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Fast Atom Bombardment Mass Spectrometry Identification of Oligomers Contained in Polysulfides and Their Complexes with Heavy Metals

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ABSTRACT: Fast atom bombardment mass spectrometry (FABMS) was used to identify cyclic oligomers formed in polycondensation reactions leading to aromatic, aliphatic, and aliphatic–aromatic polysulfides. Compounds with a molecular weight up to about 1500 daltons present in the crude polymers were detected without separation. Furthermore, the FABMS technique showed the formation of complexes between the cyclic sulfides contained in the extracted fraction from crude polymers and salts of heavy metals (Ag, Hg, and Cu). In some cases a selectivity of the $AgNO_3$ toward cyclic sulfides of particular size was also observed.

Introduction

Recently, we reported the synthesis, separation, and characterization of a series of aromatic,[1] aliphatic,[2] and aliphatic–aromatic[3] cyclic sulfides formed in the polycondensation reaction of dibromo compounds and dithiols.

Gel permeation chromatography (GPC) and electron impact/chemical ionization (EI/CI) mass spectrometry (MS) were used to detect the cyclic oligomers, and a rigorous demonstration of the correspondence of identity among the peaks obtained by these techniques was reported.[1-3]

EI/CI MS is suitable for the detection of low molecular weight compounds contained in the crude polymer samples since they are volatile under the high vacuum of the mass spectrometer at the relatively mild temperatures at which polymers remain undecomposed and therefore undetected.[4,5]

The MS method is based on the direct introduction of the crude sample into the ion source of a mass spectrometer by the direct insertion probe for solid materials. The probe temperature is then gradually increased on a linear program (generally 10 °C/min), and the low molecular weight oligomers, which evaporate undecomposed in the high vacuum of the mass spectrometer, are directly identified by repetitive mass scans.[4] The oligomers are usually detected as separated peaks in the total ion current (TIC) curves before the evolution of the thermal decomposition products originating from the polymer pyrolysis.[4,5]

However, some of the higher molecular weight cyclic sulfides previously investigated by EI/CI MS were too involatile, so that they could not be seen by the MS distillation method.[1-3] As matter of fact, GPC traces always showed more peaks than TIC curves.[1-3]

Consequently, we have resorted to fast atom bombardment mass spectrometry (FABMS)[6-8] in an attempt to detect and identify, without isolation, the cyclic sulfides formed in the synthesis of some polysulfides.

In the present case we have observed that the FABMS method provides information on all the cyclic oligomers detected by GPC, allowing identification of compounds with a molecular weight up to 1500 daltons (i.e., nearly at the cutoff of our magnet). When the polymers investigated were accurately purified from low molecular weight compounds, no significant peaks were observed in their FAB mass spectra. Instead, the FAB spectra of the mixtures extracted from the polymers were found to be very similar to those obtained for the crude polymers.[9]

Furthermore, we have found that the FABMS technique also allows detection of the complexes among the cyclic sulfides with heavy metals (Ag, Hg, and Cu).

The molecular ions of pure oligomers and those of the corresponding doped sulfides often appear in the spectra with widely differing intensities, therefore providing an analytical tool to detect specific sulfides in a mixture and, conversely, to investigate the selectivity of metals toward macrocyclic sulfides of different size.

Experimental Section

Polymer Synthesis and Oligomer Extraction. Poly(*m*-phenylene sulfide), polymer I (Table I), was prepared by starting from *m*-dibromobenzene and disodium sulfide according to the procedure of Edmonds and Hill.[10]

Poly(hexamethylene sulfide) and poly(trimethylene sulfide), polymers II and III (Table I), were synthesized from the corresponding dithiols and dibromides according to the method de-

