Evaluation of the Mode of Termination for a Thermally Initiated Free-Radical Polymerization via Matrix-Assisted Laser Desorption Ionization Time-of-Flight Mass Spectrometry

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Received October 7, 1996; Revised Manuscript Received January 16, 1997[⊗]

ABSTRACT: Styrene and methyl methacrylate have been polymerized at 90 °C with azobis(isobutyronitrile) (AIBN) as a thermal initiator. The molecular weight distributions were analyzed using matrix-assisted laser desorption ionization (MALDI) mass spectrometry and size exclusion chromatography (SEC). By synthesizing polymer of low molecular weight ($M_p = 1000$), we were able to achieve excellent agreement between molecular weight data from MALDI and SEC for the same polymer. Evaluation of the termination mode in free-radical polymerization was performed by integrating the peaks on the mass spectra which corresponded with either one or two initiator fragments per polymer chain. Evidence for some primary radical termination was noted at high initiator concentrations. An additional peak in the spectra for polystyrene was ascribed to the copolymerization of styrene with a single methacrylonitrile unit originating from the initiation process with AIBN. Two other anomalous peaks were noted in the polystyrene mass spectrum; the first relates to chain scission under MALDI conditions and the second to a Diels−Alder rearrangement thermal initiation product. The ratios of the termination modes (disproportionation to recombination, k_{td}/k_{tc}) were evaluated for methyl methacrylate and styrene as 4.37 ± 1.1 and 0.057 ± 0.032, respectively, at 90 °C. These values are in excellent agreement with data reported previously in the literature. Potential errors arising from the use of MALDI for quantitative chain end analyses are discussed.

Introduction

Several experimental approaches have been taken to determine the mode of chain termination in free-radical polymerization. These have been reviewed by Moad and Solomon.[1,2] It is widely accepted that termination can occur via either disproportionation or combination as shown in Figure 1. In the case of termination by disproportionation a chain is generated with one initiator fragment, whereas in the case of combination, a chain with two initiator fragments results. Unfortunately, identification and quantification of chain ends are not simple as they contribute only small signals (relative to the rest of the polymer chain) in spectroscopic analysis. This can be overcome to some extent by isotopic labeling of the initiator end groups or by using initiator fragments containing fluorine[3] or phosphorus as NMR-sensitive molecules. Other complications in the analysis include isolating the long-chain termination process from other chain-stopping mechanisms such as chain transfer and primary radical termination.

Because of these experimental difficulties, there remains considerable uncertainty in existing termination mode measurements and there is wide variation in results for common monomers such as styrene (STY) and methyl methacrylate (MMA) as shown in Table 1.[3−24] Solomon and Moad[1,2] conclude that despite the sparsity of reliable data the following generalizations can be made: "(A) Termination of polymerizations involving vinyl monomers occurs predominantly by combination; (B) termination of polymerizations of α-methylvinyl monomers involves a measurable amount of disproportionation." Solomon and Moad[1] point out that methacrylonitrile (MAN) may be an exception to this general statement.

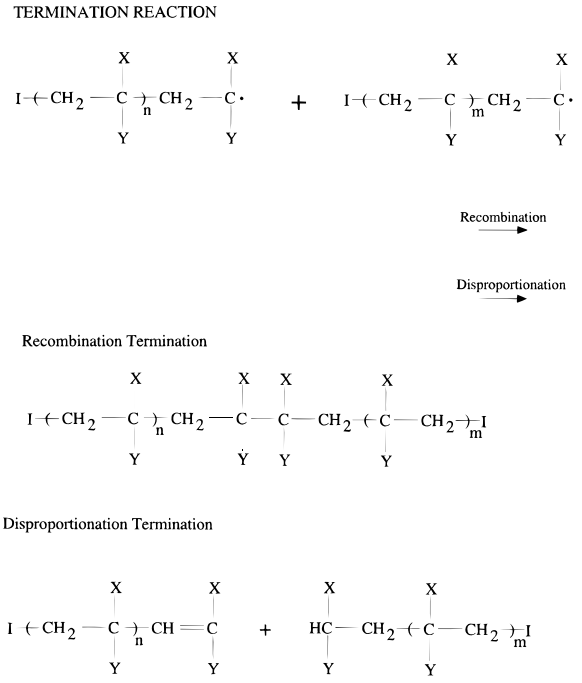

Figure 1. Schematic of the possible termination reactions of a free-radical polymerization.

