

Mass Spectrometry of Synthetic Polymers

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SCOPE

The aim of this review is to give a compact overview about the literature on mass spectrometry (MS) of polymers published during 2006/2007. The citations are drawn from *SciFinder* January 25, 2008, using the search terms “poly*” and “mass spectrometry” with restrictions to review and journal contributions in the English language including refined searches in *Web of Science*. More than 750 relevant papers, reviews, (1, 2) and historical summaries (3, 4) were published in these two years, demonstrating the importance of MS for polymer analysis. We were therefore forced to select the most important references. This is always a subjective decision and may not always represent the best choices. In contrast to the previous review in this series (5), which focused on MS principles, including matrix-assisted laser desorption/ionization (MALDI) time-of-flight (TOF), electrospray ionization (ESI) TOF, TOF secondary ion mass spectrometry (SIMS), etc., in this paper, we categorize according to applications of MS for polymer analysis. Even this choice is arbitrary.

The main chapters are focused on New Techniques and Principles, Polymer Synthesis, Copolymer Analysis, Fragmentation Techniques, Polymer Degradation, and Polymer Surface and Interface. Due to their comprehensiveness and complexity, clear classification of some papers to a single category is difficult. Thus, Copolymer Analysis exclusively deals with the

determination of the copolymer composition, whereas the synthesis of copolymers is described in Polymer Synthesis. Sometimes, making a clear decision between synthetic polymers and biopolymers, because both fields strongly overlap, is difficult. Typical examples for this overlap are papers of Boyer et al. (6) on the synthesis of well-defined protein–polymer conjugates via in situ reversible addition–fragmentation chain-transfer (RAFT) polymerization and also poly(ether–urethane) biobased sugar diols by Beldi et al. (7).

NEW TECHNIQUES AND PRINCIPLES

Mass spectrometry has been demonstrated to be powerful for characterizing the chemical compositions and frequently the molar mass distributions for certain polymer classes. For the ionization of intact macromolecules, the use of soft ionization techniques such as MALDI-TOF MS and ESI TOF MS is necessary. Thus, the choice of suitable matrixes, solvents, and new principles of sample preparation are of great interest. However, direct laser desorption/ionization can also be achieved in some instances when the analyte molecules show a strong absorption of the laser wavelength employed. Unfortunately, the complexity of polymers can be so large that it becomes impossible to characterize a sample directly by any MS method, thus requiring hyphenated analytical approaches to be employed. Solvent-based as well as solvent-free gas-phase separation methods can be used to reduce complexity permitting polymer MS analyses. Other new techniques and developments, in for example, desorption electrospray ionization (DESI), electrosonic spray ionization (ESSI), and TOF SIMS were described in the time frame covered here.

Matrix-Free Laser Methods. Several new MS methods were introduced using laser technology as the energy source for transferring the polymer as ions into the gas phase. Ma et al. applied the principle of LDI for the investigation of thermally stable conjugated polymers having transient energy transfer properties (8). The results were in good agreement with conventional MALDI mass spectral data.

Laser desorption can also be obtained using germanium nanodots (quantum dots) grown on a silicon monocrystalline substrate. This new method, introduced by Seino et al., has potential for application to thermally unstable brominated flame retardants whose effective mass spectra cannot be observed by MALDI-TOF MS or laser desorption/ionization on silicon (DIOS) MS because of fragmentation during the ionization process (9). Laser-induced silicon microcolumn arrays were presented as matrix-free substrates for soft laser desorption/ionization MS by Chen and Vertes (10). In these experiments using a nitrogen laser,

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the microcolumn arrays produced molecular ions for synthetic polymers at low laser fluence. The threshold laser fluence and ion yield were comparable to those observed in MALDI, indicating soft desorption/ionization processes. Low-femtomole sensitivity in a mass range up to 6000 Da was achieved.

The detection of micrometer-size poly(ethylene glycol) (PEG) particles using an online single-particle aerosol mass spectrometer equipped with a 266-nm Nd:YAG laser was reported by Bogan et al. (11). These data were used to develop a low-cost strategy for creating PEG-containing particles that produce an array of reproducible and easily recognizable spectra for calibrating the aerosol mass spectrometer. Another interesting application was the use of polymers as fuel for laser-based microthrusters designed for steering and propelling of small satellites (12). A special designed mass spectrometer was used to determine generated carbon "thrust" ions. For all polymers, one of the main decomposition products was positively charged carbon (C^+). The kinetic energies of the C^+ -ions were also measured with the mass spectrometer.

Fundamentals of MALDI and ESI. A split sample probe was constructed and used to demonstrate that gas-phase cationization occurs within the desorption plume during a MALDI experiment (13). Different sample preparation methods and matrixes including nonpolar anthracene, previously only applicable for nonpolar polymers, revealed that incorporation of an analyte is obstructive for an optimized MALDI effect and that intimate contact between analyte and matrix with the smallest crystallinity are essential (14). Selectivity of electrospray response for low molecular weight PEG provides additional evidence for the influence of electrospray droplet chemical composition on the equilibrium partitioning coefficient according to the model by Enke et al. (15). Ion/molecule reactions were exploited to chemically deconvolute ESI mass spectra in which 15-crown-5 was used to strip alkali cations (Na^+) from PEG 2500 to 10 225 (16). For example, charge-state distribution (+1 to +7) of PEG 4120 is reduced to primarily a single charge state aiding reduction in spectral complexity and yielding resolved oligomers and the determination of the average molecular mass and polydispersity.

Solvent-Based MALDI Methods. Wallace reported on reactive MALDI-TOF MS in which the application of a molecular solid of fullerene (C_{60}) intercalated with cobalt cyclopentadienyl dicarbonyl [$CoCp(CO)_2$] was explored as an effective matrix for the analysis of higher mass alkanes and polyethylene (17). The influence of the MALDI probe temperature on the ion yield of low molecular weight linear polyethylene samples using the C_{60} matrix system was also examined (18). An increase of sample temperature from 25 to 150 °C led to a significant growth of the total ion intensity.

A statistical approach for the evaluation of new matrixes was presented by Meier et al. (19). From a pool of more than 11 000 compounds, 59 were selected for testing individual performance. At least 10 new possible matrixes were identified. Somogyi and co-workers synthesized 10 polyfluorinated azobenzenes and stilbenes and employed them subsequently as matrixes for the analysis of condensation polymers (e.g., poly(ethylene terephthalate)s and Vectra) (20). The use of pencil leads as an inexpensive and safe matrix for poly(ethylene oxide)s (PEO)s, polystyrenes (PS)s, and sensitive silyl hydride-functionalized polymers was demonstrated

by two groups (21, 22). This method resulted in reproducible MALDI-TOF mass spectra in a molecular weight range of 300–6000, which is the most important region for end group analysis.

Wyatt and co-workers evaluated several aqueous-based sample preparation protocols for the analysis of poly(methacrylic acid) (PMAA) used as a ligand in the size-controlled synthesis of gold nanoparticles by MALDI-TOF MS (23). Their study resulted in significant improvements in the quality of MALDI-TOF data combined with greater signal-to-noise ratios when treating the sample solution with ion-exchange beads, before mixing with the matrix. An effective derivatization method for MALDI-TOF MS of poly(acrylic acid) (PAA) was presented by Arakawa et al. (24). After methylation of carboxy groups, intense molecular ions of the derivatized PAA were obtained. In achieving progress toward quantitative analysis of polymeric materials, selection of optimal MALDI instrument parameters yielding enhanced reproducibility was determined, some employing numerical approaches (25, 26).

