Anal. Chem. **2002,** *74,* 2743−2748

Mass Spectrometry of Chemical Polymers

Charles N. McEwen* and Patricia M. Peacock

Experimental Station, DuPont Corporate Center for Analytical Sciences, Wilmington, Delaware 19880-0228

Review Contents

SCOPE

The scope of this review is limited to articles published or in press from January 2000 through January 2002 and include only publications dealing with mass spectrometry of synthetic polymers. This literature review covers the use of MALDI, ESI, DCI, EI, PI, SIMS, and Py-MS methods. Applications to polymer characterization and fundamental studies directed at improving polymer analysis as well as mechanistic and kinetic studies of polymers using MS methods are included. The review does not cover papers dealing with natural materials such as proteins and carbohydrate-based polymers. Even with such a focused review, it was necessary to make subjective choices regarding which work to include and what portion of the research to mention. The intent is to provide sufficient information to point the reader to recent literature in specific areas of interest.

REVIEWS

Several in-depth reviews dealing with mass spectrometry of polymers have appeared during the covered period. A review by Hanton (*1*) extensively covers polymer characterization as well as methods for characterizing polymer surfaces. Chan and Weng (*2*) also reviewed the use of static SIMS for characterizing the surfaces of copolymers and polymer blends. Scrivens and Jackson (*3*) reviewed the use of MALDI, ESI, and FD ionization methods for polymer characterization as well as chromatographic links to MS and methods for studying polymer conformations by MS. A book on mass spectrometry of polymers edited by Montaudo and Lattimer (*4*) covers a wide range of topics including pyrolysis methods in combination with MS and GC/MS, and the use of ESI, LC-ESI, FI, FD, SIMS, LD, and MALDI methods for polymer characterization. Also discussed are mathematical concepts for quantitative applications in polymer analysis.

MALDI MASS SPECTROMETRY

The majority of papers published during the covered period used MALDI as a means of characterizing polymers. The great advantage of MALDI as a desorption/ionization method is that little or no fragmentation is observed during either desorption or ionization, and at least for lower molecular weight oligomers, only singly charged ions are observed. An additional advantage is the recent development of MALDI methods that work with insoluble polymers (*5*, *6*). In addition, developments have been reported that allow ionization of saturated polyolefins (*7*, *8*). A striking aspect during the period of this review has been the increasing integration of MALDI into laboratories involved with polymer synthesis, fundamental polymer studies, and polymer characterization. The number of papers dealing with polymer characterization and originating in traditional mass spectrometry laboratories appears to be an ever-decreasing fraction of those published.

Application to Nonpolar Polymers. Application of MALDI MS to nonpolar polymers received increasing attention during this period. Py-PI (*9*, *10*) and DCI (*11*) were applied to nonpolar polymers, but most of the attention was fundamental studies directed at using either MALDI or laser desorption/ionization methods. A solvent-free preparation method was described that used silver trifluoroacetate to cationize low molecular weight parafins and microcrystalline waxes (*12*). Both LD and MALDI were shown to be capable of ionizing low molecular weight (up to 4000) polyethylenes using either silver or copper ion attachment (*7*). Macha et al. (*13*) discussed the background signals due to silver clusters when attempting to obtain MALDI mass spectra of nonpolar polymers. These clusters can interfere with the analysis, especially for lower molecular weight oligomers. They noted that silver cluster abundance is greatly reduced by using nonpolar matrixes such as anthracene and pyrene. Bauer et al. (*8*) improved the analysis of polyethylenes by covalently attaching an organic cation to polyolefins before MALDI analysis. They reported strong MALDI signals from the modified polymer. Poly(isobutylene) was characterized by MALDI after sulfonating the end groups to increase the ion signal (*14*). MALDI was also used to determine the microstructure of butadiene copolymers after ozonolysis (*15*) and for the analysis of macrocyclic polystyrenes (*16*, *17*).

Application to Polar Polymers. Because of the ease of ionization, MALDI is more frequently applied to polar polymers containing a hetroatom functionality. An important contribution during this period was the development of a sample preparation method for insoluble polymers (*5*, *6*). The method that was used for polyamides and other poorly soluble polymers consisted of

10.1021/ac020214u CCC: $22.00
Published on Web 05/09/2002

pressing a pellet from a finely ground solid mixture of polymer and matrix (*5*). In an alternate procedure, matrix and polymer were ground together using a ball mill cooled with liquid nitrogen (*6*). Using this procedure, equivalent results were obtained for soluble polymers as were obtained with the solvent matrix preparation method. However, the solvent-free method successfully produced MALDI mass spectra from an insoluble fraction of poly(9,9-diphenylfluorene). Most reports, however, were of soluble polymers analyzed by MALDI or so-called matrix-free MALDI. Grimm et al. (*18*) applied MALDI MS to the molecular structure investigation of fluorine-containing polyazomethines, and Ming et al. (*19*) were able to observe partial fluorination of hydroxyl end-capped oligoesters using MALDI MS. MALDI was used to characterize partially transesterified poly(*β*-hydroxyalkanoate)s produced by a bacterial strain which existed on saponified vegetable oil as the only source of carbon (*20*). Poly(ethylene glycol) esters chemically modified with biologically active (2-benzothiazolon-3-yl)acetyl end groups were characterized using MALDI as well as FAB and PDMS (*21*). Mg(II), Ca(II), Cu(II), Zn(II), and Pt(II) adducts with monomethoxypoly(ethylene glycol) 5000 was studied by MALDI and thermogravimetric analysis (*22*). MALDI MS was used to monitor the biodegradability of poly(vinylpyrrolidone) (*23*), and MALDI along with ESI and tandem MS was used to characterize complex mixtures of polyols (*24*). Several papers on the characterization of silsesquioxanes were published (*25*−*28*). Nonami et al. (*29*) evaluated the use of pyridoindoles, pyridylindoles, and pyridylpyridoindoles as UV matrixes for the MALDI MS analysis of poly(ethylene glycol)s, polyesters, and polyamides. The products from low-temperature pyrolysis of poly(tetrahydrofuran) were analyzed by using DCI and MALDI (*30*).