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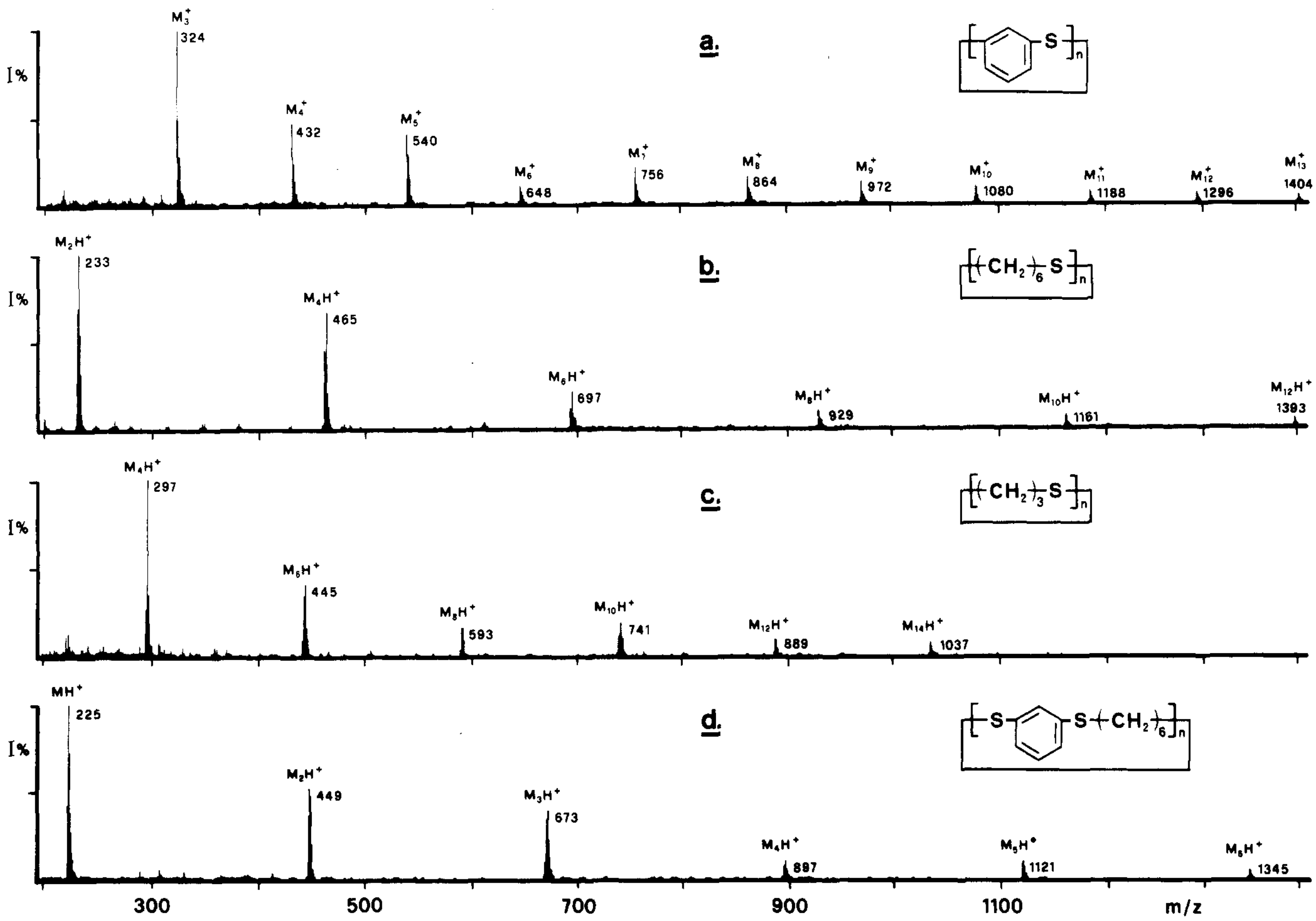
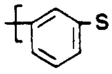
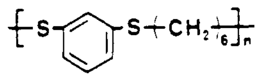


Figure 1. FAB mass spectra of the mixtures of cyclic sulfides extracted from the crude polymers: (a) poly(*m*-phenylene sulfide) (polymer I); (b) poly(hexamethylene sulfide) (polymer II); (c) poly(trimethylene sulfide) (polymer III); (d) poly(*m*-phenylene hexamethylene sulfide) (polymer IV).