Solvent-Free MALDI Methods. Solvent-free MALDI-TOF MS developed by Trimpin et al. showed significant improvements in the analysis of synthetic materials (27). By omitting the use of any solvent in the MALDI sample preparation, segregation effects were eliminated allowing analysis of poly(dimethylsiloxane) (PDMS) polymers with molecular weights up to 28 000. This work also demonstrated the usefulness of solvent-free MALDI-TOF MS for avoiding laser-induced fragmentation of fullerene-containing dendrimers as well as solvent-induced modifications of chemically active groups of dissolved polymers. The authors showed that tetrahydrofuran (THF) solvent-related modification of PS can be overcome by using an appropriate solvent, CH_2Cl_2 , or simply solvent-free MALDI analysis. Modifications of PS by peroxides in THF were also observed by Zagorewskii et al. using MALDI-TOF and ESI-TOF MS (28). By measuring self-diffusion coefficients, Mazarin et al. used pulsed gradient spin-echo nuclear magnetic resonance (NMR) for MALDI method development (29). Interestingly, samples had to be prepared according to the solvent-free MALDI method, because solvent-based methods using various matrixes and cationizing agents failed. The principle of solvent-free MALDI-TOF MS for single samples was extended to an efficient multiplexed analysis by a simultaneous homogenization/transfer method by Trimpin and McEwen (30). This multiplexed MALDI method permits reliable analysis of polymers up to 10 kDa while reducing sample consumption, preparation time and effort.

Solvent-Based Condensed-Phase Separation Methods. The marriage of liquid chromatographic (LC) separation with multisample solvent-free MALDI-TOF MS was demonstrated using a mixture of PEOs with different molecular weights and end groups (31). The mixture was separated at so-called "critical conditions of adsorption" (LACCC), and fractions containing as little as 200 pmol were collected and analyzed with the newly developed hyphenated approach, which permitted precise and simultaneous homogenization/transfer of 100 polymer fractions to the MALDI target plate without the need of a previous optimization of sample deposition. Efficient recovery of dried samples of small amounts from the wall of the sample holder device and ease of transport and storage of the MALDI sample is indicated. LC-ESI method development for the analysis of polymeric materials has also been described. A fast coupling of LC

with MS was performed by Bentayeb et al. (32). Ultraperformance liquid chromatography was coupled to ESI-TOF MS to detect nonvolatile contaminants in recycled poly(ethylene terephthalate) (PET).

Solvent-Free Gas-Phase Separation Methods. Ion mobility spectrometry TOF MS was introduced by Trimpin et al. to examine distributions of ESI-generated PEG ions with molecular weights up to 17 900 (33). The two-dimensional gas-phase separation of ions according to drift time and mass-to-charge ratios provided baseline separation of cesium cationized PEG 6550 up through charge state 10. Multiply cesiated PEG ions, $[\text{PEG}_{126}+9\text{Cs}]^{9+}$, are highly extended, linear conformations (“beads-on-a-string”) as determined by cross-section analysis and molecular simulation. The principle of this separation finally permits higher molecular weight polymer analysis including end group and molecular weight determination using ESI ionization and is shown to readily detect low-abundant compounds. Robinson et al. reported a combination of high-field asymmetric waveform ion mobility spectrometry (FAIMS) with Fourier transform ion cyclotron resonance (FT-ICR) MS (34). This combination enables lower detection limits, increased sensitivity, and improved dynamic range in the analysis of PEG 600. Different conformers of predominantly singly sodiated molecular ions could be separated and detected even with less than 0.2% relative abundance. The results indicate that interactions between the carrier gas and the cations play a role in the separation of these ions. Additional experiments showed that results for all (+1 to +7) except some of the +3 and +4 charge states of protonated PEG 300–5000 are consistent with a single gas-phase conformer (35). The structural characterization of polyhedral oligomeric silsesquioxanes (POSS) siloxane dimer and trimer were undertaken using ion mobility and molecular modeling methods by examining the gas-phase conformational properties of MALDI-generated sodiated dimer and trimer ions. X-ray crystal structures at 100 and 298 K supporting data showed that solid-state cage–cage intermolecular distances are perfectly consistent with the modeled POSS–PMA dimer and trimer structures (36).

Other Methods. DESI and ESSI, two new techniques for polymer analysis, were introduced by Nefliu et al. for measuring average molecular weights and molecular weight distributions of solid phase and solution phase of low molecular weight polymeric samples such as PEG, poly(tetramethylene glycol), and polyacrylamide (37). DESI combined with both MS and tandem mass spectrometry (MS/MS) was also employed by Jackson et al. for low molecular weight synthetic polymer analysis including PEG, poly(propylene glycol) (PPG), PMMA, and poly(α -methylstyrene) (38). Zhang et al. applied on-probe pyrolysis DESI MS to detect and analyze nonvolatile pyrolysis products of synthetic and biological samples (39). In addition, the potential for successive fragmentation analysis was shown.

By combining TOF-SIMS with depth profiling, Gillen et al. obtained three-dimensional molecular image depth profiles from thin monolayer and bilayer films of spin cast PMMA, poly(2-hydroxyethyl methacrylate) (PHEMA), and poly(lactic acid) (PLA) (40). However, the complexity of SIMS spectra is often a limitation for the identification of unknown components. For this purpose, the principle of so-called gentle-SIMS can be applied. The extrapolation of the data to low surface plasma temperature reveals

the undegraded parent fragments from the ordinary SIMS spectra providing more information. Examples on biodegradable homopolyesters and thermosetting polymers were shown by Ogaki et al. and Hawtin et al. (41, 42). Cryogenic sample handling methods for TOF-SIMS analysis have been developed and successfully applied to the study of siloxane segregation in hydrogel polymers (43).

The measurement of the carbon isotope ratio (^{14}C , ^{13}C , and ^{12}C) based on ISO 14855-2 for the investigation of the biodegradability of poly(3-caprolactone) (PCL) powder using accelerator mass spectrometry (AMS) was developed by Kunioka et al. (44). However, this method is limited to only oil-based plastic biodegradation in natural biomass. First results of positive and negative electron-stimulated ion desorption-TOF MS on poly(vinyl chloride) (PVC) induced by a variable-energy electron beam were reported by Mendes et al. (45).

Räder et al. introduced a general route to process, at surfaces, extraordinarily large carbon-based polymers, that is, synthetic nanographenes, into ultrapure crystalline architectures (46). The combination of methods relies on the soft landing of ions generated by solvent-free MALDI, purified in the MS dimension, and characterized by scanning tunneling microscopy. The observed flexibility permits the growth of ultrapure crystalline films of various systems, including organic, inorganic, and biological molecules.

POLYMER SYNTHESIS

ESI and MALDI ionization techniques are predominantly used for answering important questions with respect to the synthesis of polymers by the determination of oligomer molecular weights, thus enabling the characterization of end groups and the elucidation of reaction pathways. In this section, we discuss the use of these techniques for the analysis of copolymers, dendrimers, and hyperbranched polymers.