The evaluation of the fraction of radicals undergoing disproportionation, % *d*, has been defined by Bevington[6] and is calculated via eq 1,

$$\% \, d = \frac{(2 - n)}{n} \tag{1}$$

where *n* is the number of end groups per molecule. The

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⊗ Abstract published in *Advance ACS Abstracts,* March 15, 1997.

S0024-9297(96)01488-X CCC: $14.00

Table 1. Selection of Previous Investigations of Termination Mode for Thermal Homopolymerization of MMA and STY to Low Conversion at Temperatures Greater Than 25 °C

year	M	temp (°C)	solvent	k_{td}/k_{tc}	method	ref
1951	STY	60		pc	MWD	4
1952	STY	60		pc	^{14}C radiolabeled I	5
	MMA	50		pc		5
1954	STY	60		pc	^{14}C radiolabeled I	6
	MMA	60	benzene	5.75		6
1954	STY	25		pc	^{14}C radiolabeled I	7
	MMA	25		2.27		7
1955	STY	100	dichlorobenzene	pc	post polymerization reaction of initiator derived functional groups	8
	MMA	90	benzene	pd		8
1956	MMA	60	benzene	1.58	^{14}C radiolabeled I	9
1959	STY	60	benzene	1.38	^{14}C radiolabeled I	10
	MMA	60	benzene	pc		10
1959	MMA	80		1.3	^{14}C radiolabeled I	11
1960	STY	50	benzene	pc	^{14}C radiolabeled I	12
1960	STY	60		pc	^{14}C radiolabeled I	13
1964	STY	25		pc	difunctional I	14
1965	STY	80		pc	^{14}C radiolabeled I	15
1969	STY	25	benzene	pc	gelation technique	16
	MMA	25	benzene	1.92		16
1969	MMA	25	benzene	pd	gelation technique	17
1973	MMA	60	benzene	pd	^{14}C radiolabeled I	18
1979	STY	80	benzene	0.081	model compounds	19
1980	MMA	30		1.2	MWD analysis	20
1982	STY	60		0.21	^{13}C NMR + ^{13}C-enriched I	12
1984	STY	100		0.12−0.21	^{13}C NMR + ^{13}C-enriched I	21
1985	MMA	80	chlorobenzene	0.78	model compounds	22
1986	MMA	60	benzene	pd	^{1}H NMR + MMA-d_8	23
1993	STY	96	toluene	pc	perfluorinated-azo I	3
1995	STY	70	methanol	pc	2D-INADEQUATE NMR + ^{13}C enriched initiator	24

[a] pc = predominantly recombination, pd = predominantly disproportionation.

fraction of oligomers that have undergone recombination, % *c*, is found from eq 2,

$$\% c = \frac{2(n-1)}{n} \tag{2}$$

and the percentage of radicals undergoing disproportionation relative to recombination is calculated by eq 3,

$$\frac{k_{td}}{k_{tc}} = \frac{(2-n)}{2(n-1)} \tag{3}$$

where k_{td} and k_{tc} are the bimolecular rate coefficients for termination via disproportionation and recombination, respectively.

MALDI has been applied to qualitative chain end analyses for a number of polymers.[25−28]. Currently it is not known whether ionization efficiency is dependent on the chain ends of macromolecules. However, Belu et al.[29] reported that time-of-flight secondary ion mass spectrometry (TOF-SIMS) provided evidence for quantitative end group analyses for five PSTY samples generated by anionic polymerization and terminated with either methanol or chlorodimethylphenylsilane. In a subsequent paper, Belu et al.[30] compared MALDI and SIMS analyses for perfluoroalkyl-terminated PSTY with a dimethylphenylsilyl-terminated PSTY and noted small differences between the two ionization methods. They ascribed this to possible surface enrichment of the perfluoro species although they could not rule out some effect of chain ends on ionization yield. Belu et al.[30] noted that despite some deviation in quantitative chain end analysis at the low- and high-mass ends of the distribution, quantitative chain end analysis was possible by MALDI-MS.