Table I
Cyclic Oligomers Detected in the Synthesis of Polymers I-IV

polymer		method of detection	no. of repeating units in the cyclic sulfides 1	2	3	4	5	6	7	8	9	10	11	12	13	14
I		GPC			Y	Y	Y	Y	Y							
		FABMS			Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	
II	$-[(CH_2)_6S]_n-$	GPC		Y		Y		Y		Y		Y		Y		
		FABMS		Y		Y		Y		Y		Y		Y		
III	$-[(CH_2)_3S]_n-$	GPC		Y		Y		Y		Y		Y		Y		Y
		FABMS		Y		Y		Y		Y		Y		Y		Y
IV		GPC	Y	Y	Y	Y	Y	Y								
		FABMS	Y	Y	Y	Y	Y	Y								

scribed by Marvel and Kotch.[11]

Poly(*m*-phenylene hexamethylene sulfide), polymer IV (Table I), was obtained from 1,3-benzenedithiol and 1,6-dibromohexane as reported elsewhere.[3]

The oligomer extractions were performed by treating the crude polymer with *N*-methyl-2-pyrrolidone (NMP) (polymer I) or benzene (polymers II-IV) with stirring for 2 h at 20 °C. After filtration, the NMP- or benzene-soluble fractions were dried under vacuum.[1-3]

FAB Mass Spectrometry. FABMS analyses were performed on a double-focusing Kratos MS 50 S mass spectrometer, equipped with a standard FAB source.

Mass spectra were recorded by using a DS 55 data system. Argon was used as bombarding gas, with an energy of 8 kV. Mass resolution was about 2000. A mixture of CsI/RbI (50:50 by weight) was used as calibrant (calibration range 28-1693). Spectra were obtained by using 3-nitrobenzyl alcohol (3-NBA) as a matrix.

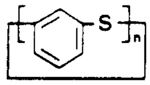
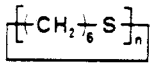
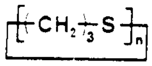
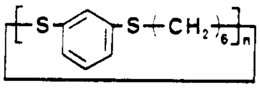
For the salt-doping experiments 1-2 mg of $AgNO_3$, $Hg(CH_3COO)_2$ or CuCl (molar concentration ratios of oligomers/metal salts about 1:10) was added to the mixtures of 3-NBA and the polymers before being applied as a thin layer on the copper target. During the preparation of the doped samples a color change of the mixtures was observed.

Results and Discussion

The positive FAB mass spectra of the mixtures of cyclic sulfides extracted from the crude polymeric samples I-IV (Table I) are reported in Figure 1.

In the mass spectrum of the poly(*m*-phenylene sulfide) (polymer I, Figure 1a), the peaks at m/z 324 + n108 correspond to molecular ions (M^+) of cyclic oligomers $M_3{}^+$-$M_{13}{}^+$ (Table II). FAB mass spectra of polymers II-IV in Figure 1 (parts b-d, respectively) show peaks due to protonated molecular ions (MH^+) of the oligomers present in mixtures (Table II).

Table II
Molecular Ions Detected in FABMS of Polymers I–IV (*m*/*z*)

		no. of repeating units in the cyclic sulfides[a]													
cyclic compd formulas	ion	1	2	3	4	5	6	7	8	9	10	11	12	13	14
	M^+			324	432	540	648	756	864	972	1080	1188	1296	1404	
	MAg^+			431	539	647	755	863	971	1079					
	$MAg_2NO_3^+$			600	708	816	924	1032	1140						
	MH^+		233		465		697		929		1161		1393		
	MAg^+		339		571		803		1035						
	MAg_2^+				677		909								
	$MAg_2NO_3^+$		508		740		972								
	MCu^+		295		527		759		991						
	MCu_2Cl^+		393		625		857								
	MH^+				297		445		593		741		889		1037
	MAg^+				403		551		699		847		995		
	MCu^+				359		507		655		803		951		
	$MHg(CH_3COO)^+$		409		557		705		853		1001				
	MH^+	224	449	673	897	1121	1345								
	MAg^+	331	555	779	1003										
	MAg_2^+		661	885	1109										
	$MAg_2NO_3^+$		724	948	1172										
	MCu^+		511	735	959										