End Groups and Fragmentation. Polymer end group masses can be inferred from the measured mass of oligomer chains if the mass of the cationizing agent is known. Combined with information from other sources, this may be sufficient information to assign end group structures. To unambiguously assign end group structures, additional information beyond oligomer mass is needed. Nandam et al. (*31*) were able to determine the end groups of poly(methylstyrene peroxide) and poly(methyl methacrylate peroxide) unequivocally using a combination of MALDI, Fourier transform infrared (FT-IR) spectrometry, and thermochemical calculations. Trimpin et al. (*23*) used PSD fragmentation to determine the end groups of poly(vinylpyrrolidone). MALDI was used to study the end groups that formed upon photoinitiation of methyl methacrylate monomers using 2,2-dimethoxy-2-phenylacetophenone and benzoin as initiators (*32*). Analysis of fragment ions using postsource decay (PSD) determined that the secondary series of ions that are observed in the MALDI spectrum of polystyrene arise at least in part from fragmentation of matrix adducts of polystyrene (*33*). The study was unable to determine whether the main series of ions (PS + cation) underwent fragmentation under normal MALDI conditions, but fragmentation was noted to occur under conditions of high laser flux typically used with PSD. End group fragmentation was suggested to be the cause of unexpected peaks observed in the MALDI, ESI, and SIMS spectra of synthetic nylon-6 oligomers (*34*).

Molar Mass Analysis. Reports on the use of MALDI MS for determining molar mass and polydispersity continue despite the limitation that accurate values are only obtained for relatively narrow (<1.2−1.4) polydisperse polymers. A NIST-sponsored interlaboratory comparison study involving 23 laboratories using the same narrow polydispersity polystyrene polymer standard found good agreement between MALDI laboratories (*35*). However, while the results fell within the estimated error limits for light scattering and NMR, all of the MALDI results were below the average for the classical methods. Byrd et al. (*36*) studied the limitation of MALDI-TOF MS for the molecular weight characterization of wide polydisperse polymers using conditions in which only the ion detectors were changed. Their findings were that a major limitation of MALDI for the analysis of wide polydisperse polymers is related to the detector mechanism (e.g., number fraction in MS vs weight fraction in SEC) and the poor signal-to-noise for the high-mass tail of the distribution. MALDI MS was nevertheless used to successfully determine the average molecular weights of polyethylene−poly(ethylene glycol) copolymers used as surfactants (*37*). The molar masses obtained by MALDI closely corresponded to that specified by the manufacturer. Molar mass distributions of silicon oils were also obtained by MALDI MS (*38*) as were the molecular weight distributions of PEG oligomers chemically modified with (2-benzothiazolon-3-yl)acetyl end groups (*21*).

Although MALDI MS in its present form is not suitable for determining the molar mass distribution of wide polydisperse polymers, combined with SEC, it provides an absolute molecular weight calibration. Off-line SEC has been used to collect fractions for subsequent analysis by MALDI MS (*39*). The parameters affecting the SEC fractionation performance with wide polydisperse polymers were studied, and equations to optimize the SEC in combination with MALDI were reported. Guidelines for enhancing the performance of SEC-MALDI were also given. Hanton et al. (*40*) combined SEC and MALDI MS using a LC interface. They found the combination of SEC-MALDI with a LC interface helped verify the presence of low-abundance, high-mass oligomers and aided in the detection of minor series of oligomers. SEC-MALDI was applied to analyze random copolyesters with either butylene succinate or butylene sebacate repeat units (*41*) and for the determination of cyclic polyester oligomers (*42*).

Separation methods other than SEC were combined with MALDI for polymer characterization. Several groups coupled liquid chromatography at the critical point of adsorption with MALDI MS (*17, 43*−*45*). Keil et al. (*44*) used the method to analyze poly(propylene oxide)s while Lee et al. (*45*) applied it to a triblock copolymer. Supercritical fluid chromatography (SFC) was combined with MALDI to determine the molar mass distribution of silicon oils (*38*).

Copolymers. Analysis of copolymers was well represented during the covered period even though, or because, the characterization of copolymers is more difficult than that of homopolymers. In addition to the molecular information desired for all polymers (e.g., molar mass distribution, repeat unit and end group composition, and branch points), additional information is desired for copolymers (e.g., molar fraction of each type of repeat unit, the average length of chains of each polymer type, and the variation of composition as a function of molecular weight). Although several mass spectrometric techniques other than

MALDI were applied to copolymer characterization (*10*, *46*−*50*), MALDI MS was well represented.