As the findings of Belu et al.[30] are consistent with quantitative chain end analyses for synthetic polymers, we decided to investigate the possibility of using MALDI to measure the ratio of disproportionation to combination in free-radical polymerization. An earlier communication[31] on MALDI analysis of polymer produced by pulsed-laser polymerization indicated that the resolution obtained from the MALDI Kompact III was sufficient to identify end-group fragments in PMMA.

Experimental Section

Materials. Monomers. Styrene (Aldrich) was washed with aqueous sodium hydroxide, dried over calcium hydride, and distilled under reduced pressure immediately prior to use. Methyl methacrylate (MMA) (ICI) was passed through a column of activated alumina and stored over molecular sieves (4 and 13 Å) under an inert atmosphere in the dark. The thermochemical initiator 2,2′-azobis(isobutyronitrile) (AIBN) was purchased from BDH and used as received.

Solvents. Toluene was refluxed over sodium metal and benzophenone until dry and distilled prior to use. Freshly dried, distilled and stabilized tetrahydrofuran (THF) was used as the SEC eluent.

Polymerizations. Purified monomer, solvent, and initiator were charged to Pyrex glass sample vials (2.5 cm diameter) and deaerated by bubbling with N_2 for 5 min. Isothermal polymerization conditions were maintained at 90 °C in a water bath. Total conversion to polymer in all cases was less than 10%. The polymer was isolated, dried, and dissolved in THF for quantitative SEC and MALDI analyses.

Analysis. Size Exclusion Chromatography (SEC). SEC analyses were performed on a modular system comprising an ICI Instruments LC1110 high-performance liquid chromatography pump, a Rheodyne 7125 injection valve with a 20 μL loop, and a differential refractive index detector (DRI) (ICI instruments LC1240). The eluent was tetrahydrofuran (THF) at a flow rate of 1 mL min^{-1}. The data were collected at 1 point/s and analyzed using Polymer Laboratories Calibre GPC/SEC software. The column set consisted of a PL 5 μm bead size guard column (50 × 7.5 mm) and a PL 3 μm bead size

Mixed-E column (300 × 7.5 mm). The system was calibrated with Polymer Laboratories PMMA standards and PSTY standards up to 30 000 Da, and at the low molecular weight region with MMA dimer, trimer, tetramer, and pentamer prepared by the catalytic chain transfer (CCT) method.[32]

Matrix-Assisted Laser Desorption Ionization Time-of-Flight (MALDI-TOF) Mass Spectrometry. Mass spectrometry was carried out on a Kratos Kompact III MALDI-TOF MS (Kratos, Manchester, UK), incorporating a 337 nm nitrogen laser with a 3 ns pulse duration and an electron multiplier detector. The instrument was operated in the positive ion reflectron mode with an accelerating potential of +20 kV. The mass scale was calibrated using bovine insulin.

For each sample the spectrum was averaged over 175 laser shots. Moderation of the laser power through the laser firing is a critical part of the experiment, and it was found that laser power regulation was best achieved by viewing continuously the "single laser shot" spectrum and moderating the power about the critical threshold energy level. With laser power too low, no mass spectrum will be accumulated, and with too high power, the baseline will severely distort and accumulation of lower MWT's will be favored. The polymer and matrix were prepared on a number of sample slide positions, and several mass spectra for each polymer were accumulated.

MALDI-TOF Sample Preparation. The matrix and cation used for PMMA was 2,5-dihydroxybenzoic acid (Aldrich) and sodium cations, respectively. The optimum PSTY matrix found was a combination of 9-nitroanthracene (Aldrich) and Ag^+ cations (silver trifluoroacetate, Aldrich). Polymer solutions in THF were made up at a concentration of 0.1 mg of polymer per mL. The polymer solutions (0.5 μL) were deposited on the matrix (or mixed with the matrix) and allowed to dry.

Results and Discussion

Comparison of the Evaluated MWD between MALDI-TOF-MS and SEC. Several studies have shown that there is often a discrepancy in the analyses of molecular weight averages determined by SEC and MALDI methods; see for example Lloyd et al. and references therein.[33] It is commonly found that MALDI underestimates the high molecular weight tail in broad molecular weight distributions, i.e. where the polydispersity is greater than 1.3. A number of explanations have been tendered, and the problem may be to some extent dependent on instrumentation and/or sample preparation. In this study it was important to identify a molecular weight range where the MALDI response matched the SEC result so that accurate integration of all signals across the mass spectrum could be achieved. This is important for termination mode studies as it may be expected that chains terminating by combination contribute heavily to the higher molecular mass end of the spectrum.

