Instrumentation

Polymer Analysis Using Pyrolysis-GC-FTIR-MS and GC-AED

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1 Introduction

During the last decade. analytical instruments employed in polymer analysis have developed greatly. Fourier transform nuclear magnetic resonance spectroscopy (FTNMR) and Fourier transform infrared spectroscopy (FTIR) are often used to obtain structural information needed for the Identification of monomers, and the determination of copolymer cornposition and differences in isomeric structure [1-6].

Pyrolysis GC has recently become popular for polymer analysis because of its simplicity and its capacity for providing important structural information. A typical system consists of a low dead-volume pyrolyzer. a high resolution capillary GC and a detector. Polymers are degraded in the pyrolyzer and the volatile pyrolysates are swept into the high resolution GC for separation and detection. The advantage of this system is that both monomer and polymer composition can be investigated qualitatively.

The value of pyrolysis GC data is very much dependent upon the GC detector employed The most popular detector has been the mass spectrometer because it can provide structural information about the pyrolysis fragments. More recently. a compact FTIR spectrometer has been combined with a mass spectral detector to construct a tandem GC-FTIR-MS system. This system can provide both mass spectral and complementary infrared data from a single GC injection. Another powerful system consists of a pyrolysls GC equipped with an atomic emission detector (AED)

Key Words:
Capillary gas chromatography
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Polymer analysis

Summary

Volatile pyrolysates of a methyl meth-Acrylate-butadiene-styrene copolymer (MBS) have been analyzed using a capillary gas Chromatograph equipped with a and a gas Chromatograph-atomic emis-Among the volatile compounds observed were monomers used for synthesis of the polymer. Numerous oligomers of higher boiling point were also found; identification of these could be used to give structural information about the parent polymer.
Combining information from these techniques was found to be extremely useful for the analysis of polymer pyrolysis useful for the analysis of polymer pyrolysis products. In characterizing each compound it was found paeticularly helpful to juxtapose feature-specific chromatograms (e.g., single ion monitoring from the mass-selective detector and the selected wavelength chromatography frome the infrared detector.)

The AED is an element-selective GC detector which can be used to determine the elemental composition corresponding to each GC peak Column eluate enters a microwave-induced helium Plasma where the very high temperatures cause the molecules to become atomized In this process. the molecules constituent atoms are raised to electronically excited states or are ionized by the plasma as they return to lower electronic energy levels photons are emitted at wavelengths that are characteristic of the particular element. A photodiode-array-based optical emission spectrometer is used to measure the wavelength and intensity of the emitted light. This data may be used to identify the elements present and determine their relative amounts It is possible. in principle, to detect any element in the periodic table, except helium. present in molecules which can be eluted from a GC So far methods have been developed for 23 different elements and four isotopes (^{13}C. ^{14}C. ^{15}N. and D) [7-13].
In this study au three spectral detectors (IR, MS, and AED) were used to characterize compounds eluting following pyrolysis of an MBS copolymer.
MBS copolymer is one of the most popular plastics because of its good transparency and high strength. It can be molded into many different components and is often added to other polymers as a modifier It

can be produced with a wide variety of polymer compositions, depending upon the amounts of butadiene, styrene, and methyl methacrylate used, and also because various graft ratios are possible. Tsuge and Otani [1] have reported the analysis of one MBS copolymer using pyrolysis capillary GC. The chromatogram obtained from our study was similar to theirs, except that the pattern of compounds of low volatility was different. Differences in monomer sequence and polymer additives may be responsible for this discrepaney.

2 Experimental

MBS copolymer pellets were obtained from a molding factory. The sample. consisted of a straight chain MBS copolymer with no grafts, a type of MBS copolymer widely used in industry. Pyrolysis was performed with a JHP-3 Curie Point Pyrolyzer (Japhn Analytical Industry Corp.. Tokyo, Japan). Approximately 1 mg of MBS polymer was cut from the pellet and wrapped in metal foil. The sample was pyrolyzed for 5 s at 590°C: volatiles were swept into the GC inlet by a flow of helium through a length of 0.53 mm i.d. fused silica tubing which was held at 200°C.