MALDI was used to determine the average molecular weight of standard polyethylene−poly(ethylene glycol) copolymers (*37*), but others have found MALDI to be problematic for determining the relative mole fraction of each monomer type in a copolymer. Storey et al. (*51*) reported only observing homopolymer of caprolactone in the MALDI mass spectrum of a triblock copolymer composed of caprolactone and isobutylene (as the middle block). Falkenhagen et al. (*43*) observed small errors in the quantitation for copolymers having only small differences in composition. Polce et al. (*52*) studied three copolymers of quinoxaline/ethersulfone having different ratios of monomers. Ion abundances for ethersulfone-rich chains were lower than expected, which they attributed to the poorer gas-phase basity of ethersulfone-rich chains versus quinoxaline-rich chains. Ethylene oxide/propylene oxide copolymer chains with different end groups were noted to change in abundance with matrix composition, solvent composition, and even different analyte-to-matrix ratios (*53*). However, it was also noted that as long as the sample preparation is identical, small differences in composition can be determined by MALDI MS. The latter two studies seem to support the concept that the relative ion abundances of copolymer chains can be a function of sample preparation and the relative ability of the monomers to hold a charge. It is expected that copolymers made from similar monomers (especially in solubility and ability to hold a charge) behave best in MALDI MS.

The compositions of a number of copolymers have been studied using MALDI MS. Przybilla et al. (*54*) used MALDI MS and fragment ion analysis to determine the block length of poly(ethylene oxide)-*b*-poly(phenyleneethynylene) diblock copolymer. A number of studies have suggested that more fragment ions are generated from random copolymers than from block copolymers.-(*47*, *53*, *55*−*58*) Biodegradable random copolyesters were characterized using SEC-MALDI (*41*) as were the triblock copolymer poly(L-lactide)poly(ethylene oxide)poly(L-lactide) (*45*) and block copolymers of poly(ϵ-caprolactone-*b*-isobutylene-*b*-ϵ-caprolactone (*51*). Various silsesquioxane copolymers were characterized by MALDI (*25*, *27*) or laser desorption (*26*). A comparative study of the thermal degradation of poly(ethylene oxide−propylene oxide−ethylene oxide) triblock copolymer was conducted using MALDI MS, SEC-NMR, and SPME-GC/MS. MALDI was used to determine the hard segment length distribution in poly(urea−urethane) polymers (*59*). Partial degradation of polyurethane block copolymers with ethanolamine and polyesterurethane with phenyl isocyanate was found to be totally selective, thus allowing analysis of the soft blocks by MALDI MS (*60*). Ozonolysis of butadiene copolymers allowed the microstructure of butadiene copolymers to be determined (*15*).

Fundamental Studies. Several papers dealt with fundamental applications of MALDI MS to polymer characterization. Tatro et al. (*61*) found MALDI MS to be the optimum absolute molecular weight method accompanying viscometry for determining Mark−Houwink−Sakurada parameters. These authors proposed using the ratio of the distribution breadth at half-height to the molecular weight of the monomer unit as a superior method versus M_w/M_n for describing the breadth of distribution of polymer standards. Factors relating to the success of MALDI-TOF MS for describing wide polydisperse polymers were reported (*36*). New solvent-free matrix preparation methods were presented (*5*, *6*, *62*), some of which are applicable to insoluble polymers (*5*, *6*). Residue mass plots and abundance plots were combined with accurate mass measurements to detect isobaric interferences in the MALDI mass spectra of complex polymer mixtures (*63*). The effects of experimental conditions on obtaining quantitative composition analysis of ethylene oxide/propylene oxide copolymers using MALDI was presented (*53*). Barner-Kowollik et al. (*32*) investigated the end groups formed upon laser-induced photoinitiation of methyl methacrylate monomer using different initiators and were able to determine by MALDI MS markedly different reactivity for the two initiators. Ruthenium(II)-mediated living radical polymerizations of methyl methacrylate, methyl acetate, and styrene were analyzed by MALDI (*64*) as were the living cationic polymerizations of vinyl ethers (*65*). A mechanistic study of catalytic chain-transfer polymerization of methy acrylate with BF_2-bridged cobaloxime using MALDI found that the low molecular weight products isolated during the induction period were poly(methyl acrylate) oligomers bound to a single cobaloxime (*66*). The cobalt was found by MALDI to be displaced upon further reaction with methylstyrene. Mechanistic aspects of the Suzuki polycondensation of thiophenebisboronic derivatives (*67*) and the ring chain equilibrium in melt polymerized D,L-lactic acid (*68*) were also studied using MALDI MS.

ELECTROSPRAY IONIZATION MASS SPECTROMETRY

ESI is another method that can successfully ionize polymers with little or no fragmentation. A drawback of ESI is the requirement that the polymer being analyzed be soluble in a solvent that can be electrosprayed. Another reason that ESI is less used for polymer characterization than MALDI is its strong tendency to form multiply charged ions that especially complicate the analysis of polymers having molecular masses above a few kilodaltons. The multiply charged ions also complicate quantitation by ESI. One study found that ESI was not quantitative for standard polyethylene−poly(ethylene glycol) copolymers when standard cone to skimmer voltages were used (*37*). Interestingly, they were able to circumvent this problem by using high cone voltages and monitoring low-mass fragment ions (m/z 45 and 59). One distinct advantage of ESI is the ease with which it can be interfaced to liquid separation methods. For example, LC/ESI MS was employed to analyze the cyclic oligomer content of two commercial polyesters (*69*).