Copolymers. New potentially biodegradable, thermoplastic multiblock copolymers from poly(lactic acid), poly(ϵ -caprolactone), or poly(lactic acid– ϵ -caprolactone) copolymers were synthesized by Borda et al. and characterized by MALDI-TOF MS (47). These authors reported that some mechanical properties, e.g., tensile strength, Young’s modulus, and Shore A hardness of these copolymers clearly exceed those of conventional polymers. MALDI-TOF MS was also used by Bozovic-Vukic and co-workers who investigated the formation of low molecular weight poly[(styrene-*co*-acrylonitrile)–(4-vinylpyridine)] SAN-*b*-P4VP block copolymers synthesized by chain extension from reversible addition fragmentation chain transfer (RAFT)-functional P4VP (48). The attachment of sulfonate groups, which can transfer protons and confer ion-exchange properties of new polypyrrole copolymer membranes with exceptional thermal stabilities up to 900 °C, was investigated using TOF-SIMS by Clochard et al. (49). Ihara et al. applied MALDI-TOF MS for the analysis of poly(vinyl alcohol-*ran*-styrene) copolymers formed by a novel synthetic strategy comprising a radical copolymerization of alkoxyvinylsilanes with styrene and successive oxidative transformation of C–Si(OR)₂Me into C–OH (50). The characterization of possible shape-memory polymers containing short aramid hard segments and poly(3-caprolactone) soft segments was partially performed by MALDI-TOF MS (51). This MS technique was also used for monitoring the synthesis of poly[poly(ethylene glycol)-*co*-cyclic acetal]-based

hydrogels (52), melt copolymers including polyesters (53), as well as in the microwave-assisted formation of poly(ether-ester)s of aliphatic isosorbide diols (54), in the synthesis of biodegradable A-B-A triblock copolymers containing poly(ϵ -caprolactone) A blocks and poly(*trans*-4-hydroxy-L-proline) B blocks (55), for structure analysis of amphiphilic poly(ethylene oxide)-*graft*-polystyrene and poly(ethylene oxide)-*graft*-poly(methyl acrylate) copolymer brushes (56, 57), for poly(styrene-vinylpyrrolidone) and poly(methyl methacrylate-vinylpyrrolidone) diblock copolymers (58), and for the characterization of poly(fluorooxetane-*co*-THF) (59). Furthermore, this technique was employed for the analysis of electrosynthesized poly[1-(thiophene-2-yl)benzothieno[3,2-*b*]benzothophene], which represents a novel fluorescent and conducting polymer (60). The molecular weights of precursor molecules of amphiphilic poly(ethylene glycol)-poly(acrylic acid)-poly(*n*-butyl acrylate) triblock copolymers used for morphology control in the crystallization of calcium carbonate were verified by MALDI-TOF MS (61). The continuous monitoring of polymer end groups (initiating and chain growth species) at various times by ESI-TOF MS was used to determine that the sterically hindered strong organic base acts as an initiator of polymer chain growth in the copolymerization of CO₂ and propylene oxide catalyzed by Salen-Cr(III) complexes (62). ESI-TOF MS was also used in the electrochemical synthesis and characterization of 2-biphenyl-3-octylthiophene copolymers (63).

Dendrimers and Hyperbranched Polymers. Clark et al. presented a divergent polyphenylene dendrimer synthesis of the largest chemically monodisperse molecules to date, up to 28 nm at 271.6 kDa for the sixth generation. A combination of molecular and polymer characterization tools, namely size exclusion chromatography (SEC), atomic force microscopy (AFM), ultrahigh-mass MALDI-TOF MS (64), and dynamic light scattering were employed for establishing the monodispersity, conformational flexibility, and an assembly behavior reminiscent of multimeric proteins for the locally stiff, macroporous dendrimers (65).

The metal-free synthesis of amphiphilic poly(L-lactide)-*b*-poly(L-lysine)s dendrimers was investigated by MALDI-TOF and ESI-TOF MS (66). MALDI-FTMS revealed that no appreciable intermolecular chain transesterification occurred during the ring-opening polymerization. In addition, MALDI-TOF MS was successfully used to calculate the number of terminal groups of surface-functionalized poly(amidoamine) [PAMAM] dendrimers (67) and for the structure analysis of synthesized hyperbranched poly(glycerol-diacid) oligomers (68). MALDI-TOF mass spectra of multifunctionalized PAMAM dendrimers with hydrazide-terminated spacer arms could be recorded up to the fourth dendrimer generation (69). These dendrimers are intended to be used for the metal-carbonyl multilabeling of immunological reagents such as antibodies. The molecular weights of multifunctional PAMAM dendrimer-taxol conjugates designed for use in drug delivery systems could be investigated up to the fifth generation by MALDI-TOF MS (70). PAMAM from generation 2 (G2) to 10 (G10) dendrimers were determined by MALDI-TOF MS and nanoelectrospray gas-phase electrophoretic mobility molecular analysis (nES-GEMMA) using nanogram amounts. Molecular weights up to 580 000 with a precision below $\pm 0.9\%$, a spherical size (from 3.3 to 14.0 nm with a precision of ± 0.2 nm) and the calculation of their densities were reported (71).

Marquez et al. reported the formation of supramolecular complexes of resorcinarene dendrimers and fullerene C₆₀. The structure of the first and the second dendrimer generation was confirmed by MALDI-TOF MS and FAB+ MS (72). Molecular weights of different generations of poly(ether amide) dendrimer with different core sizes were successfully carried out by MALDI-TOF MS (73). Additional measurements of the dendrimer mixture demonstrated a distinct decrease of the signal quality at higher molecular weights, which represents a typical discrimination of species with higher masses in samples with broad polydispersities. Another class of spherical, hydrophilic dendrimer-like PEG copolymers demonstrated pH responsiveness at the nanometer-size range. The molecular weight of the first generations was confirmed by MALDI-TOF MS (74).

High-performance liquid chromatography-ESI-TOF MS was used to confirm the synthesis of novel monodisperse PEG-dendrons with amino or carboxylic terminal groups (75). Novel fluorescent dendrimers bearing a conjugated oligo(phenylenevinylene) core and peripheral allyl chains as dendrons represents a possible candidate for application in organic light emitting diodes. Molecular weights up to the third generation could be confirmed by MALDI-TOF and FAB+ MS (76). The advantage of MALDI-TOF MS compared to SEC was demonstrated by Degoricija et al. (77). With SEC, an accurate measure of the molecular weight of dendrimers, consisting of PEG core and dendritic wedges of succinic acid and glycerol, was more difficult to obtain, partly because the calibration is based on linear PEG standards. The poor molecular weight measurement is probably a result of the copolymers that, with increasing molecular weights, adopt a more globular structure in solution. In contrast, MALDI-TOF MS gave accurate molecular weights. The formation of hyperbranched poly(ether ketone)s (PEKs) exclusive of cross-linked products, synthesized via a A(3) + B-2 polymerization approach, was reported by Choi et al. (78). MALDI-TOF MS confirmed that there was no trace of networks in the low molecular weight region but cyclics with various sizes of were detected.

Other Polymers. There were many MS applications in support of the synthesis of polymers mainly using MALDI and ESI techniques. MALDI-TOF MS played an important role in the elucidation of the mechanism of MMA polymerization in ionic liquids. It was ascertained, for example, that a chain transfer to ionic liquids occurs, and the imidazolium ionic liquids are not neutral solvents (79). MALDI-TOF MS of the reaction products of the free-radical polymerization of MA in the presence of novel cyclic dioxanthe under γ -ray irradiation (80 Gy min⁻¹) at different temperatures reveals the formation of at least three different distributions and may be related to the reduced diffusion rate and the suppressed chain-transfer reaction at low temperature (80, 81). Nondimeric byproducts in the synthesis of epoxy end-capped PMMA could be detected by MALDI-TOF MS (82). The synthesis of PMMA was also extensively monitored by Buback et al. by means of ion trap ESI MS and ESI-FT-ICR (83). A simple thin-layer chromatography (TLC) was used to separate primary amine end-functionalized PSs and PMMAs synthesized by living anionic polymerization prior to analysis employing MALDI-TOF MS (84).