The tandem GC-IR-MS system used in this study consisted of a Hewlett-Packard 5890A Gas Chromatograph, an HP5965A Infrared Detector (IRD) equipped with a 100µ L internal volume Pyrex light-pipe and an HP5970B Mass Selective Detector (MSD). The IRD and MSD were connected in series by means of a 1 m length of 0.1 mm i.d. fused silica capillary tubing extending from the light-pipe to- the MSD. The MBS copolymer was also analyzed using a system consisting of the pyrolysis unit coupled to an HP5890A gas chr6matograph equipped with an HP5921A atomic emission detector. Although AED can monitor up to 23 different elements and four isotopes (^{13}C, ^{14}C, ^{15}N and D), 5 channels (carbon, hydrogen, oxygen, nitrogen, and sulfur) were used for this study. MBS pyrolysis products could be monitored using the carbon, hydrogen, and oxygen channels while heteroatom-containing additives to the polymer could be observed with the nitrogen and sulfur channels.

A 30 m x 0.32 mm i.d. x 0.53µm film HP-5 (5 % diphenylpolydimethyl siloxane) fused silica capillary column was used in both GC systems under the same conditions. All conditions and parameters used for this study are listed in Table l.

Table1

Analytical conditions used in the investigation.

GC	
Chromatograph oven temperature	40°C (1 min) –4°/min–250°C
Injection method	Split, split ratio 1: 50
Injection temperature	250°C
Column head pressure	103 kPa
GC-MS	
Transfer line temperature of MSD	250°C
GC-IR	
Light-pipe temperature	280°C
Make-up gas	Inlet: helium 0.5 ml/min
Scan speed	Outlet: helium 0.1 ml/min
Transfer line temperature (of IRD)	3 scans/s
GC -AED	280 ‘C
Transfer line temperature (of AED)	280°C
Make-up gas	30 ml/min
Reagent gases	oxygen, hydrogen for carbon, sulfur, and nitrogen oxygen for carbon and hydrogen hydrogen 10% methane in nitrogen for oxygen

3 Results and Discussion

3.1 Chromatographic-Analysis

Figure 1 shows the total ion chromatogram (TIC) and total response chromatogram (TRC) obtained from the GC-IR—MS system following pyrolysis of MBS-

Figure 2 shows the 5 elemental profiles obtained from the GC-AED system.

The TIC and the carbon and hydrogen profiles from the AED showed more than 50 peaks. Fewer peaks were observed in the TRC and in the oxygen- end sulfur-specific chromatograms : no peaks were observed in the nitrogen-specific chromatogram, suggesting that the polymer had no nitrogen-containing additives such as acrylonitrile. The six peaks observed in the sulfur-specific chromatogram a[e, in fact, indicative of sulfur- containing compounds and do not result from imperfect selectivity of the AED: many of the large peaks in the carbon chromatogram (such as 19. 24, and 42) do not have corresponding peaks in the sulfur chromatogram. Neither the TIC nor the TRC gave sufficient information to enable determination of the structures of the compounds generating the sulfur-specific peaks.

Several of the peaks observed in the TIC (e.g. , 11 , 31 , and 44) were from compounds generating only a small response in the TRC. Several others (e.g., 12, 13, 14, and 36) were not observed at all in the TRC. Interestingly, the compounds which were not detected by the IRD probably contained no oxygen since they gave no peaks in the AED oxygen-specific chromatogram.

MBS pyfolysis can generate two types of volatile compound. One group contains oxygen and is derived from methyl methacrylate while the other. .containing only