[a] The molecular weight of each complex is referred to the more abundant metal isotope (Ag, 107; Hg, 202; Cu 63).

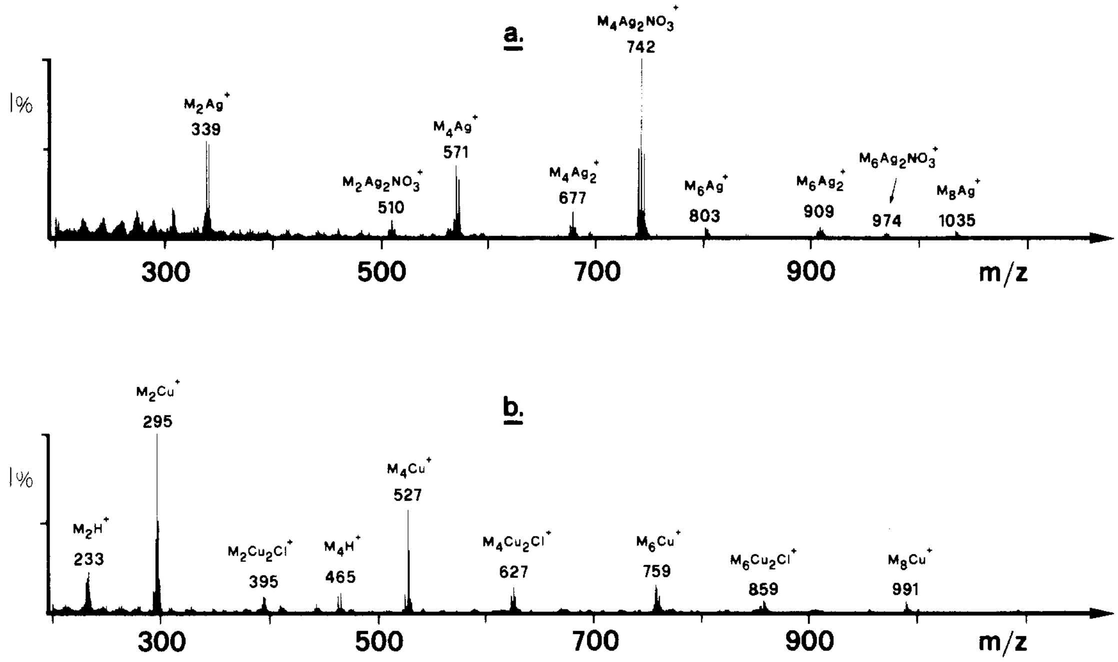


Figure 2. FAB mass spectra of the extracted material from polymer II doped with (a) $AgNO_3$ and (b) CuCl.

In all cases the FAB spectra are constituted exclusively by peaks due to molecular ions (M^+ or MH^+), indicating that these macrocycles are very stable toward the FAB desorption method, without producing fragmentation.

In Figure 2a the FAB mass spectrum of the extracted material from polymer II doped with $AgNO_3$ is reported. If it is compared with the corresponding spectrum of the pure sample (Figure 1b), a series of drastic changes can be noticed, as specified in Table II. In particular, peaks corresponding to protonated molecular ions are absent in the $AgNO_3$-doped spectrum (Figure 2a); they have been replaced by peaks due to macrocycles containing Ag^+, Ag_2^+, or $Ag_2NO_3^+$ ions.