As separation in SEC is achieved according to the size of molecules in solution, the distributions obtained by SEC and MALDI are not directly comparable. Several transformations of the MWD derived from SEC can be made to facilitate a direct comparison, which has been discussed by Lloyd et al.[33]

Broad MWT polymers of PMMA and PSTY were prepared in toluene solutions (40 vol %) using an AIBN concentration of 0.017 mol/L. The molecular weights of these polymers were determined using SEC, yielding peak maxima (M_p), in the number distributions, of 2025 (PMMA) and 1450 Da (PSTY). The transformed chromatograms and their corresponding mass spectra are shown in Figures 2 and 3. The molecular weight data derived from the two analytical methods are shown in Table 2.

From these data it is apparent that MALDI analysis fails to resolve the high molecular weight region of the distributions. This is clearly shown by comparison of the third moment of the molecular weight distribution (M_z), which shows the limitation of MALDI detector response at high molecular masses. It was evident that termination mode studies based on these polymers would lead to erroneous results.

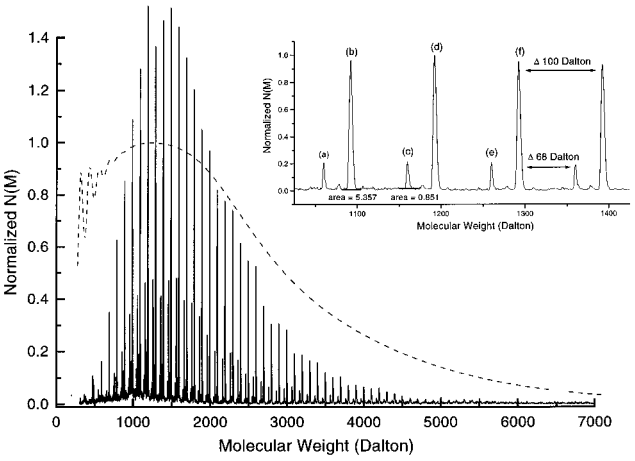

Figure 2. Analysis of PMMA via MALDI-MS with SEC analysis overlay (see Table 2 for MWD averages for both techniques). Inset is an expansion of the mass spectrum showing disproportionation and recombination series of oligomers and integration of a termination pair (see Table 4 for symbols).

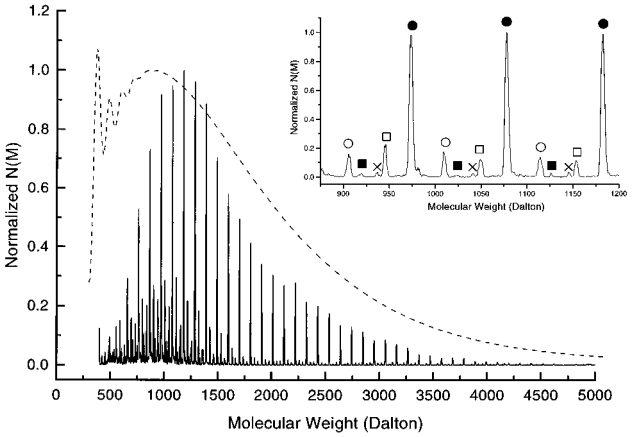

Figure 3. Analysis of PSTY via MALDI-MS with SEC analysis overlay (see Table 2 for MWD averages for both techniques). Inset is an expansion of the mass spectrum showing several oligomer series. See Table 5 for explanation of symbols.

Table 2. Comparison of SEC and MALDI Analysis Techniques for MWD Averages of PMMA and PSTY

sample	analysis technique	M_n	M_w	M_p	M_z	PDI[a]
PMMA	SEC	1365	2314	2025	3569	1.69
	MALDI	1684	1927	1495	2197	1.14
PSTY	SEC	1109	1691	1450	2555	1.52
	MALDI	1309	1560	1191	1834	1.19

[a] PDI is polydispersity index.