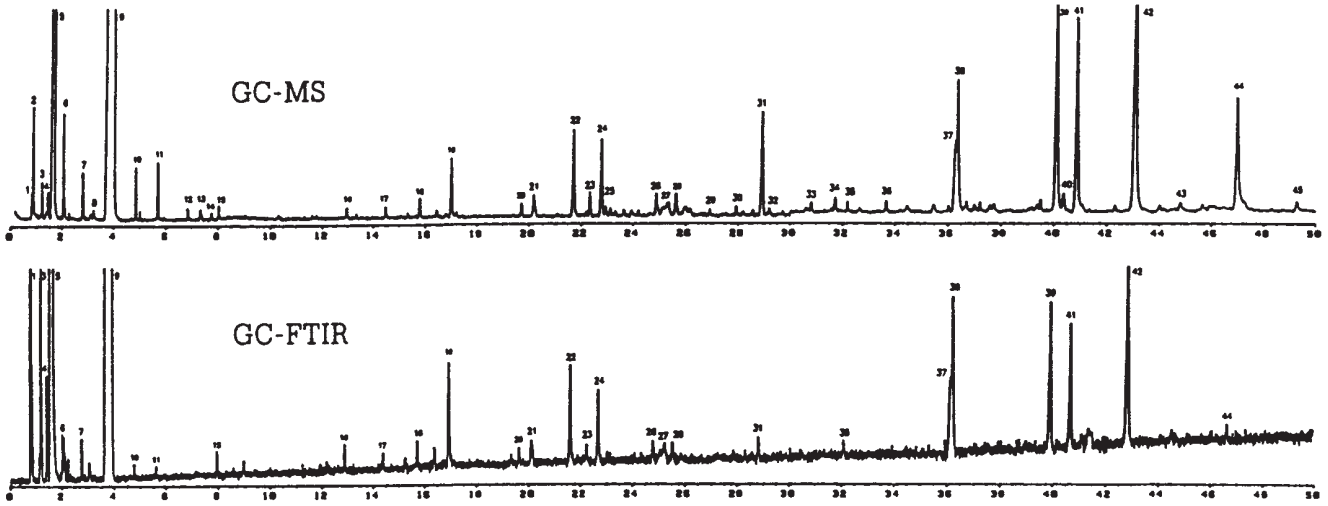

Figure 1

MSD total ion chromatogram (upper) and IRD total response chromatogram (lower) following pyrolysis (590 °C) of methyl methacrylate-butadiene-styrene copolymer (MBS). Peak number corresponds to those given in Table 3.

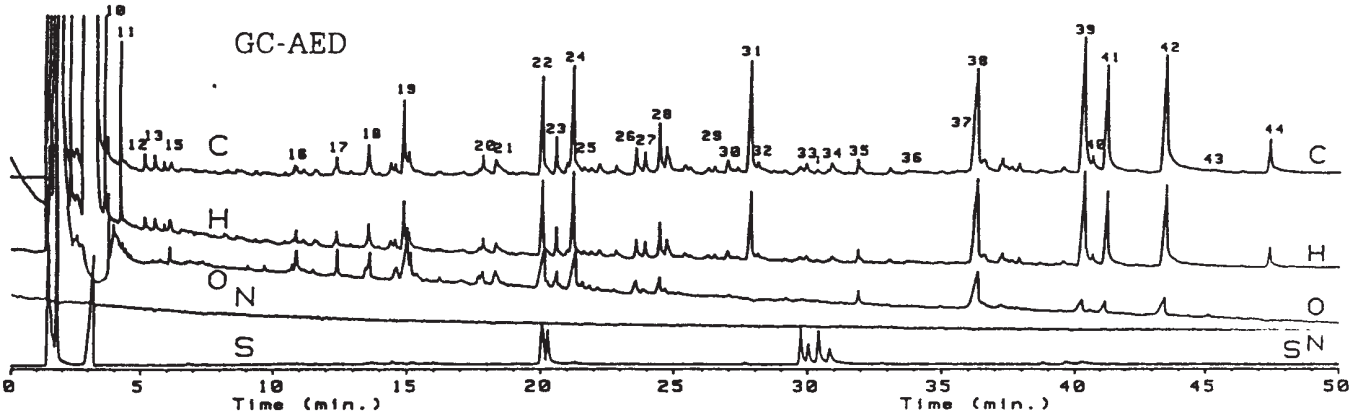

Figure 2

Carbon, hydrogen, oxygen, nitrogen, and sulfur profiles of volatile MBS copolymer pyrolysate (590 °C) obtained by GC-AED; the results from three injection were combined: run 1, carbon monitor (496 nm), hydrogen monitor (486 nm), run 2, nitrogen monitor (174 nm), sulfur monitor (181 nm), run 3, oxygen monitor (777 nm). Peak numbers on the carbon profile correspond to those given in Table 3.

hydrocarbons. is derived from butadiene arid styrene. Compounds generating little IR response are hydrocarbons While those producing a greater response are mostly esters. Peaks from compounds containing ester functions could be identified by selected wavelength chromatography (SWC) in the 1700-1780 cm^{-1} and 1100-1280 crn^{-1} regions. Using this procedure the major peaks in the IRD trace. except for Peak 15. were all shown to be produced by esters. SWC showed the presence of a carbonyl group but no ester bond in the compound generating peak 15 while the mass spectrum was indicative of a phenyl group (m/z77). From the infrared and mass spectra. peak 15 was identified as that of acetophenone: this was consistent with its elemental content determined by GC-AED.