Furthermore, the intensity of the peak at m/z 742 ($M_4Ag_2NO_3^+$) is much higher than that at m/z 510 ($M_2Ag_2NO_3^+$), indicating a selectivity in the formation of complexes between these cyclic sulfides with the Ag salt. In fact, the relative abundance of dimer (M_2H^+) and tetramer (M_4H^+) appear reversed in the FAB mass spectrum of the pure mixture (Figure 1b).

In Figure 2b the FAB mass spectrum of the same material doped with CuCl is reported. Protonated molecular ions at m/z 233 (M_2H^+) and 465 (M_4H^+) (Table II) are still present here, although with reduced abundance, whereas the most intense peaks in the spectrum appear at m/z 295 + n232 corresponding to the M_nCu^+ species. These last peaks maintain the same relative intensity observed in the FAB mass spectrum of the undoped material for the M_nH^+ species, indicating a lack of selectivity of copper salt toward these cyclic sulfides.

Similar results have been obtained for the mixture of cyclic oligomers extracted from polymer IV (Table I). Figure 3 shows the FAB mass spectrum of doped mixture with $AgNO_3$. If it is compared with the spectrum of the pure sample (Figure 1d), an inverse abundance of peaks corresponding to cyclic monomer [(m/z 225 (MH^+), Figure 1d; m/z 331 (MAg^+), Figure 3)] and dimer [(m/z 449 (M_2H^+); m/z 555 (M_2Ag^+)] can be noted, indicating also in this case a selective interaction between the macrocycles and the $AgNO_3$.

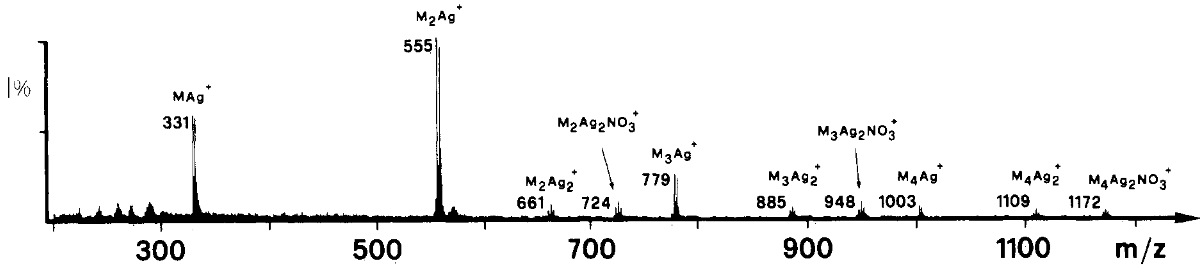


Figure 3. FAB mass spectrum of the extracted material from polymer IV doped with $AgNO_3$.