Fragmentation. Another advantage of ESI has been the ease of MS/MS and MS^n fragmentation experiments versus PSD for MALDI fragmentation. However, this has recently been less of an advantage with the introduction of TOF−TOF MALDI instruments and MALDI ion sources interfaced to orthogonal TOF and trap-type mass spectrometers. ESI and tandem MS were used to aid the characterization of complex polyol mixtures (*24*). Adamus et al. (*55*) used ESI and multistep MS^n on an ion-trap mass spectrometer to study sequence distributions in bacterial copolyesters, and Koster et al. (*47*) analyzed the structures of synthetic homo- and copolyesters using ESI and FTMS. ESI-FTMS and MS^n were also used to characterize four hyperbranched synthetic polyesteramides and gain insight into their fragmentation pathways (*70*). ESI with tandem MS was used to characterize and

identify ethoxylated surfactants (*71*) and to analyze mixtures of isomeric products formed in side reactions during the synthesis of poly(propyleneimine) dendrimers (*72*). An intriguing study employing ESI for end group structural analysis used source fragmentation produced in the cone−skimmer region to produce low-mass oligomers. High-energy CID of these low-mass oligomers induced fragment ions that aided end group structure determination (*73*).

Fundamental Studies. A very interesting application of ESI has been its use to screen for polymerization catalysts. In one study, ESI was used to observe two distributions of ions from metal-bound oligomers of Pd(II) homogeneous Ziegler−Natta catalysts (*74*). The authors used kinetic equations to fit the distributions and determine the absolute rates of initiation, propagation, and chain transfer. The rates were then used to calculate the average molecular weight and the extent of polymerization as a function of time. In a similar experiment, Adlhart and Chen (*75*) used charged substrates to fish for active catalytic species in the ring-opening metathesis polymerization of norbornene oligomers. Cerda et al. (*76*) studied the fragmentation of multiply charged poly(alkene glycol) ions and reported that Coulombic repulsion was not a specific driving force for fragmentation. Instead, fragmentation is consistent with charge site or radical site initiation. In another study of polyglycols by ESI, it was found that low-energy CID was more effective using lithium and transition metal cationization rather than sodium or higher mass alkali metal ions (*77*). A comparison of electrospray and nanospray FTMS for the analysis of poly(dimethylsiloxane)/poly(ethylene glycol) oligomer blends was conducted by Maziarz et al. (*78*). The spectral results showed a strong dependence on end group functionality, drying gas flow, skimmer potential, surface tension/hydrophilicity, and solvent heat of vaporization.

GAS-PHASE IONIZATION METHODS

Analysis of polymers using ionization methods that require gas-phase ions is necessarily preceded by some method that reduces the polymer to volatile components. The most common means of achieving this goal is through pyrolysis. While pyrolysis products can be analyzed by MALDI (*30*), or theoretically ESI, most pyrolysis experiments use EI, CI, or PI methods. Lattimer (*30*) used both MALDI and DCI to analyze the thermal breakdown products of poly(tetrahydrofuran) upon low-temperature pyrolysis. Both direct in-source pyrolysis and Py-GC/MS were used to analyze random block polysulfide copolymers containing different mole fractions of each repeat unit (*79*). Mignard et al. (*80*) studied the kinetics of the thermal degradation of copolymers of vinylidene cyanide and para-substituted styrenes using thermogravimetric analysis (TGA) and GC/MS. Py-GC/MS was also used to predict the degree of degradation of low-density polyethylene and poly(lactic acid) exposed to chemical or biological hydrolysis and oxidation (*81*). The thermal decomposition of polyethylene and polystyrene in the presence of wood, cellulose, lignin, and charcoal were studied by Py-GC/MS and TGA-MS. (*82*) The composition analysis of poly(D,L-lactic/glycolic acid) copolymer by Py-GC/MS combined with thermally assisted hydrolysis and methylation in the presence of tetramethylammonium hydroxide has been reported (*83*). Py-GC/MS for the detection of polymers in environmental samples (*84*, *85*) and paints (*86*) was also reported. Py-GC/MS was even used to obtain number-average molecular weight through end group analysis (*87*). Direct Py-MS of acrylonitrile−cellulose graft copolymers were reported by Badawy et al. (*48*). Py-PI/MS was used by Cox et al. (*10*) to quantitatively determine the methyl acrylate content in ethylene−methyl acrylate copolymers and by Zoller (*9*) to determine the deuterium distribution in deuterated polyolefines. Chemical or biological means of degrading polymers prior to analysis by MS has also been reported as has the degradation kinetics of poly(ethylene terephthalate) in supercritical methanol using GC/MS, SEC, and HPLC (*88*).

SECONDARY ION MASS SPECTROMETRY

Surface characterization of polymer films was a common application of SIMS. The surfaces of various styrene−methylacrylate random copolymers were analyzed using SIMS and X-ray photoelectron spectroscopy (XPS) in an effort to detect surface segregation of one of the copolymer components (*50*). A similar study of a thin film of symmetrical poly(styrene-*co*-isoprene) diblock copolymer found isoprene to be the sole surface constituent when the high-mass region of the SIMS spectrum was examined (*49*). However, detectable amounts of polystyrene were observed in the low-mass region. This suggested to the authors that low-mass ions were sampled from a greater depth than were high-mass ions. SIMS was also used to observe the rearrangement of surface bromine atoms attached to the ends of polymer chains in the condensation polymerization of bisphenol A and 1,8-dibromooctane (*89*). In another surface study, a different SIMS pattern was observed for monolayers of isotactic poly(methyl methacrylate) (PMMA) than for syndiotactic or atactic forms (*90*). This was attributed to the double-helical tertiary structure of isotactic PMMA. SIMS was employed to study the surface properties of modified polyurethane (*91*) as well as freeze-dried and thermally cured melamine−formaldehyde resins (*92*). Cationized polymers on self-assembled monolayer substrates were studied by SIMS, and one finding was that the abundances of the cationized fragments was dependent on the metal ion used for cationization (*93*). A systematic study of sulfonated poly(*N*-vinylcarbazole) samples using SIMS and XPS found that sulfonate groups were chemically attached to the carbazole moiety (*94*). The data suggested that the sulfonation reaction can be followed quantitatively. A surface characterization and quantitation study of poly(4-vinylphenol) and poly(4-vinylpyridine) blends using SIMS and XPS suggested that the surface of blends of high molecular weight polymers may not be in thermodynamic equilibrium (*95*). A SIMS study of sequential polymers with well-defined segmental length demonstrated that the characteristics of positive and negative spectra are related to the chemical structures of the sequential polymers (*96*). The phase domain structure (*97*) and surface morphology (*98*) of polymer blends were studied using SIMS. SIMS was also employed to study the effects of ion energy on air-aged polymers (*99*) and the kinetics of the hydrolytic degradation of poly(glycolic acid) (*100*).