Before the individual compounds were actually identified, they could be grouped into distinct classes based on the results obtained using the AED. selected ion monitoring (SIN) arid SWC. The TIC. TRC. and AED elemental profiles were then used to identify individual peaks,

3.2 Identification

More than halt the compounds were identified by combining information from GC-IR-MS and GC-AED analyses The identification of the compound generating peak 19 carl be used to illustrate how data from the three detectors were combined to provide the tentative identifications. For this compound the top three choices horn the MS library search were an aromatic ester and two aromatic hydrocarbons (Table 2). Only the first, methyl 2-methenyl-3-phenylpropionate. has a match quality large enough for serious consideration and even its value of 83 left some doubt about the compound's identity.

The IRD library search gave six choices with match qualities between 862 and 889 since the IR spectral library is considerably smaller than the MS library, the chances of its containing the correct compound were lower. Such library search results are. however, still very useful because the compounds selected usually have func-

tional groups similar to those present in the unknown. For peak 19. none of the choices matched the MS results. but all of the top choices were esters In addition, the first two choices were esters of itaconic acid. a compound having a terminal methylene group. The remaining choices were au aromatic. Only the first MS library choice, methy1 2-methenyl-3-pherlylpropionate. was consistent with the functional groups indicated by the IR library search.

The AED showed that the compound contained carbon. hydrogen. and oxygen which eliminated the hydrocarbons chosen by the MS library search. No sulfur or nitrogen were found.
Several authors have discussed using the AED to determine approximate empirical formulas [4-16].

Using procedures already described [14-16]. C : H : O ratio of the unknown was found to be 11 : 11.57 : 2.21 suggesting empirical formulas of $C_{11}H_{12}0_2$, $C_{11}H_{11}0_2$. or $C_{22}H_{23}0_4$. The last two had odd molecular weights and could thus be ignored. The first possibility. $C_{11}H_{12}0_2$, is the correct molecular formula for methy1 2-methenyl-3-phenylpropionate.

Methyl 2lmethy1-4-phenyl-4-pentenoate (peak 22) was used as the calibration standard for determining the elemental ratios since it could be identified reliably by all three detectors. While it is helpful to include an internal standard for this purpose. the use of such a standard was proscribed by the nature of the pyrolysis experiment. Any known compound in the sample may. however. be used as the calibration standard as long as it contains all the elements of interest and can be resolved chromatographically.

The three spectral detectors provide complementary evidence for compound identification. Far more confidence may be placed in structural determinations When data from all three detectors are consistent.

3.3 Monomers. Diners and Trimers

From their retention times and molecular weights. the pyrolysates could be easily categorized into three groups. The first included compounds generating peaks 2 to 15: these had molecular weights between 54 and 132 and were identified by MS and IR as monomers and monomer derivatives produced by pyrolysis. Peak 2 was butadiene and 3. 4 arid 5 were identified as being from methyl propionate. methyl isobutyrate, and methyl methacrylate monomer respectively. Esters 3 and 4 are probably pyrolysis products from methyl methacrylate units in the polymer Compound 9. the major pyrolysis product. was found to be styrene and 6. 10. 11. 12, 13, 14. and 1 5 were from minor pyrolysis products related to styrene.

Diners span the region from peaks 16 to 36. The early peaks were assigned as methyl methacrylate diners (MM). followed by methyl methacrylate-styrene diners (MS), and then, at the end of the range. styrene diners (SS).
The trimers elute in the last region of the chromatogram. From the infrared and mass spectra and the element-specific chromatogram for carbon, hydrogen. and oxygen it was possible to determine the monomeric constituents of the trimers; a more detailed structural analysis was, however. beyond the scope of this study-While the total peak area attributed to the diners was less than that for monomers or trimers. nearly half the peaks were found in this range. This complexity arises because styrene can dimerize in at least-five different ways to Produce the structures shown in **Table 3**. These styrene-based dimers, compounds 25. 29. 31, 32. and 34. could be detected easily because they had no carbonyl absorbances or peaks in the oxygen-specific chromatogram. The variety of diners present suggests that the MSS polymer had a complex composition. The compounds identified in the MBS pyrolysates are listed in Table 3.