Lovestead et al. gained a detailed mechanistic insight into the RAFT-mediated methyl acrylate and butyl acrylate polymerization initiated via ⁶⁰Co γ -irradiation using ESI quadrupole time-of-flight

(Q-TOF) and ion trap ESI MS (85). PMMA and PS were also produced by monoacylphosphine oxide photoinitiation (86). The analysis of gel permeation chromatography fractions by MALDI-TOF MS indicated that a combination of PS radicals with the highly reactive diphenylphosphine oxide group at one end of the chains was the predominant mode of termination, whereas MALDI-TOF MS results for PMMA fractions provided evidence for termination primarily by disproportionation. Ranucci et al. investigated poly(vinylpyrrolidone) (PVP) oligomers prepared with different esters as chain-transfer agents (87). MALDI-TOF MS provided the conclusive evidence that all the molecular species present in the samples carried a terminal ester-derived group. MALDI-TOF MS after functionalization of poly(styryl)lithium with thiiranes indicates a ring-opening mechanism, in contrast to a sulfur extrusion mechanism for the reaction of organolithium compounds with propylene sulfide (88).

In the characterization of thermoresponsive poly(*N*-isopropylacrylamide) (P-NIPAM) functionalized with pyrenyl end groups, the number-average molecular weights calculated from MALDI-TOF MS were in a good agreement with the theoretical data, in contrast to SEC results, which gave significantly higher molecular weights (89). Kricheldorf et al. applied MALDI-TOF MS to prove the formation of multicycles as the main reaction products in the polycondensation of oligo(ethylene glycol)s and trimesoyl chloride and to monitor the synthesis of different lactones (90–92). The ring-opening polymerization of macrocyclic (arylene thioether ketone) oligomers was confirmed by MALDI-TOF MS (93). The same MS method was used to investigate the effect of long time aging on the chain end of poly(*p*-methoxystyrene) (94). Furthermore, the characterization of poly(ether imide)s (95, 96), poly(amidoamines) (97), poly(ester amide)s (98), poly(epichlorohydrin) (99), telechelic poly(*N*-isopropylacrylamides) (100), cyclic poly(lactides) (101), enantiomeric poly(α -methyl- α -ethyl- β -propiolactones) (102), and multicyclic poly(ether sulfone)s (103) by MALDI-TOF MS was reported. Liu and Mishra described the atom-transfer radical polymerization of menthyl acrylate (104). The release of the menthyl group at higher temperatures, monitored by gas chromatography (GC) MS, provides an alternative route to synthesize poly(acrylic acid) with controlled structures.

Temperature-dependent product distributions in the octylthiol-mediated polymerization of poly(butyl acrylate) were investigated by ESI-MS (105). At lower temperatures, the main product peak could be assigned to the expected transfer to thiol product, whereas at elevated temperatures additionally four β -scission products can be identified. Poly(L-lactide)s and poly(D-lactide)s of high optical purity were synthesized with an excellent control on the number-average degree of polymerization by Jalabert et al. (106). The MALDI-TOF mass spectra of these polymers revealed two distributions of linear chains with even and odd numbers of lactic acid repeat units, which are the result of intermolecular transesterification occurring at the very beginning of the polymerization. Ihara et al. showed that, although a cationic polymerization mechanism was expected, MALDI-TOF MS of the resulting poly(isobutyl vinyl ether)s revealed the presence of H at the α -chain end (107). Evidence for intermediate radical termination in the RAFT polymerization of *n*-butyl acrylate (BA) was presented by Geelen and Klumperman by means of MALDI-TOF MS of fractions taken from SEC (108). Gies and co-workers

applied MALDI-TOF MS using an evaporative grinding method for studies of aromatic poly(*p*-phenylene terephthalamide) and Kevlar fibers due to the low solubility of these materials (109).

COPOLYMER ANALYSIS

The analysis of copolymers is considerably more challenging than that of homopolymers. In addition to the molecular weight and end group distribution of comparatively simple homopolymers, copolymers exhibit a topology distribution. Thus, random, block, alternating, or gradient copolymers can be synthesized. As noted in the copolymer section under Polymer Synthesis, MS can be useful in determining these structures. Nevertheless, MS frequently requires a suitable combination of LC separation methods and other spectroscopic methods such as NMR for structural analysis.

Huijser et al. investigated by MALDI-TOF MS the formation of poly(lactide-*co*-glycolide) (PLGA), which is a copolymer used extensively in the medical sector as a material for drug delivery, implants, bone screws, and absorbable sutures (110, 111). Software developed in-house enabled the elucidation of individual chain structures and a full characterization of the copolymer, including even its chemical composition and topology. A similar approach was used by Weidner et al. for the investigation of poly(ethylene oxide)–poly(propylene oxide) copolymers (PEO-*co*-PPO) in which different chromatographic separation techniques (e.g., SEC and chromatography at “critical” conditions of adsorption, LACCC) were coupled to MALDI-TOF and ESI-TOF MS (112). In addition to copolymer composition, end groups, and molecular weights, different modes of separation for each polymer structure of the copolymer could be easily detected. Due to the previous chromatographic separation, narrow distributed fractions were obtained. The investigation of adipinic acid–neopentyl glycol-*co*-adipinic acid–hexanediol polyesters resulted in resolved MALDI spectra up to 20 000 Da (113). Another coupling approach was presented by van Leeuwen and co-workers (114). LACCC coupled to ESI and atmospheric pressure chemical ionization in the positive and negative ion modes was used for the characterization of methoxy poly(ethylene oxide) (mPEO)– ϵ -caprolactone (CL) block copolymers. This combination enabled the determination of the polymer backbone composition as well as the block length distribution. An offline coupling of SEC with MALDI-TOF MS for the detailed characterization of poly[(*RS*)-3-hydroxybutyrate-*co*-L-lactic acid], P[(*RS*)-3HB-*co*-LA], and poly[(*R,S*)-3-hydroxybutyrate-*co*- ϵ -caprolactone], P[(*R,S*)-3HB-*co*-CL], copolymers was described by Adamus and co-workers (115). The composition of the copolyesters was additionally determined by ^1H NMR. Both MALDI-TOF MS and NMR values showed good agreement. The degree of transesterification was determined based on sequence analysis. The formation and analysis of poly(ϵ -caprolactone-*co*-L-lactide) P(CL-LLA) and poly(ϵ -caprolactone-*co*-D-valerolactone) P(CL-VL) as new degradable binders used for antifouling paints was reported by Fay et al. (116). MALDI-TOF MS of SEC fractions showed that the molecular weights calculated from the conventional SEC calibration are strongly overestimated. In contrast to other reports, no cyclic structures were observed. Narrowly dispersed molecular mass SEC fractions were used to characterize random and microblock poly[(*R*)-3-hydroxybutyrate-*co*- ϵ -caprolactone] [P(HB-*co*-CL)] copolymers by MALDI and ESI-TOF MS (117). The higher resolution of ESI MS of lower molecular weight

fractions permitted the identification of those oligomer species hypothesized in the assignment of the corresponding MALDI mass spectra.