To overcome the limitations of MALDI analysis, a second pair of polymer samples was prepared in toluene solution (5 vol %) using an AIBN concentration of 0.068 mol/L. Strong agreement was observed in the molecular weight distributions obtained from SEC and MALDI, as shown in Figure 4, which shows the transformed SEC analysis for PMMA overlaid on the MALDI mass spectrum of the same polymer. A similar result was obtained for PSTY, as shown in Figure 5. The molecular weight moments calculated from the MALDI and SEC data are given in Table 3.

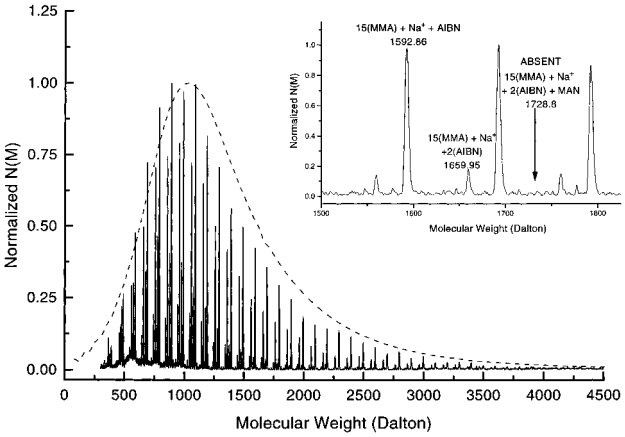

Figure 4. Analysis of PMMA via MALDI-MS with SEC analysis overlay (see Table 3 for MWD averages for both techniques). Inset is an expansion of the mass spectrum indicating the absence of copolymerized methacrylonitrile.

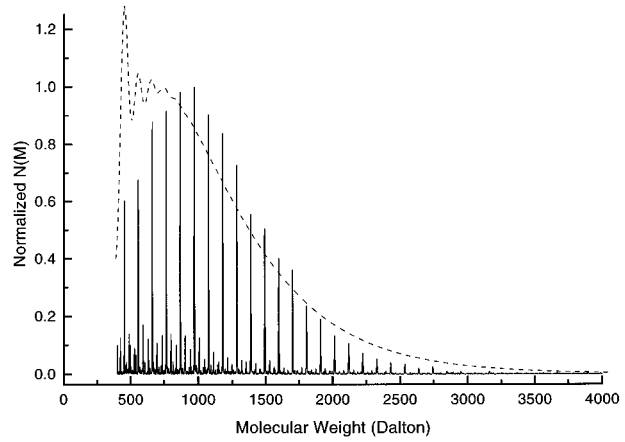

Figure 5. Analysis of PSTY via MALDI-MS with SEC analysis overlay (see Table 3 for MWD averages for both techniques).

Table 3. Comparison of SEC and MALDI Analysis Techniques for MWD Averages of PMMA and PSTY

sample	analysis technique	M_n	M_w	M_p	M_z	PDI[a]
PMMA	SEC	878	1341	1167	1991	1.51
	MALDI	1211	1451	890	1725	1.19
PSTY	SEC	886	1121	950	1456	1.26
	MALDI	1005	1173	970	1349	1.16

[a] PDI is polydispersity index.

Thus by restricting the polymer molecular weight to the oligomer region, it is possible to match SEC and MALDI data; i.e. the difference in M_p between the two analytical methods is ±1 monomer unit (based on the number distributions). More importantly, the first three molecular weight moments (M_n, M_w, and M_z) also concur. There are slight differences among the M_n values, which can be explained by the loss of low oligomeric material under the high-vacuum conditions of MALDI analysis.

Evaluation of the Termination Mode from a MALDI-TOF Mass Spectrum. The scheme for termination in free-radical polymerization is shown in Figure 1. If termination is the sole chain-stopping mechanism, then polymer chains are formed with three possible different chain end structures, viz: (a) a primary radical fragment on both ends of the chain (recombination), (b) a primary radical fragment on one end and a saturated end group on the other (disproportionation), or (c) a primary radical fragment on one end and an unsaturated end group on the other (disproportionation). It should be noted that the MALDI instrument used throughout this work has a resolution of 3−4 Da, and thus cannot discriminate between chain ends labeled as (b) and (c) above. When considering oligomers arising from a disproportionation mechanism, peak areas must be divided by 2 to account for the fact that a single disproportionation event produces two dead chains.

