity of our estimation of molecular sizes. Detection of very large PDSIs and their quantification will encounter difficulties because of their low solubility to the eluents currently used.

Figure 4 shows a TSP mass spectrum of quasi-molecular ions of PDSI contained in the KF-96-100CS

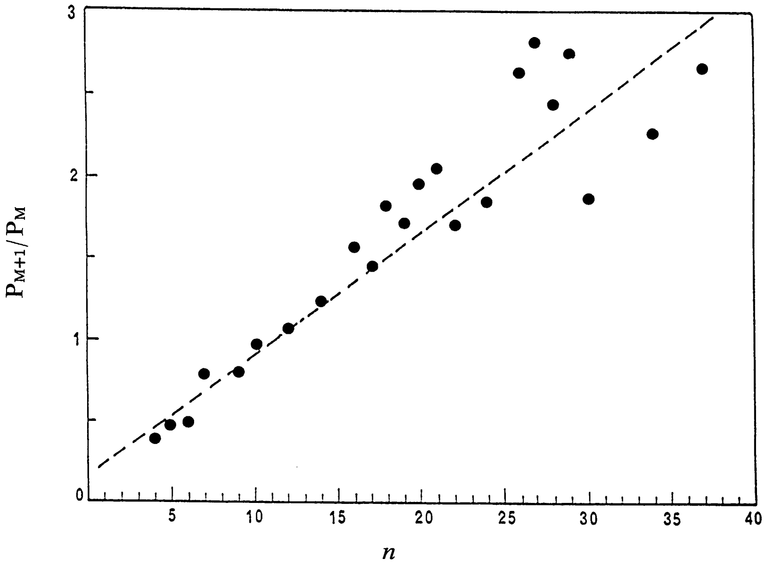

Fig. 3. Experimental isotope ratios $[P_{M+1}/P_M]$ (closed circles) together with theoretical calculations (dashed line).

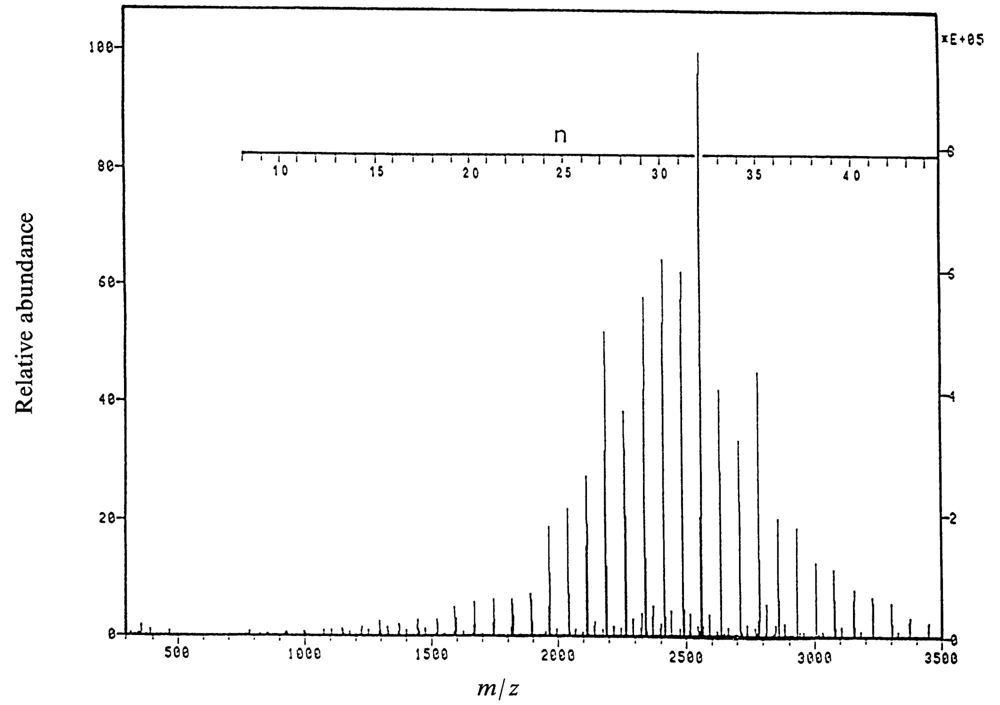

Fig. 4. A TSP mass spectrum of a large size silicone oil antifoam (Shin Etsu KF-96-100CS).