Jacquín et al. combined several analytical techniques including NMR, MALDI-TOF MS, GPC, LC at the point of exclusion adsorption transition (PEAT), and capillary electrophoresis CE) to analyze and quantify the characteristics of amphiphilic diblock poly(butyl acrylate)-*b*-poly(acrylic acid) (PBA-*b*-PAA) and poly(di(ethylene glycol) ethyl ether acrylate)-*b*-poly(acrylic acid) (PDEGA-*b*-PAA) copolymers synthesized by macromolecular design via interexchange of xanthate (MADIX) (118, 119). This combination of analytical methods allowed the quantification of side products as well as an improvement in reaction conditions through a better knowledge of the reaction mechanism. Several techniques, including LC, MALDI-TOF MS, IR, and NMR spectroscopy, as well as combined techniques such as 2D chromatography have been used to determine the end groups of polyacetal copolymers (120). Cyclic oligomers and polymers with formyl, hydroxy, and aliphatic end groups were identified.

The results of ^{13}C NMR spectroscopy based on diad and triad analysis and the ESI-MSⁿ technique used by Zagar et al. for sequence distribution analysis of comonomer units in microbial poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) copolyesters (121) were also in a good agreement. ESI and MALDI-TOF MS and ^1H NMR were used to monitor the composition changes that occur during copolymerization of poly(butyl acrylate/vinyl acetate) (PBA/PVAc), poly(methyl methacrylate/vinyl acetate) (PMMA/PVAc), and poly(butyl acrylate/methyl methacrylate) (PBA/PMMA) copolymers (122). ESI MS was useful in end group analysis, which could not be obtained by NMR, and for the determination of the copolymer composition. Due to inherently different ionization efficiencies in MALDI, different monomer and copolymer end group ratios were found for PBA/PMMA copolymers in ESI MS and MALDI-TOF MS spectra. Full characterization (molar mass distribution and block sequence) of a multiblock (2,6-dimethyl-1,4-phenylene oxide)-*b*-(bisphenol A carbonate) (PPO-*b*-PC) copolymer was reported by Semperi et al. (123). MALDI-TOF analysis showed that the synthesized PPO-*b*-PC copolymers were composed of multiblock PPO-*b*-PC chains and of some nonreacted PC oligomers terminated with methyl carbonate groups. MALDI-TOF MS was also applied for the analysis of synthesized vinyl acetate (VAc) and *N*-vinylpyrrolidone (PVAc-PVP) copolymers. Only end groups of copolymers with a PVAc blocks could be successfully analyzed by MALDI-TOF MS because significant fragmentation occurred with the PVP-containing polymers (124). The composition of a thermosensitive poly(2-isopropyl-2-oxazoline) copolymer synthesized via gradient copolymerization was revealed by MALDI-TOF MS (125, 126). In combination with ^1H NMR, monomer reactivity ratios were derived from the cumulative and instantaneous compositions of the copolymers.

Spin-cast films of random copolymers of styrene and 2,3,4,5,6-pentafluorostyrene (PS-5FPS) were analyzed using TOF-SIMS (127). Using relative signal intensities, the authors showed that ion intensity ratios are linearly proportional to the copolymer mole ratio when characteristic ions of PS and 5FPS were selected. This suggests that quantitative analysis is possible in such copolymer system.

Adamus characterized the molecular architecture of individual copolyester macromolecules and structures of end groups (hydroxyl and carboxylate) of two random poly[(*R,S*)-3-hydroxybutyrate-*co*-L-lactide] (P[(*R,S*)-3HB-*co*-LA]) copolyesters by ESI ion trap mass spectrometry (IT-MS) (128). Detailed studies were performed by means of collision-induced dissociation (CID). The arrangement of comonomer units was evaluated by the respective ESI-MS/MS fragmentation pathways. This last reference again demonstrates the difficulties encountered structuring categories. In addition to being relevant for copolymer analysis, it could just as well have been classified to fragmentation techniques, which is surveyed in the next chapter.

FRAGMENTATION TECHNIQUES

In contrast to biopolymers where fragmentation is used extensively for sequence determination, the fragmentation analysis of synthetic polymers is sparingly reported. One possible reason is that polymers often undergo rearrangement(s) after dissociation, which leads to additional signal series, making spectra elucidation more complicated. Additional challenges are that the fragment ion yield of informative backbone cleavages is comparatively low, especially in the case of singly charged ions preferentially formed by MALDI, and the simple dissociation of the charge carrier (metal cation) is a competitive pathway for energy release in MS/MS experiments. Recently, first attempts to establish a common nomenclature of fragments have been undertaken. Nevertheless, the potential of polymer fragmentation appears not to be fully explored as expressed by the low number of publications with only one dozen contributions in total for the time frame reviewed.

For the first time, the development and application of novel software for the interpretation of ESI-MS/MS data of synthetic polymers (including acrylics, polyethers, and styrenes) was described by Thalassinou et al. (129). This software aids the interpretation of MS/MS spectra from polymers with known fragmentation pathways and reduces significantly the time for interpretation. The same software was successfully used by Williams et al. for DESI Q-TOF MS of polyglycol esters and ethers (130). Lee et al. developed a nomenclature for assigning fragment ions produced by electron capture dissociation of a third-generation PAMAM dendrimer (131).

A number of polyethers with various end groups were characterized by Jackson et al. using MALDI-CID (132). Different series of fragment ions were detected with abundances being dependent on the functionality at the chain ends. Additionally, the authors found that the fragmentation of PEG samples with ester end groups produced significant series of ions with neither of the original end groups. In contrast to these results, Rizzarelli et al. reported no influence of different end groups on the fragmentation of sodiated PBA oligomers in MALDI-TOF MS/MS experiments (133). Similar experiments to determine the end group functionality of PMMA polymers made with both brominated and chlorinated initiators by means of ATRP indicated the formation of lactone-ring end groups, partly generated by fragmentation of the carbon-to-bromine bond in the MALDI process and partly from intact oligomers that are present in the sample prior to analysis for PMMA (134).

MALDI-CID was also used to examine the fragmentation patterns of poly(amic methyl ester) oligomers (135). It was shown

that both molecular weight and end groups affected the fragmentation, whereas the use of different CID gases (helium, argon, xenon) had no effect on the fragmentation pattern. The same principle was used by Weidner et al. for fragmentation analysis of PEG–PPG copolymers (112). In contrast to the expected randomlike structure, fragment series were observed providing evidence for a rather blocklike composition. In order to examine the influence of molecular weights and collision kinetic energy on the degradation mechanisms of hydroxylated polystyrene, MALDI-TOF/TOF CID experiments were conducted on a variety of precursor ions up to $n = 30$ by Gies et al. (136). Different depolymerization mechanisms were presented in detail with experimental and computational data showing the complex interrelationships between the various pathways. In addition, pyrolysis (Py)-GC/MS data were presented to compare the unimolecular fragmentation reactions of MS/MS with the multimolecular free-radical reactions in pyrolysis. Experiments on a series of ethoxylated surfactants showed the utility of atmospheric pressure MALDI quadrupole ion trap (QIT) by Hanton et al. (137). MS/MS analysis was also obtained stressing the possibility of completing these experiments on relatively inexpensive QIT instruments.