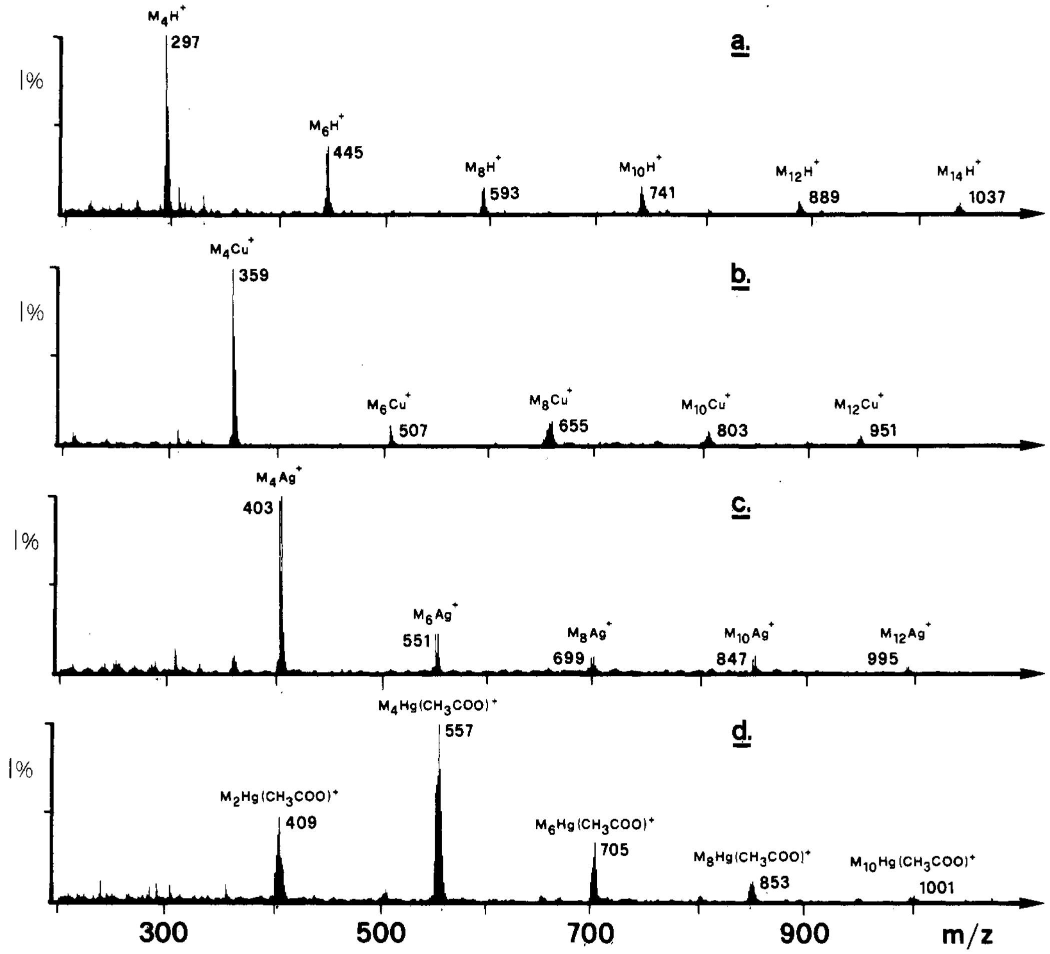


Figure 4. FAB mass spectra of the extracted material from polymer III: (a) pure sample; (b) doped with $AgNO_3$; (c) doped with CuCl; (d) doped with $Hg(CH_3COO)_2$.

In Figure 4 the FAB mass spectra of the mixture of oligomers extracted from polymer III (Table I), pure and doped with different metal salts, are reported. Also in these cases, peaks due to protonated molecular ions (Table II) are absent in the doped spectra. Moreover, $Hg(CH_3COO)_2$ is the only salt capable of retaining, in FAB conditions, the anion in the complexes with these macrocycles (Figure 4d and Table II).

The foregoing data show the ability of the FABMS technique to detect oligomers contained in a mixture, allowing identification of compounds with a molecular weight up to about 1500 daltons (Tables I and II).

In the case of poly(*m*-phenylene sulfide) (polymer I) the FAB mass spectrum (Figure 1a) also shows peaks due to molecular ions of compounds present in trace amounts not resolved in the GPC trace (Table I).

Furthermore, the FABMS method also allows detection of the complexes of cyclic sulfides with heavy metals (Ag, Hg, and Cu).

In the case of polymers II and IV, it has also been ascertained that $AgNO_3$ induces a selective formation of some species between cyclic sulfides of a particular size and the salt.

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Registry No. I (copolymer), 113584-75-1; I (SRU), 32027-35-3; II (copolymer), 71693-88-4; II (SRU), 57514-74-6; III (copolymer), 104035-44-1; III (SRU), 28758-48-7; IV (copolymer), 108250-29-9; IV (SRU), 108250-39-1; Ag, 7440-22-4; Hg, 7439-97-6; Cu, 7440-50-8.