Table 4. Comparison of Experimental versus Theoretical Mass for PMMA[a]

peak	origin	theor mass (Da)	exptl mass (Da)
a	Na^+ + 1(AIBN) + 9(MMA)	1059.561	1060.257
b	Na^+ + 2(AIBN) + 9(MMA)	1091.563	1092.555
c	Na^+ + 1(AIBN) + 10(MMA)	1159.613	1160.164
d	Na^+ + 2(AIBN) + 10(MMA)	1191.616	1192.620
e	Na^+ + 1(AIBN) + 11(MMA)	1259.666	1260.231
f	Na^+ + 2(AIBN) + 11(MMA)	1291.668	1292.676

[a] MMA = methyl methacrylate.

Unless exceptional conditions prevail, then other chain-stopping processes, such as transfer, need to be considered when interpreting chain end data. Complications can arise in assigning chain end structures to termination mechanisms. If, for example, transfer occurs by hydrogen abstraction (or addition), the resulting chain will be identical to an oligomer produced by termination via disproportionation, leading to an overestimate of disproportionation. On the other hand, if termination by combination with primary radical occurs, this could lead to an overestimation of combination.

Accurate quantification of the termination mode requires total integration of all the peaks across the mass spectrum. MALDI resolves two separate MWDs, one arising from disproportionation and one arising from combination, as seen in the expansion of Figure 2. The inset in Figure 2 is labeled to show the two series of peaks, a, c, and e with one initiator fragment and b and d with two initiator fragments. It should be noted that although the polymers were prepared at high dilution in toluene, no end groups derived from transfer to toluene are evident. Also note the small peak between a and b, c and d, etc. This corresponds to the lithium adduct of the disproportionation series of peaks and is found as an impurity in the cation source used in the analysis.

Termination Mode in MMA Homopolymerization. The individual peaks in the expansion of Figure 2 have been fully assigned and collated in Table 4. The mass of the polymer chains comprises the monomeric MMA units, one or two initiator fragments, and a sodium cation originating from the MALDI ionization process.

To investigate the possibility of transfer to initiator and/or primary radical termination, the effect of initiator concentration on chain end analysis was studied. Three different PMMA polymers were prepared using different initiator concentrations. The data are plotted in Figure 6 showing at each degree of polymerization the ratio of 1 to 2 initiator fragments per chain length for the three polymers.

These data strongly suggest that at the high initiator concentration there is a significant contribution from primary radical termination as a chain-stopping mechanism. However, at the two lower initiator concentrations the results are congruent, indicating that the chain end structure is independent of initiator concentration. The value for ρ ($= k_{td}/k_{tc}$) (which was obtained by summing all the disproportionation peak areas and dividing by the sum of all the recombination peak areas)

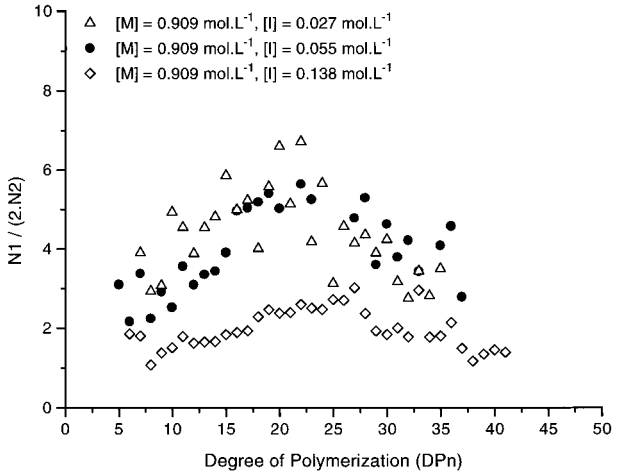

Figure 6. Termination mode versus degree of polymerization for three PMMA samples prepared with different initiator concentrations.