Among other spectroscopic methods, Kawauchi et al. applied MALDI-TOF MS for detecting isotactic and syndiotactic C_{60} -end-capped PMMA (it- and st-PMMA- C_{60} 's). These polymers form a supramolecular nanosphere and nanonetwork by a formation of a stereocomplex combined with self-assembly of the terminal C_{60} (138). The MS/MS analysis of a PMMA- C_{60} peak revealed the loss of a C_{60} , clearly indicating that one C_{60} unit was covalently attached to the polymer chain end. PAMAM dendrimers were intensively studied by Giordanengo et al. using MALDI-TOF and ESI-TOF MS (139). ESI-TOF MS/MS measurements, based CID revealed that in addition to the commonly reported “missing arm” and “molecular loop”, new impurities were detected from first generation dendrimer sample. Pulsed laser deposition was used to obtain thin films of PMMA and PS, doped with fluorescent probes (140). ESI-MS/MS and MS/MS/MS experiments were performed to confirm the presence and the structure of the probes in the polymeric targets.

As a link between Fragmentation Techniques and the following chapter, Polymer Degradation, the paper of Osaka et al. should be mentioned (141). The authors used ESI-TOF MS and MS/MS and MALDI-TOF PSD fragmentation analysis for the characterization of solvolysis products of linear and cyclic poly(lactic acid)s.

POLYMER DEGRADATION

The stability of polymers regarding thermal, photooxidative, and other treatment is of great importance in determining their lifetime and durability in applications. MS is extensively used for the detection of degradation products formed by those processes. The improved degradation of biocompatible polymers for medical purposes or for environmental protection objectives represents another important field of application of polymer MS. Similar to fragmentation analysis, the degradation of polymers could provide additional information on their structure. Aside from MALDI and ESI-TOF MS, various other MS techniques, including thermogravimetry (TG)-MS or GC/MS were used for the detection of lower molecular weight degradation products.

Archodoulaki et al. investigated the influence of different stabilizer on the degradation behavior of poly(oxyethylene) (142). The TG-MS traces of the aged samples showed degradation at an earlier time. The authors concluded that degradation led to the formation of shorter chains, which decompose at lower temperatures, as well as to the formation of chains, which are thermally more stable. Bennet et al. proposed a degradation mechanism of PMMA at 95 °C in an ambient atmosphere involving epoxidation of the terminal vinyl bond and subsequent elimination of formaldehyde and 2-oxopropionic acid methyl ester (143). ESI quadrupole ion trap and ESI Q-TOF MS were applied for this study. MALDI-TOF MS was employed to determine the structures of thermo-oxidized Nylon 6 and Nylon 66 at 180 and 250 °C in air. The results indicated that the degradation of both polymers proceeds through a hydrogen abstraction and subsequent formation of hydroperoxide intermediates yielding oligomers containing aldehydes, amides and methyl terminal groups, and finally carboxylic end groups (144).

The influence of fullerene C_{60} additives on thermal behavior and thermal degradation of aromatic polyesters was investigated by Zuev and Bertini by means of Py-GC/MS revealing different degradation mechanisms at the beginning and at higher temperatures (145). The same technique was used for aliphatic biodegradable poly(propylene succinate) polyesters (146), for substituted polyacetylene (147), and for poly(4-hydroxybutyric acid) (148), for determining the influence of PF_6^- and BF_4^- dopants on the stability of electrochemically prepared poly(3-methylthiophene) (149), for monitoring the thermal degradation behavior of PLA blended with PE (150), and for the determination of the pyrolysis of acrylonitrile–butadiene rubber with different acrylonitrile contents (151).

Direct py-MS of electrochemically synthesized thiophene-functionalized polystyrene and pyrrole (PS/PPy) and their copolymers revealed the growth of polypyrrole onto the pendant thiophene moiety of polystyrene (152). The same technique was also used to study the thermal behavior of copolymers of thiophene with decanedioic acid bis-(2-thiophen-3-yl-ethyl)ester (DATE) and terephthalic acid bis(2-thiophen-3-yl-ethyl)ester (TATE) prepared by potentiostatic polymerization. The evolution of degradation products above 400 °C characteristic of TATE and DATE together with thiophene-based products confirmed copolymer formation (153).

A few papers dealt with the investigation of the flame-retardant behavior of specially equipped polymers. The influence of thermal degradation of covalently bonded phosphorus in poly(methyl methacrylates), of cyclic poly(butylene terephthalate) oligomers (154, 155), of brominated epoxy resins cured with different nitrogen-containing hardeners (156), of tri(acryloyloxyethyl) phosphate blended in different ratios with epoxy acrylate and polyurethane acrylate (157), and of a potentially new UV-curable flame-retardant resin composed of poly(bisphenyl acryloxyethyl phosphate) blended in different ratios with urethane acrylate (158) was determined by py-GC/MS and direct insertion probe pyrolysis MS. The latter method was also applied by Samperi et al. for the characterization of thermal decomposition products of copoly(arylene ether sulfone)s (159), by Uyar et al. and Nur et al. for monitoring thermal degradation processes of poly(carbonate)/PMMA and PC/PMMA/polyvinylacetate (PVAc) blends (160, 161),

of poly(*p*-phenylene-*graft-ε*-caprolactone) (PPP), poly(phenylene)s (PP) with PCL and PCL/PS copolymers (162, 163).

Fluorinated materials are found at low levels in human serum and in wildlife making exposure pathways and optimal analytical conditions important issues. Thermal treatment of poly(tetrafluoroethylene) fluoropolymer before pressurized solvent extraction with methanol at 150 °C for 24 h significantly enhanced the quantity of perfluorooctanoate removed as determined by LC/MS/MS methods (164).

The influence of nanoparticles on the degradation of polymer was studied by various authors. An approach to suppress the emission of dioxin formed by incineration of PVC with TiO₂-encapsulating polystyrene was presented by Choi et al. (165). The results show that the addition of TiO₂ nanoparticles into these systems reduces the concentration of the dioxin and its precursors in exhaust gases. Furthermore, the results of the studies showed that the addition of nanostructured organometallic macromer trisilanolisobutyl-POSS to PET increases the thermooxidative stability and consequently prevents discoloration of the material. MALDI-TOF MS combined with TLC, DIOS MS, and TOF-SIMS results confirmed that the stabilization is achieved by covalent interaction and branching of the nanostructured additive to PET (166, 167). By means of different methods (among them GC/MS), it was found by Costache et al. that the presence of clay or carbon nanotubes in PMMA [in contrast to other polymers, such as polyamides (PA), etc.] did not change the degradation pathway, since PMMA undergoes thermal degradation by a single process (168). Lee et al. demonstrated that uniformly dispersed Pd nanoparticles retarded the thermal decomposition of PS, PP, and PMMA, whereas the thermal decomposition of PA 6 and PET was accelerated (169). No major changes in the molecular weight distribution of polymers were detected by MALDI-TOF MS, indicating that the metal-loading process did not cause any degradation or cross-linking of the polymer. The introduction of SiO₂ nanoparticles to polyvinyl alcohol (PVA) led to a remarkable change in the degradation mechanism (170). The degradation products were identified among others by FT-infrared (IR)/TGA and Py-GC/MS.