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End Groups in Acrylic Copolymers. 1. Identification of End Groups by Carbon-13 NMR

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ABSTRACT: The end groups of acrylate copolymers prepared by free-radical polymerization have been identified by ^{13}C NMR in a number of different copolymer preparations. In order to increase the relative abundance of end groups and to facilitate spectral assignments, we have used two different procedures to isolate a low M_n copolymer component: size exclusion chromatography and fractional extraction. Integration of quantitative NMR spectra was used to measure the relative concentration of the different classes of end groups.

Introduction

The initial event in the photooxidation of acrylic–melamine coatings in the outdoors is the absorption of sunlight to form free radicals.[1] Since neither the acrylate ester nor the melamine cross-linker components of these coatings absorb sunlight, their photolysis does not contribute directly to photoinitiation. Rather, photoinitiation in unweathered coatings is attributed to the presence of trace chromophoric components: inadvertent impurities, initiator fragments, end groups, and oxidation products introduced either during synthesis or subsequent cure.[1] Such chromophores have not been identified in acrylic–melamine coatings largely due to the chemical complexity of coating formulations. A typical acrylic–melamine automotive enamel may be formulated with 10 or more components, each with its own set of trace chromophores. The task of identifying trace components in such mixtures is, therefore, a formidable one, even for modern spectroscopic techniques.

In addition, it is generally believed that painstaking identification of specific chromophores in polymers is futile since photooxidation will cause changes in chromophore composition. Overall durability, consequently, may not be strongly related to the initial composition. These conclusions are based on photooxidation studies in polyolefins,[2–4] where considerable research has identified chromophoric impurities present prior to weathering and their subsequent photochemistry. In polyolefins, the presence of small amounts of chromophoric impurities triggers free-radical oxidation. During an initial induction period, characterized by low free-radical initiation rates and long kinetic chain lengths, free-radical oxidation leads to the buildup of oxidation products such as hydroperoxides. At some point, these oxidation products dominate the oxidation and autoxidation begins. The length of the induction period prior to autoxidation has been found to be nearly independent of the concentration of initial chromophore. The greatest gain in the weatherability of the polyolefins has come through the use of hindered amine light stabilizers,[5] HALS, and ultraviolet (UV) light absorber additives.[6] These additives can increase weatherability of polyolefins by a factor of 10 or more by delaying the onset of the autocatalytic oxidation phase.

The study of photooxidation in cross-linked coatings such as acrylic–melamines has been less extensive than that in polyolefins.[7–13] Nevertheless, sufficient data exist to conclude that oxidation behavior in these coatings is quite different from that of the polyolefins. Rather than exhibiting an induction period followed by autoxidation, acrylic–melamine coatings photooxidize at near constant rate throughout their usable life as evidenced by a constant increase in carbonyl functionality,[13] constant rate of weight loss,[14,15] and constant rate of oxygen uptake.[16] The addition of light stabilizers provides a relatively modest improvement in weatherability compared to that of the polyolefins.[5]

In previous work on developing rapid tests of coating weatherability, a clear, positive relationship has been established between the photoinitiation rate of free radicals measured in coatings during the first few hours of exposure and their long-term weatherability.[2] Coatings with low initial photoinitiation rates are invariably more durable than coatings with high initial photoinitiation rates. Thus, it would appear that specific information about the origin and nature of chromophoric centers present prior to weathering could lead to improvements in performance. Recent work has shown that the photoinitiation rate is strongly correlated to acrylic copolymer molecular weight and polymerization conditions.[17] These results suggest that the chromophores responsible for photoinitiation in acrylic–melamine coatings may be end groups on the copolymer chain.[17]

The present two-part work initiates a study of synthesis-derived chromophores in acrylic–melamine coatings and their relation to weatherability. In part 1, a ^{13}C NMR procedure is presented that is used to identify and quantify end groups in acrylic copolymers. The procedure involves fractionating the copolymer into low and high molecular weight components. This facilitates the identification of end groups, since the contribution of end groups increases with decreasing molecular weight. Carbon-13 NMR spectra of the components for different acrylic copolymers

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