Table 5. Comparison of Experimental versus Theoretical Mass for PSTY[a]

peak	origin	theor mass (Da)	exptl mass (Da)
○	$Ag^+ + 1$(AIBN) + x(STY)	1007.455	1009.200
■	Ag^+ + methylene + x(STY)	1022.455	1023.554
×	Ag^+ + MAN + $(x-1)$(STY)	1039.492	1040.717
□	Ag^+ + H−$(x-1)$(STY)−H (Diels−Alder initiation)	1047.255	1049.357
●	$Ag^+ + 2$(AIBN) + x(STY)	1075.505	1077.973

[a] STY = styrene and x = number of styrene units in oligomer (example in Table 5 is for $x = 8$).

for the lower initiator concentration run is 4.37 ± 1.1 (at 90 °C). This value is consistent with data reported in Table 1.

Termination Mode in STY Homopolymerization. A MALDI analysis for PSTY is shown in the expansion of Figure 3. The mass of the polymer chains comprises the monomeric STY units, one or two initiator fragments, and a silver cation originating from the MALDI ionization process. The peak assignments corresponding with the labeled peaks in the inset Figure 3 are given in Table 5.

It is apparent that there are additional peaks in the PSTY mass spectrum, when compared with the PMMA spectrum. The PSTY spectrum shows the expected one and two initiator fragment oligomers, together with significant signals for three additional structures.

The peak labeled (×) corresponds to a third initiator fragment which can be ascribed to a single unit of copolymerized methacrylonitrile (MAN)[21,34] arising from the initiation process. This is generated as a disproportionation product from the primary AIBN radicals,[35] as shown in Figure 7. The absence of this peak in the PMMA spectrum (see expansion of Figure 4) can easily be explained. If a methyl methacrylate chain initiated by a primary radical subsequently copolymerizes with a MAN unit and terminates by disproportionation, then the dead chain will contain two initiator fragments and will be subsumed within the peak arising from termination by combination. Therefore it is likely that the value for ρ of 4.37 for PMMA is a slight underestimate.

The series denoted by the filled square "■" can be ascribed to MALDI-induced PSTY scission. It has been shown by Craig et al.[36] that PSTY will fragment in a MALDI analysis by leaving a vinyl group on the chain end, as shown in Figure 8. The PSTY chains tend to rupture near the chain ends, thus causing some error

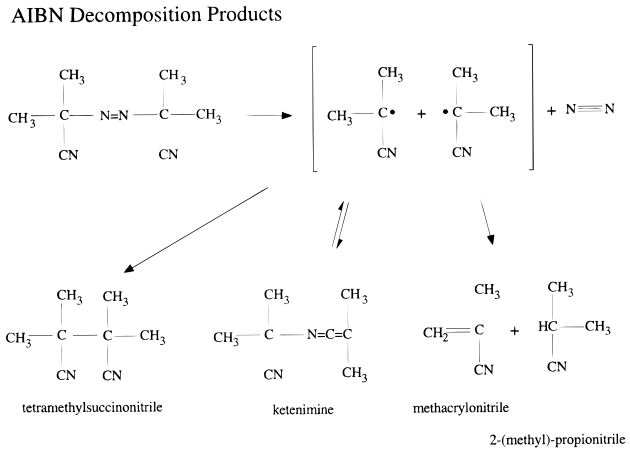

Figure 7. AIBN decomposition products.

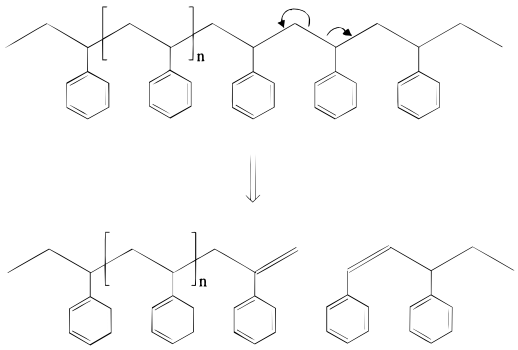

Figure 8. PSTY fragmentation mechanism under MALDI analysis conditions.

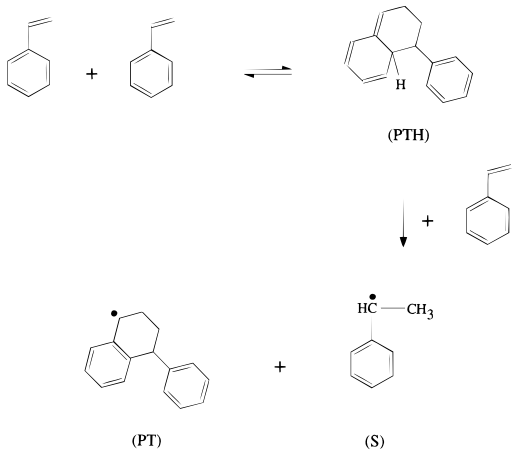

Figure 9. Diels−Alder dimerization reaction of styrene.

in the molecular weight determination of PSTY by MALDI.