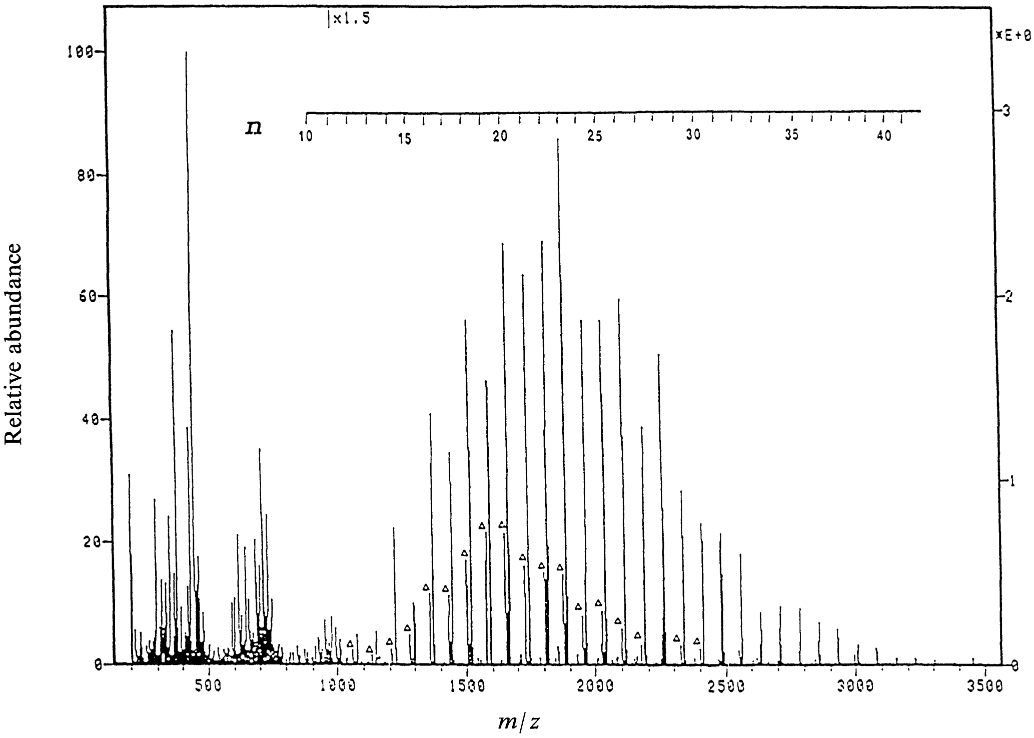

Fig. 5. A TSP mass spectrum of the antifoam emulsion formulation (Shin Estu KM-72A).

silicone oil. Its distribution maximum lay around n=30, and the mass spectrum showed the size of PDSI much larger than those in the KF-96-10CS formulation.

Figure 5 is a typical TSP mass spectrum of the KM-72A water-dilutable antifoam. Its distribution of PDSI quasi-molecular ions spreads from n=12 to n=44, and has a distribution center around n=22 to n=25. Additionally, a considerable amount of cyclic PDSIs