CONCLUSION

Publications relating to synthetic polymer/copolymer characterization using mass spectrometry favored MALDI as the ionization method. LD/matrix-free MALDI MS was increasingly applied to the characterization of low-mass polymers. The development

of solvent-free matrix preparation methods applicable to insoluble polymers as well as methods for obtaining MALDI results from hydrocarbon-based polymers shows considerable potential. ESI was a growing area, especially for studying fundamental polymer processes. The use of ESI to follow polymer reaction kinetics and observe polymer chains growing on active catalyst substrates is expected to see continued study. Separation and pyrolysis methods were effectively combined with mass spectrometry to aid polymer characterization. SIMS continued to see activity as a method for characterizing polymer surfaces. Methods such as inductively coupled plasma (ICP) MS (*101*), PDMS (*102*), Fast atom bombardment (FAB) MS (*102*), FD MS (*103*), and laser ablation in combination with MS (*104*) were used infrequently as polymer characterization tools during the period covered by this review. Overall, however, it appears that mass spectrometry is growing in importance as a technique for characterizing synthetic polymers.

Abbreviations used: CID, collision-induced dissociation; DCI, desorption chemical ionization; EI, electron impact ionization; ESI, electrospray ionization; FD, field desorption; FI, field ionization; GC, gas chromatography; LC, liquid chromatography; LD, laser desorption; MALDI, matrix-assisted laser desorption/ionization; MS, mass spectrometry; MS/MS and MS^n, multistage mass spectrometry for fragment ion analysis; PI, photoionization; Py, pyrolysis; PSD, postsource decay; SEC, size exclusion chromatography; SIMS, secondary ion mass spectrometry; TOF, time of flight.

Charles N. McEwen *is a Research Fellow in the Dupont Corporate Center for Analytical Sciences in Wilmington, Delaware. He is the author or co-author of scientific papers dealing with diverse areas of mass spectrometry and is coauthor or coeditor of several books and book chapters. His interests are in the use of mass spectrometry to characterize synthetic and natural polymers. He received a B.S. degree in chemistry from the College of William and Mary, M.S. in chemistry from Atlanta University, and Ph.D. in chemistry from the University of Virginia. He is a member of the American Chemical Society and the American Society for Mass Spectrometry.*

Patricia M. Peacock *is a Staff Technologist in the Dupont Corporate Center for Analytical Sciences in Wilmington, Delaware. She studied materials engineering at Virginia Polytechnic Institute and State University and chemistry at the University of Delaware. She has 8 publications and 17 years experience in polymer characterization. Her current research interests include practical applications of mass spectrometry for the characterization of a wide variety of industrial and research polymers. Other areas of interest include structure elucidation of small organic molecules using mass spectrometry and laser light scattering analyses of macromolecules. She is on the board of directors of the Delaware Valley Mass Spectrometry Discussion Group.*