The series of peaks labeled "□" arise from the Diels−Alder type thermal initiation of STY at 90 °C. The self-initiation mechanism for styrene polymerization has been firmly established.[37,38] The first step is formation of the Diels−Alder dimer 1-phenyl-1,2,3,4-tetrahydronaphthalene (PTH), followed by transfer of a hydrogen atom in a molecule-induced homolysis to produce a styryl (S) and a 1-phenyltetralyl (PT) radical, as shown in Figure 9. The styryl radical can then initiate polymerization as usual. If termination is by combination with a second chain containing an initiator fragment, the resulting oligomer will contain only one initiator fragment, whereas if termination is via disproportionation (or transfer), the resulting oligomer will have a H−STY_x−H arrangement. The series of oligo-

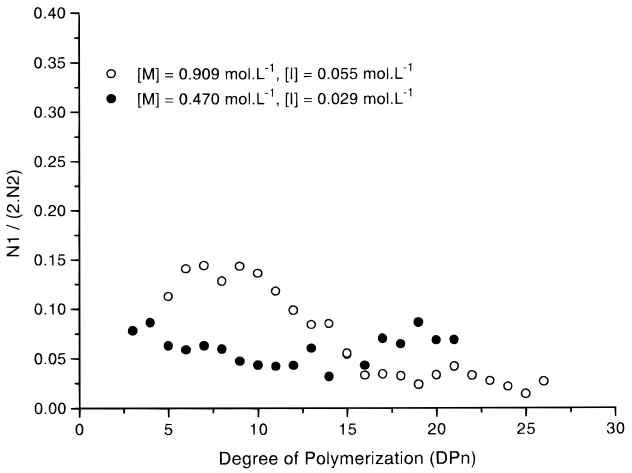

Figure 10. Termination mode versus degree of polymerization for two PSTY samples prepared with different initiator concentrations.

mers at 942, 1046, and 1150 Da (corresponding to x = 8, 9, and 10, plus silver adduct) correspond to the Diels–Alder initiated oligomers denoted in the inset of Figure 3 by "□".

As the mass spectrum of PSTY has identified a chain-stopping process other than bimolecular termination, as well as copolymerized MAN and fragmented chains, results for the termination mode will be slightly in error. Despite these problems, we have calculated a k_{td}/k_{tc} ratio of 0.057 ± 0.032 for PSTY based on Figure 10, which shows the ratio of 1 to 2 initiator fragments per chain length at each degree of polymerization originating from different starting initiator concentrations. In this instance, both distributions yield the same value for ρ (to within experimental error) for the termination ratio.

Conclusions

The data we report in this paper for the termination mode at 90 °C are consistent with the numbers reported previously in the literature (see Table 1). MALDI is a fast and simple technique for qualitative chain end analyses; however, there are still questions related to the precision and accuracy of quantitative data derived from mass spectrometric measurements which this study does not address. The specific issues relating to ionization efficiency were discussed in the Introduction. The other area of concern is that the entire mass spectrum should be resolved in order to accurately assign termination processes. We believe that it is possible to do this by carefully designing the experimental procedure. MALDI has some advantages over alternative methods for calculating the termination mode as it is model-independent and it can identify competing (interfering) mechanisms (such as copolymerization of MAN), which can then be taken into account. It is evident that with the rapid developments in MALDI analysis, some of the problems/ambiguities discussed in this paper will be resolved; viz., the availability of Fourier transform methods can yield isotopic resolution and the use of delayed extraction will enhance both resolution and the extent of molecular range which can be studied.

Acknowledgment. We acknowledge the support of the British Council in awarding a bursary to M.D.Z. and Kratos for access to the Kompact MALDI-TOF III mass spectrometer in the United Kingdom. Also, we wish to thank Prof. P. J. Derrick for experimental facilities and Mr. Dax Kukulj for data reanalysis.

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MA961488K