Table 2

MS and IR library search results for peak 19 together with elemental information from the AED.

Detector	Compound	Match quality	Formula
MS	Methyl 2-methenyl-3-phenylpropionate	83	$C_{11}H_{12}O_2$
	1-Ethynyl-4-methylbenzene	37	C_9H_8
	1,2,3,4-Tetrahydro-1,4-methanonaphthalene	25	$C_{11}H_{12}$
IR	Itaconic acid, dimethyl ester	889	$C_7H_{10}O_4$
	Itaconic acid, dibutyl ester	874	$C_{13}H_{22}O_4$
	Diphenic acid, dimethyl ester	870	$C_{16}H_{14}O_4$
	o-Toluic acid, methyl ester	868	$C_9H_{10}O_2$
	m-Methylbenzoic acid, methyl ester	865	$C_9H_{10}O_2$
	Cinnamic acid, 3-phenylpropyl ester	862	$C_{18}H_{18}O_2$
AED	Elements present carbon, hydrogen, oxygen		
	Elements not present nitrogen, sulfur		
	Empirical formula $C_{11}H_{11.57}O_{2.21}$ or $C_{11}H_{12}O_2$		

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Table 3

Compounds identified following pyrolysis of MBS

Peak No.	Compound (molecular weight)	Related monomer unit[a]	Structure[b]
1	[Air]		
2	Butadiene (54)	B	C=CC=C
3	Methyl propionate (88)	M	mCC
4	Methyl isobutyrate (102)	M	mC(C)C
5	Methyl methacrylate (100)	M	mC(C)=C
6	Toluene (92)	S	PhC
7	4-Vinylcyclohexene (108)	BB	
8	Ethylbenzene (106)	S	PhCC
9	Styrene (104)	S	PhC=C
10	2-Propenylbenzene (118)	S	PhCC=C
11	Isopropenylbenzene (118)	S	PhC(C)=C
12	1-Propenylbenzene (118)	S	PhC=CC
13	3-Butenylbenzene (132)	S	PhCCC=C
14	2-Phenyl-1-butene (132)	S	PhC(C=)CC
15	Acetophenone (120)	S	PhC(=O)C
16	Unknown (–)	MM[c]	–
17	Unknown (–)	MM[c]	–
18	Methyl 2-methyl-3-phenylpropionate (178)	MS	PhCC(C)m
19	Methyl 2-methenyl-3-phenylpropionate (176)	MS	PhCC(=C)m
20	Unknown (–)	–	–
21	Methyl 2-methenyl-4-phenylbutanoate (190)	MS	PhCCC(=C)m
22	Methyl 2-methyl-4-phenyl-4-pentenoate (204)	MS	PhC(=C)CC(C)m
23	Unknown (218)	MS	
24	Methyl 2-methyl-5-phenylpentanoate (206)	MS	PhCCCC(C)m
25	1,2-Diphenylethane (182)	SS	PhCCPh
26	Unknown (204)	MS	–
27	Unknown (–)	–	–
28	Unknown (218)	MS	–
29	1,3-Diphenylpropane (196)	SS	PhCCCPh
30	Unknown (–)	–	–
31	2,4-Diphenyl-1-butene (208)	SS	PhC(C=)CCPh
32	2,4-Diphenyl-1-pentene (222)	SS	PhC(C=)CCPh(C)
33	Unknown (–)	–	–
34	1,4-Diphenyl-1-butene (208)	SS	PhCCC=CPh
35	Unknown (–)	–	–
36	Unknown (–)	–	–
37	Unknown (304)	MMS	–
38	Unknown (304)	MMS	–
39	Unknown (308)	MSS	–
40	Unknown (–)	–	–
41	Unknown (308)	MSS	–
42	Unknown (308)	MSS	–
43	Unknown (–)	–	–
44	2,4,6-Triphenyl-1-hexene (312)	SSS	PhC(C=)CC(Ph)CCPh
45	Unknown (–)	–	–

[a] M = Methyl methacrylate S = Styrene B = Butadiene
[b] Ph = Phenyl m = Methyl ester ($CH_3-O-CO-$)
[c] tentative determination

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