Matsumoto et al. synthesized SiN-based ceramic nanoparticles by cross-linking and pyrolysis of novel silazane block copolymers micelles and applied TG-MS for examination of the pyrolysis process (171). TG-MS was also used for investigating the thermal-oxidative induced degradation behavior of POM, revealing different mechanisms in air and under nitrogen atmosphere (172) as well as for examining the pyrolysis of an amorphous poly(ethylene glycol-*co*-cyclohexane 1,4-dimethanol terephthalate) copolyester (173). Huang and Li employed this method for studying the thermal decomposition of a PEG 8000/NiCl₂ mixture, before the thermal process of in situ synthesis of graphite nanofibers was initiated (174).

By means of GC/MS, the long-term hydrolytic degradation of homogeneous disks of linear PCL, porous scaffolds of linear PCL, and cross-linked PCL networks at 37 °C and pH 7.4 was investigated by Hoglund et al., revealing different degradation profiles and susceptibilities toward hydrolysis depending on the macroscopic and macromolecular biomaterial design (175). In another paper, these authors altered the hydrophilicity of cross-linked PCL by copolymerization with poly(1,5-dioxepan-2-one)

(176). This alteration made degradation profiles and migration of degradation products controllable. A combination of GC/MS and FT-IR was used to show that the IR laser ablation of PET led to the formation of various low molecular weight products and was accompanied by ablative deposition of solid materials composed of soluble oligomer and insoluble polymer (177).

Ultrasonic degradation of synthetic and biopolymers has become increasingly interesting, because no chemicals are used, no purification is necessary, and the process itself is very simple to perform. One of the first mass spectrometric investigations of the ultrasonic degradation PEG and PMMA was established by Kawasaki et al. (178). The use of MALDI-TOF MS offered the opportunity to study structural changes induced by ultrasonic degradation directly.

A combination of MALDI-TOF MS and evolved gas analysis (EGA) GC/MS was used to study the cyclodehydration of polybenzoxazole and poly(benzoxazoleamide) precursors. Cyclodehydration, structure of end groups and structure modifications by decarboxylation and branching were detected by MALDI-TOF MS, whereas EGA/GC/MS indicated mass loss caused by chain rupture and evolution of low molecular weight material, which led to branching (179). The results demonstrate the potential of this combination of methods for examining thermal, chemical, and photodegradation pathways of high molecular weight condensation polymers. Poly(*p*-phenylenevinylene) (PPV) represents another type of highly conjugated polymer. The thermal degradation of PPV films deposited by chemical vapor deposition was investigated by Gedelian et al. (180). These authors proved that degradation proceeded through densification and removal of nonpolymerized or weakly bonded fragments (toluene and xylene) and not by dehydrobromination.

The emission of volatile organic compounds in magnetic tapes based on poly(urethane-ester)s after several decades of natural aging at room temperature was determined by headspace solid-phase microextraction-MS (181). Homologous series of carboxylic acids, furanones, and aldehydes were identified, which are most likely the source of the characteristic smell.

The need to find transparent and photostable polymers for use as pellicles (i.e., membranes to protect photomasks from contamination during the manufacture of integrated circuits) in the 157-nm lithography was the background for investigating the photodegradation of Teflon AF at that wavelength (182). The results, obtained by electron spin resonance, NMR, FT-IR, X-ray photon spectroscopy (XPS), Raman spectroscopy, and GC/MS could have some important implications for the design of suitable polymeric materials.

Polymer-on-metal friction was studied by thermodesorption mass spectrometry (TDMS) (183). Polytetrafluoroethylene (PTFE), PS, and PMMA predominantly degraded by depolymerization. Using TDMS data, it is also possible to distinguish between transferred materials worn via different mechanisms (e.g., involving the transfer of damaged and intact macromolecules) and to measure the rates of wear according to these mechanisms.

Typical application of TOF-SIMS are surface and interface analysis as described in the following chapter; however, it has been more recently also used for studying polymer degradation processes. A series of methyl methacrylate–ethylene glycol dimethacrylate (MMA-*co*-EGDMA) films were characterized by

Wagner et al. using positive and negative ion TOF-SIMS (184). The results proved the hypothesis that the presence of cross-linker can impede degradation by depolymerization during SF⁵⁺ bombardment, which leads to an accumulation of damaged material. Owing to the widespread use of PTFE in nuclear facilities, a study was performed by Fisher et al. to determine the suitability of PTFE as a sealing material in a radiological environment (185). Chemical images and high-resolution TOF-SIMS spectra were collected and analyzed to reveal the effects of α -particle radiation (5.5 MeV ⁴He²⁺ ions) on the chemical structure. Depending on radiation doses, different degradation effects could be observed that were responsible for hardness and elastic modulus decline of the polymer.

POLYMER SURFACE AND INTERFACE

The influence of ¹³C-labeling for SIMS was investigated in depth by Harton et al. (186–189). Changes in interfacial properties as well as thermodynamic interactions in various polymer blends and immiscible polymers were observed. Evidence led to the conclusion that deuterium labeling resulted in changes in the thermodynamic properties of the system (e.g., segregation effects). Furthermore, results confirm that ¹³C-labeling can be used for quantitative analysis of molecular movement in heterogeneous organic systems containing matrix-enhancing heteroatoms such as nitrogen. The extension of this method to more complicated biological systems, layers, and heterogeneous interfaces, as well as two- and three-dimensional profiling and imaging using SIMS, can be envisioned. The interpretation of TOF-SIMS spectra and images of selectively ion-etched PMMA films were simplified using cautious application of multivariate analysis (190).

The effect of different end groups on surface and interfacial segregation in PS–PMMA blend thin films was studied using SIMS by Kailas and Bertrand (191). The results gave evidence for a reactive compatibilization of both polymers. Although phase separation phenomena in PS–PMMA systems have been extensively investigated, the early stages of this process had not been studied. To resolve this problem, thin polymer films of a deuterated PS/PMMA blend, mixed with various amount of diblock copolymers PS–PMMA were prepared from suitably sized nanoparticles. Through annealing, the early stages of phase evolution were initiated. By means of SIMS and AFM, a schematic model of structure evolution in thin polymer films prepared from miniemulsions was presented by Raczkowska et al. (192). This work demonstrated that TOF-SIMS, similarly to XPS, can provide quantitative results. In order to assess the composition of PLA/PMMA blends, a comparative study of XPS and TOF-SIMS was performed by Cossement et al. (193). Both methods coincidentally show that there is no segregation of one of the two polymers onto the surface. Roerding et al. studied the topographically induced ordering of amorphous poly(isoprene-*block*-ferrocenylsilane) (PI-*b*-PFS) block copolymer domains (194). SIMS was used for compositional analysis and depth profiling as well. TOF-SIMS and contact angle measurements were used to study coverage and protection of glass surfaces treated with various hydrophobizing microemulsions containing, for example, polyisobutylene as a hydrophobe emulsified by dimethyl dicoco ammonium chloride (i.e., mimicking commercial car wash practices) (195). Contact angle studies indicated that, for drying of surfaces (beading of water), a partial coverage by a hydrophobe is sufficient; however,

MS showed that, if the surfaces are not fully saturated with hydrophobes, the unprotected areas remain vulnerable to environmental damage.

TOF-SIMS using buckminsterfullerene (C₆₀) as the primary ion beam was applied for depth profiling of the outermost layers of poly(vinylidene difluoride)-based coil coatings and additive segregation in those coatings (196, 197). Evidence for the formation of three layers with different chemical composition were found. A similar source was used for the investigation of PMMA, Teflon AF1600, and poly(3-hexylthiophene) films (198). The results showed that the use of C₆₀ ions in SIMS may enhance analysis of polymer films by increasing film conductivity and thereby reducing charging effects. This was also reported by Braun et al. for depth profiling of a taxol-loaded poly(styrene-*b*-isobutylene-*b*-styrene) triblock copolymer using Ga and C₆₀ ions (199). Other cluster ions (Au⁺) were used to analyze a new type of self-assembled fluorocarbon-grafted PET monolayer (200). This led to an enhanced sputter efficiency combined with in a larger information depth.