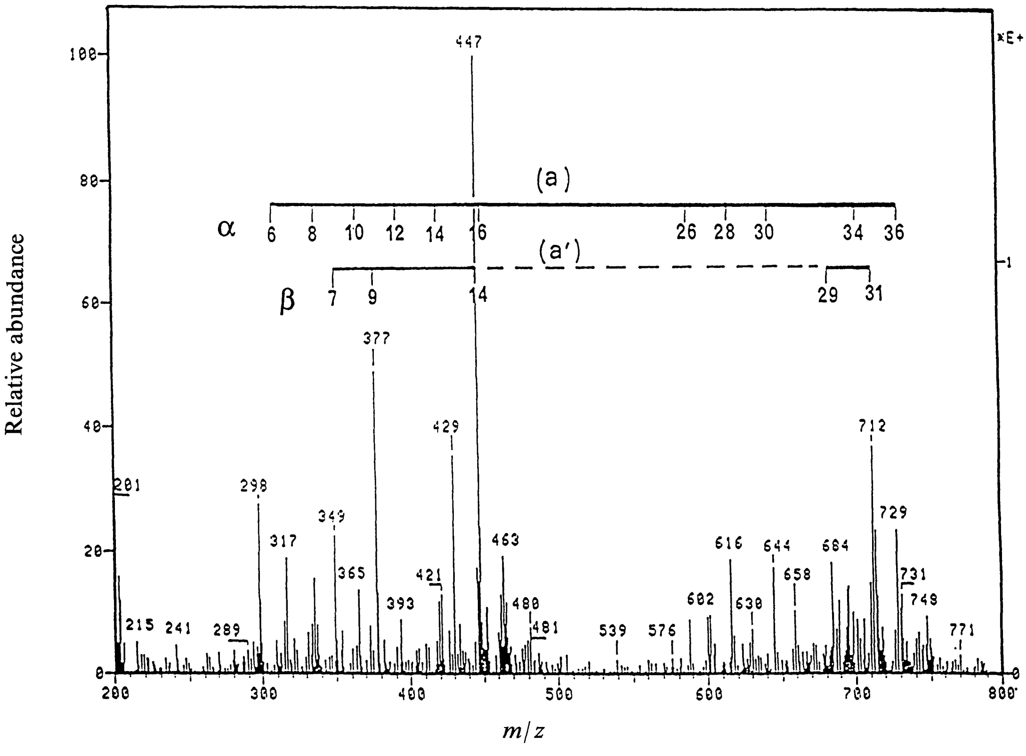

Fig. 6. A mass spectrum of fatty acid esters contained in the antifoam emulsion (Shin Etsu KM-72A): (a) and (a′) denote saturated and unsaturated fatty acid esters with sorbitol, respectively.

(indicated by open triangles) were also observed together with those of linear PDSIs in its mass spectrum.

For the KM-82F, which is another example of antifoam emulsions, its distribution of PDSIs lies from n=7 to n=38, indicating the size of PDSIs slightly smaller than those in the KM-72 formulation. Its distribution center of PDSIs is located around n=20, and the amount of cyclic PDSIs contained is considerably lower than that in the KM-72A formulation.

Fatty Acid Esters in Antifoam Emulsions. Commercial antifoam emulsions (oil-in-water emulsion) contain fatty acid esters as emulsifiers. Species and amounts of these emulsifiers are specific to a type of antifoam emulsion. Their quasi-molecular ions were observed in the mass regime less than 1000 daltons. The TSP mass spectra obtained were characterized by series of molecular protonated ions with the separation of m/z 28 or 14 due to size difference of fatty acid chains.

Typical emulsifiers are esters of fatty acids

Saturated fatty acids

$$CH_3(CH_2)_\alpha COOH \qquad (9)$$

Unsaturated fatty acids

$$CH_3(CH_2)_aCH=CH(CH_2)_bCOOH$$
$$\beta=a+b \qquad (10)$$

with sorbitan, glycerol and sucrose. TSP mass spectra obtained for commercial antifoam emulsions containing sorbitan fatty acid esters often showed quasi-molecular ions of sorbitol fatty acid esters. These sorbitol fatty acid esters seems to be formed via elimination of a water molecule from a sorbitan ester under TSP ionization conditions.

TSP mass spectra of the KM-72A formulation (Fig. 6) showed an inclusion of both sorbitol saturated fatty acid esters (α=6, 8, 10, 12, 14, 16, 26, 28, 30, 34, and 36) and sorbitol unsaturated fatty acids (β=9, 11, 16, 31, and 33) in the region less than 800 daltons. The base ion peak was ascribed to the sorbitol ester with an unsaturated fatty acid, that is sorbitol oleate (MH^+= m/z 477).

In contrast with the KM-72A formulation, both glycerol saturated fatty acids (α=14, 16, and 21) and sucrose saturated fatty acid esters (α=12, 14, and 16), were observed in a TSP mass spectrum of the KM-82F antifoam formulation. The base peak corresponds to the glycerol stearate (m/z 360).

Conclusion

The TSP ionization technique provided mass spectra reflecting molecular weight distribution of polydimethylsiloxane polymers and fatty acid esters contained in emulsion formulations. Both cyclic PDSIs and fatty acid esters observed were found to be characteristic to individual water-dilutable formulations. TSP mass spectrometric analysis of PDSI antifoams thus seems useful to identify a particular type of antifoams contained in aqueous samples.

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