LITERATURE CITED

(1) Hanton, S. D. *Chem. Rev.* **2001**, *101*, 527−569.
(2) Chan, C. M.; Weng, L. T. *Rev. Chem. Eng.* **2000**, *16*, 341.
(3) Scrivens, J. H.; Jackson, A. T. *Int. J. Mass Spectrom.* **2000**, *200*, 261−276.
(4) Montaudo, G., Lattimer, R. P., Eds. *Mass Spectrometry of Polymers*; CRC Press: Boca Raton, FL, 2002.
(5) Skelton, R.; Dubois, F.; Zenobi, R. *Anal. Chem.* **2000**, *72*, 1707−1710.
(6) Trimpin, S.; Rouhanipour, A.; Az, R.; Rader, H. J.; Mullen, K. *Rapid Commun. Mass Spectrom.* **2001**, *15*, 1364−1373.
(7) Chen, R.; Yalcin, T.; Wallace, W. E.; Guttman, C. M.; Li, L. *J. Am. Soc. Mass Spectrom.* **2001**, *12*, 1186−1192.
(8) Bauer, B. J.; Wallace, W. E.; Fanconi, B. M.; Guttman, C. M. *Polymer* **2001**, *42*, 9949−9953.
(9) Zoller, D. L.; Johnston, M. V.; Qian, K.; Lohse, D. J. *Macromolecules* **2000**, *33*, 5388−5394.
(10) Cox, F. J.; Feudale, R. N.; Johnston, M. V.; McEwen, C. N.; Hauptman, E. *J. Anal. Appl. Pyrolysis*, in press.
(11) Vincenti, M. *Int. J. Mass Spectrom.* **2001**, *212*, 505−518.
(12) Pruns, J. K.; Vietzke, J.-P.; Strassner, M.; Rapp, C.; Hintze, U.; Konig, W. A. *Rapid Commun. Mass Spectrom.* **2002**, *16*, 208−211.
(13) Macha, S. F.; Limbach, P. A.; Hanton, S. D.; Owens, K. G. *J. Am. Soc. Mass Spectrom.* **2001**, *12*, 732−743. Macha, S. F.; Limbach, P. A.; Savickas, P. J. *J. Am. Soc. Mass Spectrom.* **2000**, *11*, 731−737.
(14) Ji, H.; Sato, N.; Nakamura, Y.; Wan, Y.; Howell, A.; Thomas, Q. A.; Storey, R. F.; Nonidez, W. K.; Mays, J. W. *Macromolecules* **2002**, *35* (4), 1196−1199.
(15) Zoller, D. L.; Johnson, M. V. *Macromolecules* **2000**, *33*, 1664−1670.
(16) Lepoittevin, B.; Dourges, M.-A.; Masure, M.; Hemery, P.; Baran, K.; Cramail, H. *Macromolecules* **2000**, *33* (22), 8218−8224.
(17) Cho, D.; Park, S.; Kwon, K.; Chang, T.; Roovers, J. *Macromolecules* **2001**, *34* (21), 7570−7572.
(18) Grimm, B.; Kruger, R.-P.; Schrader, S.; Prescher, D. *J. Fluorine Chem*, **2002**, *113*, 85−91.
(19) Ming, W. H.; Lou, X. W.; Van de Grampel, R. D.; Van Dongen, J. L. J.; Van der Linde R. *Macromolecules* **2001**, *34*, 2389−2393.
(20) Saeed, K. A.; Ayorinde, F. O.; Eribo, B. E.; Gordon, M.; Collier, L. *Polymer* **2001**, *42*, 6841−6849.
(21) Mincheva, Z.; Hadjieva, P.; Kalcheva, V.; Seraglia, R.; Traldi, P.; Przybylski, M. *J. Mass Spectrom.* **2001**, *36*, 626−632.
(22) Mwelase, S. R.; Bariyanga, J. *J. Mol. Struct.* **2002**, *608*, 235−244.
(23) Trimpin, S.; Eichhorn, P.; Rader, H. J.; Mullen, K.; Knepper, T. P. *J Chromatogr., A* **2001**, *938*, 67−77.
(24) Chen, R.; Tseng, A. M.; Uhing, M. Li, L. *J. Am. Soc. Mass Spectrom.* **2001**, *12*, 55−60.
(25) Williams, R. J. J.; Erra-Balsells, R.; Ishikawa, Y.; Nonami, H.; Mauri, A. N.; Riccardi, C. C. *Macromol. Chem. Phys.* **2001**, *202*, 2425.
(26) Kim, H. J.; Lee, J. K.; Park, S. J.; Ro, H. W.; Yoo, D. Y.; Yoon, D. Y. *Anal. Chem.* **2000**, *72*, 5673−5678.
(27) Techlenburg, R. E.; Wallace, W. E.; Chen, H. P. *Rapid Commun. Mass Spectrom.* **2001**, *15*, 2176−2185.