Other SIMS applications were reported by Mahoney et al., e.g., the temperature-controlled depth profiling of PMMA, PS, and PLA, as well as of polymers used in drug-eluting stents, like poly(ethylene-*co*-vinyl acetate), PLGA, and various poly(urethanes) (201–203). Best profiles were obtained at –75 °C. These effects were associated primarily with changes in physical properties at low temperatures, leading to decreased sputter-induced topography formation. As a direct method, SIMS was used by Jeremic et al. to detect the penetration of PEG into wood, showing that even higher molecular mass PEGs (20 000 Da) were capable of penetrating cell walls (204).

In order to detect photopolymerization-induced phase separation from a homogeneous blend of acrylate monomers and liquid crystals, multivariate statistical analysis was used to interpret static-SIMS spectra (205). The reactive blending of amine end-functional polystyrene (dPS-NH₂) and anhydride end-functional poly(2-vinylpyridine) (P2VP-ah) during extrusion was investigated by dynamic SIMS (206). The interfacial excess (*z*^{*}) of the formed block copolymer, reaction rate constants, and activation enthalpy could be determined. Dynamic SIMS was also used to obtain diffusion coefficients of self-diffusion of PS–PE–PS triblock and pentablock (PS–PE–PS–PE–PS) copolymers with a cylindrical domain structure (E cylinders) and its dependency on the chain architecture of copolymers (207).

Well-ordered monolayers of PDMS with molecular masses of >1000 Da and narrow polydispersity were produced by anionic polymerization and investigated by SIMS (208). Depending on the ternary structure (random coil, helically coiled, or hairpin), differences in fragment intensities were observed. Similar results for different tertiary structures of PDMS-2400, formed in Langmuir–Blodgett films, were reported by Piwowar and Gardella (209).

Polymer-based coatings are widely used to protect surfaces, to modify surfaces for further modifications, and to avoid a segregation of phases. The principle of plasma polymerization and deposition of allylamine films was studied by “in situ” TOF-SIMS before exposure to air by Oran et al. (210). The results indicated a partially transformation of the allylamine monomer’s primary amino groups into other nitrogen functionalities. The same

principle was applied for acrylic acid (AA) monomers. The resulting polymer films were used for surface modification of TiO₂ nanoparticles (211). By means of SIMS, it was shown that AA films contain low molecular weight oligomeric components. Additional GC/MS data showed that most of the oligomers had molecular weights not higher than three monomer units. The influence of 3-aminopropyltriethoxysilane on the adhesion of a PA 11 powder coating was investigated by Guicheney et al. (212). The powder coating was modified by direct addition of the liquid aminosilane into the powder stock, which led to a significant enhancement of the coating durability. Aliphatic polyesters like PLA, poly(glycolic acid), and their copolymer (PLGA) are an important class of biodegradable polymers for bone repair (213). To buffer in vivo degradation products, bioceramics such as hydroxyapatite (HA) are blended with these polyesters. To improve the binding strength of the inorganic nano-HA and degradable polymer matrix, a nanothickness degradable polymer film on the surfaces of nano-HA particles was created by plasma polymerization and investigated by SIMS. The modification of PMMA by water vapor–plasma-based surface activation using trichlorosilane was studied by Long and co-workers (214). The results indicated that these layers are uniform and stable under ambient conditions without evidence of surface deterioration. A combination of both Py-GC and TOF-SIMS was applied in surface characterization on spherical PMMA-coated iron microparticles used in the powder metallurgy (215). The results showed that the thin polymer layer did not uniformly cover the surface. The exposure of cross-linked PDMS to UV/ozone was used by Song et al. to reduce surface hydrophobicity and control of the surface wettability (216). The average chemical composition of the surface, depending on the treatment time, was quantitatively investigated by SIMS. The results showed that silanol functional groups were the most probable ionizable groups on the surface. A simple method of surface modification for controlling interfacial penetration of polyimide/epoxy interfaces was described by Gurumurthy et al. (217). Depth profiling and analysis of fracture surfaces using SIMS showed that converting a thin surface of polyimide back to its precursor resulted in an increasing strength of the interface by creating a broader interpenetrating region. A method to minimize the transfer of silicone from PDMS stamps during microcontact printing was presented by Hale et al. (218). The analysis of the stamped surfaces was performed by TOF-SIMS. It was found that curing the PDMS at elevated temperatures minimized the amount of silicone transferred.

In situ polymerization allows efficient coating of fibers, textiles, and noble metals. The investigation of poly(2-methoxyaniline) growth on gold by ESI-MS revealed the exclusive formation of the linear trimer in bulk of the reaction mixture, although other species were also expected (219). In contrast to the polymerization on metals, the opposite principle (metallization of polymers) was applied by DeMondt et al. for depositing thin Au or Ag layers on nonconducting samples (220). This process prior to analysis improves the secondary ion yields of organic analytes.

Changes in the surface chemical composition of a copolymer consisting of poly(bisphenol A-co-octane) and 4,40-(hexafluoroisopropylidene)diphenol (6FBA) were measured by Cheung et al. using TOF-SIMS (221). In the amorphous state, the surface of the copolymer is enriched with the low surface energy 6FBA units,

but a migration of these units away from the surface can be observed as the copolymer crystallizes. Novel self-organized structures of polymer crystals containing micrometer-sized concentric rings (or bands) were observed in poly(bisphenol A hexane ether) (BA-C6) thin films (222). Molecular fractionation as a direct consequence of the crystallization process led to segregation of molecules. End group and molecular weight distribution in those structures were successfully investigated by SIMS. Spin-coated blends of poly(3-butylthiophene-2,5-diyl) and PS (1:1 w/w) were exposed to solvent vapors and moisture (223). Changes in film morphologies were examined by mapping and depth profiling modes of dynamic SIMS. The results might lead to improved morphological control of technologically important conjugated polymer blends.

The effect of the substrate on the vertical phase separation in spin-coated thin films of poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-5,5–40,70-di-2-thienyl-20,10,30-benzothiadiazole] (APFO-3) blended with [6,6]-phenyl-C61-butyric acid methyl ester was investigated by Bjorstrom et al. (224). Because of specific interactions between the polymer (APFO-3) and the gold substrate surface, the change from silicon to gold also changed the composition profile near the substrate interface. However, the composition profile in the area away from the substrate interface, as well as the enrichment of the free surface with APFO-3, remained unaffected. Two blends of PVP and partly brominated polystyrene (1:1 and 5:3 w/w) were spin-cast onto two chemical patterns of microcontact printed stripes of hexadecanethiol self-assembled monolayers on gold (225). A selective adsorption of PVP on the hydrophilic gold regions and interactions between the polymer phases were found.

CONCLUSION

Numerous applications in which MS is used in the analysis of synthetic polymers and dendrimers, such as in the study of polymerization and degradation mechanisms, identification of additives, and polymer structure characterization, demonstrate the value of this methodology in real world problems. The large number of new technique and method developments in polymer analysis using a mass spectrometric approach demonstrates that there is still room for improvements.

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