(28) Fasce, D.P.; Williams, R. J. J.; Erra-Balsells, R.; Ishikawa, Y.; Nonami, H. *Macromolecules* **2001**, *34* (11), 3534−3539.
(29) Nonami, H.; Wu, F.; Thummel, R. P.; Fukuyama, Y.; Yamaoka, H.; Erra-Balsells, R. *Rapid Commun. Mass Spectrom.* **2001**, *15*, 2354−2373.
(30) Lattimer, R. P. *J. Anal. Appl. Pyrolysis* **2001**, *57*, 57−76.
(31) Nandam, A. K.; Ganesh, K.; Kishore, K.; Surinarayanan, M. *Polymer* **2000**, *41*, 9063−9072.
(32) Barner-Kowollik, C,; Vana, P.; Davis, T. P. *J. Polym. Sci. A: Polym Chem.* **2002**, *40*, 675−681.
(33) Goldschmidt, R. J.; Wetzel, S. J.; Blair, W. R.; Guttman, C. M. *J. Am. Soc. Mass Spectrom.* **2000**, *11*, 1095−1106.
(34) Shan, L.; Murgasova, R.; Hercules, D. M.; Houalla, M. *J. Mass Spectrom.* **2001**, *36*, 140−144.
(35) Guttman, C. M.; Wetzel, S. J.; Blair, W. R.; Fanconi, B. M.; Girard, J. E.; Goldschmidt, R. J.; Wallace, W. E.; VanderHart, D. L. *Anal. Chem.* **2001**, *73*, 1252−1262.
(36) Byrd, H. C.; McEwen, C. N. *Anal. Chem.* **2000**, *72*, 4568−4576.
(37) Takats, Z.; Vekey, K.; Hegedus, L. *Rapid Commun. Mass Spectrom.* **2001**, *15*, 805−810.
(38) Chmelik, J.; Planeta, J.; Rehulka, P.; Chmelik, J. *J. Mass Spectrom.* **2001**, *36*, 760−770.
(39) Lou, X.; van Dongen, J. L.; Meijer, E. W. *J. Chromatogr., A* **2000**, *896*, 19−30.
(40) Hanton, S. D.; Liu, X. M. *Anal. Chem.* **2000**, *72*, 4550−4554.
(41) Carroccio, S.; Rizzarelli, P.; Puglisi, C. *Rapid Commun. Mass Spectrom.* **2000**, *14*, 1513−1522.
(42) Laine, O.; Osterholm, H.; Selantaus, H.; Vainiotalo, P. *Rapid Commun. Mass Spectrom.* **2001**, *15*, 1931.
(43) Falkenhagen, J. Friedrich, J. F.; Schulz, G.; Kruger, R. P.; Much, H. Weidner, S. *Int. J. Polym. Anal. Charact.* **2000**, *5*, 549.
(44) Keil, C.; Esser, E.; Pasch, H. *Macromol. Mater. Eng.* **2001**, *286*, 161.
(45) Lee, H. J.; Chang, T. Y.; Doosung, L.; Shim, M. S.; Ji, H.; Nonidez, W. K.; Mays, J. W. *Anal. Chem.* **2001**, *73*, 1726−1732.
(46) Gallet, G.; Carroccio, S.; Rizzarelli, P.; Karlsson, S. *Polymer* **2002**, *43*, 1081−1094.
(47) Koster, S.; Duursma, M. C.; Boon, J. J.; Nielen, M. W. F.; DeKoster, C. C.; Heeren, R. M. A. *J. Mass Spectrom.* **2000**, *35*, 739−748.
(48) Badawy, S. M.; Dessouki, A. M.; El Din, H. M. N. *Radiat. Phys. Chem.* **2001**, *61*, 143.
(49) Mehl, J. T.; Hercules, D. M. *Macromolecules* **2001**, *34* (6), 1845−1854.
(50) Eyend, X. V.; Bertrand, P.; Penelle, J. *Macromolecules* **2000**, *33* (15), 5624−5633.
(51) Storey, R. F.; Brister, L. B.; Sherman, J. W. *J. Macromol. Sci. Pure Appl. Chem.* **2001**, *38*, 107.
(52) Polce, M. J.; Klein, D. J.; Harris, F. W.; Modarelli, D. A.; Wesdemiotis, C. *Anal. Chem.* **2001**, *73*, 1948−1958.
(53) Chen, R.; Zhang, N.; Tseng, A. M.; Li, L. *Rapid Commun. Mass Spectrom.* **2000**, *14*, 2175−2181.
(54) Przybilla, L.; Francke, V. Rader, H. J.; Mullen, K. *Macromolecules* **2001**, *34*, 4401−4405.
(55) Adamus, G.; Sikorska, W.; Montaudo, M. S.; Scandola, M.; Kowalczuk, M. *Macromolecules* **2000**, *33*, 5797−5802.
(56) Keki, S.; Bodnar, I.; Borda, J.; Deak, G.; Batta, G.; Zsuga, M. *Macromolecules* **2001**, *34*, 7288−7293.

(57) Zaia, J.; McClellan, J. E.; Costello, C. E. *Anal. Chem*. **2001**, *73*, 6030−6039.
(58) Dasaire, H.; Sirick, T. L.; Leary, J. A. *Anal. Chem*. **2001**, *73*, 3513−3520.
(59) Yontz, D. J.; Hsu, S. L. *Macromolecules* **2000**, *33* (22), 8415−8420.
(60) Mehl, J. T.; Murgasova, R.; Dong, X.; Hercules, D. M.; Nefzger, H. *Anal. Chem*. **2000**, *72*, 2490−2498.
(61) Tatro, S. R.; Baker, G. R.; Fleming, R.; Harmon, J. P. *Polymer* **2002**, *43*, 2329−2335.
(62) Thomas, J. J.; Shen, Z.; Blackledge, R.; Siuzdak, G. *Anal. Chim. Acta* **2001**, *442*, 183−190.
(63) Meyer, T.; Kunkel, M.; Frahm, A. W.; Waidelich, D. *J. Am. Soc. Mass Spectrom*. **2001**, *12*, 911−925.
(64) Nonaka, H.; Ouchi, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2001**, *34*, 2083−2088.
(65) Katayama, H.; Kamigaito, M.; Sawamoto, M. *J. Polym. Sci. A.: Polym. Chem*. **2001**, *39*, 1249.
(66) Roberts, G. E.; Heuts, J. P. A.; Davis, T. P. *Macromolecules* **2000**, *33* (21), 7765−7768.
(67) Jayakannan, M.; Van Dongen, J. L. J.; Janssen, R. A. J. *Macromolecules* **2001**, *34*, 5386−5393.
(68) Keki, S.; Bodnar, I.; Borda, J.; Deak, G.; Zsuga, M. *J. Phys. Chem. B* **2001**, *105*, 2833−2836.
(69) Holland, B. J.; Hay, J. N. *Polymer* **2002**, *43*, 1797−1804.
(70) Koster, S.; de Koster, C. G.; van Benthem, R. A. T. M.; Duursma, M. C.; Boon, J. J.; Heerena, R. M. A. *Int. J. Mass Spectrom*. **2001**, *210*, 591−602.
(71) Socher, G.; Rissler, K.; Walter, U.; Lankmayr, E. *Tenside, Surfactants, Deterg.* **2001**, *38*, 80.
(72) McLuckey, S. A.; Asano, K. G.; Schaaff, G.; Stephenson, J. L. *Int. J. Mass Spectrom*. **2000**, *195*, 419−437.
(73) Yalcin, T.; Gabryelski, W.; Li, L. *Anal. Chem*. **2000**, *72* (16), 3847−3852.
(74) Hinderling, C.; Chen, P. *Int. J. Mass Spectrom*. **2000**, *195*, 377−383.
(75) Adlhart, C.; Chen, P. *Helv. Chim. Acta* **2000**, *83*, 2192−2196.
(76) Cerda, B. A.; Breuker, K.; Horn, D. M.; McLafferty, F. W. *J. Am. Soc. Mass Spectrom*. **2001**, *12*, 565−570.
(77) Chen, R.; Li, L. *J. Am. Soc. Mass Spectrom*. **2001**, *12*, 832−839.
(78) Maziarz, P., III; Baker, G. A.; Mure, J. V.; Wood, T. D. *Int. J. Mass Spectrom*. **2000**, *202*, 241−250.
(79) Sundarrajan, S.; Surianarayanan, M.; Srinivasan, K. S. V.; Kishore, K. *Macromolecules* **2002**, *35*, 3331−3337.
(80) Mignard, N.; Zerroukhi, A.; Boinon, B. *Eur. Polym. J.* **2001**, *37*, 1591.
(81) Westphal, C.; Perrot, C.; Karlsson, S. *Polym. Degrad. Stab.* **2001**, *73*, 281−287.
(82) Jakab, E.; Blazso, M.; Faix, O. *J. Anal. Appl. Pyrolysis* **2001**, *58*, 49−62.
(83) Urakami, K.; Higashi, A.; Umemoto, K.; Godo, M.; Watanabe, C.; Hashimoto, K. *Chem. Pharm. Bull.* **2001**, *49*, 203−205.
(84) Fabbri, N. *J. Anal. Appl. Pyrolysis* **2001**, *58*, 361−370.
(85) Tienpont, B.; David, F.; Vanwalleghem, F.; Sandra, P. *J. Chromatogr., A* **2001**, *911*, 235−247.
(86) Nakamura, S.; Takino, M.; Daishima, S. *J. Chromatogr., A* **2001**, *912*, 329−334.
(87) Wang, F. C.-Y.; Meunier, D. M. *J. Chromatogr., A* **2000**, *888*, 209.
(88) Goto, M.; Koyamoto, H.; Kodama, A.; Hirose, T.; Nagaoka, S.; McCoy, B. J. *AICHE J.* **2002**, *48*, 136−144.
(89) Li, L.; Ng, K.-M.; Chan, C.-M.; Feng, J.-Y.; Zeng, X.-M.; Weng, L.-T. *Macromolecules* **2000**, *33* (15), 5588−5592.
(90) Nowak, R, W,; Gardella, J. A., Jr.; Wood, T. D.; Zimmerman, P. A.; Hercules, D. M. *Anal. Chem*. **2000**, *72* (19), 4585−4590.
(91) Sidouni, F.-Z.; Emch, R.; Nurdin, N.; Chabrececk, P.; Lohmann, D.; Vogt, J.; Xanthopoulos, N.; Mathieu, H. J.; François, P.; Vaudaux, P.; Descouts, P. *Surf. Sci.* **2001**, *491*, 355−369.
(92) Coullerez, G.; Léonard, D.; Lundmark, S.; Mathieu, H. *J. Surf. Interface Anal.* **2000**, *29*, 431−443.
(93) Michel, R.; Luginbühl, R.; Graham, D. J.; Ratner, B. D. *Langmuir* **2000**, *16* (16), 6503−6509.
(94) Weng, L.-T.; Wong, P. C. L.; Ho, K.; Wang, S.; Zeng, Z.; Yang, S. *Anal. Chem*. **2000**, *72* (20), 4908−4913.
(95) Zeng, X. M.; Chan, C. M.; Weng, L. T.; Li, L. *Polymer* **2000**, *41*, 8321−8329.
(96) Li, L.; Chan, C. M.; Lei, Y.; Weng, L. T. *Polymer* **2001**, *42*, 6841.
(97) Bernasik, A.; Rysz, J.; Budkowski, A.; Kowalski, K.; Camara, J.; Jedlinski, J. *Macromol. Rapid Commun*. **2001**, *22*, 829.
(98) Zeng, X. M.; Weng, L. Y.; Li, L.; Chan, C. M.; Liu, S. Y.; Jiang, M. *Surf. Interface Anal.* **2001**, *31*, 421.
(99) Brookes, P. N.; Fraser, S.; Short, R. D.; Hanley, L.; Fuoco, E.; Roberts, A.; Hutton, S. *J. Electron Spectrosc. Relat. Phenom*. **2001**, *121*, 281−297.
(100) Chen, J.; Lee, J.-W.; Hernandez de Gatica, N. L.; Burkhardt, C. A.; Hercules, D. M.; Gardella, J. A., Jr. *Macromolecules* **2000**, *33* (13), 4726−4732.
(101) Vanhaecke, F.; Resano, M.; Verstraete, M.; Moens, L.; Dams, R. *Anal. Chem*. **2000**, *72* (18), 4310−4316.
(102) Mincheva, Z.; Hadjieva, P.; Kalcheva, V.; Seraglia, R.; Traldi, P.; Przybylski, M. *J. Mass Spectrom*. **2001**, *36*, 1076−5174.
(103) Qian, K.; Edwards, K. E.; Siskin, M. *Energy Fuels* **2001**, *15* (4), 949−954.
(104) Lippert, T.; David, C.; Dickinson, J. T.; Hauer, M.; Kogelschatz, U.; Langford, S. C.; Nuyken, O.; Phipps, C.; Robert, J.; Wokaun, A. *J. Photochem. Photobiol. A: Chem*. **2001**, *145*, 145−157.

AC020214U