Initiation of Methyl Methacrylate Polymerization by the Nonvolatile Products of a Methyl Methacrylate Plasma. 3. Characterization of Initiator Structure

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ABSTRACT: The free radical polymerization of methyl methacrylate (MMA) can be initiated by an oily substance produced by passage of MMA vapor through a radio frequency (rf) plasma. NMR spectroscopy (^{1}H and ^{13}C) has been used to estimate the functional group composition of the oil, from which a prototypical structure was drawn. The oil bears little resemblance to MMA. It contains about half the oxygen content, most of which is still in the original methyl ester form. About 6% of the carbon atoms are olefinic. Few if any PMMA sequences are present. The various functional groups exist in a wide variety of chemical environments, due to the diversity of chemical reactions that take place in the rf plasma.

Introduction

Osada et al.[1] have reported that addition-polymerization initiators can be formed in the low-pressure plasma (or glow discharge) of certain vinyl compounds. Subsequently, other reports of this phenomenon have appeared, using both vinyl[2–5] and saturated[6,7] compounds. With methyl methacrylate (MMA), it has been established that the initiator is present in a nonvolatile oily deposit formed on the walls of the plasma zone.[2] A recent study[7] using this oil to initiate MMA polymerization found that the oil generates initiating free radicals unimolecularly. The initiator appears not to be a single compound, since size exclusion chromatography yields fractions, all of which are effective as initiators. While their effectiveness varies, the activation energy for radical generation is about the same for each fraction and close to that for the unfractionated oil. The present paper describes the results of an investigation aimed at determining the structure of the oil produced in an MMA plasma. The principal techniques used were elemental analysis and both ^{1}H and ^{13}C NMR.

Experimental Section

The systems and conditions employed to produce, collect, and fractionate the nonvolatile oily product of an MMA plasma were those previously described.[7] The discharge was created with two parallel-plate electrodes (10 cm × 15 cm) outside a 0.9-cm-o.d. Pyrex tube through which MMA vapor was flowing at a pressure of ~9 torr and with a residence time of 4–9 s. The power was 40 W and the frequency 13.56 MHz. The oily deposit dripped from the plasma zone into a collection vessel. Several grams were collected over a period of 1–3.5 days. The weight percent of carbon, hydrogen, and nitrogen in the plasma-produced oil was determined with a Perkin-Elmer Model 240 combustion analyzer. The weight percent of oxygen was obtained by difference.

^{1}H NMR. Two spectrometers were used to record ^{1}H NMR spectra. One operates at 202 MHz and the other at 251 MHz. The plasma-produced oil was dissolved in chloroform-*d* or pyridine-d_5 (Aldrich Chemical Co.) to concentrations of up to 0.25 g of oil per milliliter of solution and then added to 5-mm-o.d. NMR tubes.

Inversion–recovery experiments utilized a composite 180° pulse[8] and a 90° pulse that was phased shifted 180° (relative to the inversion pulse) on alternate scans.[9] These procedures help to correct for both inhomogeneities in the pulse field and differences in the effective pulse field experienced by protons resonating at different frequencies. Inversion–recovery ^{1}H NMR experiments were conducted on both degassed and nondegassed samples. The results were almost identical, probably because nondegassed solutions contained only small amounts of atmospheric oxygen—a paramagnetic relaxation agent. Wherever possible, atmospheric exposure of the solvent, $CDCl_3$, and the plasma-produced oil was minimized. Furthermore, containers for both liquids were purged with a stream of nitrogen after each opening.

Table I
Elemental Composition of the Plasma-Produced Oil and MMA

element	mol % plasma-produced oil	mol % MMA
C	33.7 ± 0.60	33.3
H	59.8 ± 1.53	53.3
O	6.5 ± 0.41	13.1
N	0.016 ± 0.016	0

The delay between scans was 16.9 s for the inversion–recovery experiment in which proton T_1 values were determined. This delay allowed even the most slowly relaxing peak ($T_1 \sim 1.4$ s) to recover to greater than 99.9% of its magnetization between scans. For the other proton NMR experiments, the radio-frequency (rf) pulses (45° for the 202-MHz machine and 39° for the 251-MHz machine) and delays (6.7 and 4 s, respectively) were such that the most slowly relaxing peak could still recover >97% of its magnetization between scans.

The rf pulse power of the 202-MHz and 251-MHz machines was sufficient that the inequality[10]

$$t_{90} < 1/4\Delta \tag{1}$$

was always satisfied. In eq 1, t_{90} is the rf pulse time required to produce a 90° tip in the magnetization vector, and Δ is the sweep width (size of the frequency interval, in hertz, swept by the spectrometer). Because the delay times were sufficiently long to allow nearly complete relaxation of all peaks between pulses and because the rf pulse power was sufficiently great (eq 1 was satisfied), all ^{1}H NMR spectra were quantitative—peak areas were proportional to the number of protons contributing to the peak.

^{13}C NMR. The spectrometer used to record ^{13}C spectra operates at a carbon nuclear resonance frequency of 45 MHz. The plasma-produced oil was dissolved in Aldrich Chemical Co. chloroform-*d* and transferred into a 10-mm NMR tube. A relaxation agent [Aldrich Chemical Co., chromium(III) acetylacetonate or $Cr(acac)_3$] was added to the sample solution, on which a quantitative spectrum was taken. The rf pulse power was sufficient to satisfy eq 1, and therefore it was possible to obtain quantitative spectra. To distinguish between various CH_n evironments ($n = 0, 1, 2, 3$) an INEPT (insensitive nucleus enhancement by polarization transfer) experiment was conducted with refocusing pulses (INEPTR) in the manner described by Bolton.[11]

Results and Discussion

Elemental Analysis. Elemental analyses of four different batches of oil yielded the average composition given in Table I. In comparison with the starting material, MMA, the plasma-produced oil has the same carbon content, a hydrogen content that is about 10% greater, but about half the content of oxygen. The trace of nitrogen

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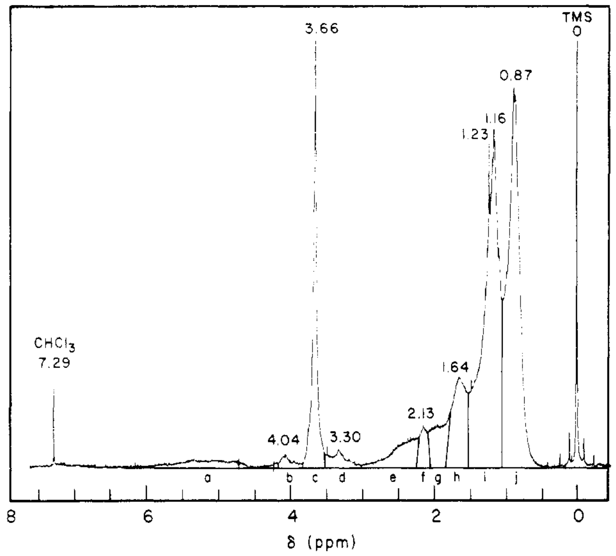

Figure 1. ^1H NMR spectrum (251 MHz) of the plasma-produced oil dissolved in $CDCl_3$ (<0.1 g/mL).

Table II
^1H NMR Peak Assignments for the Plasma-Produced Oil

absorpn area[a]	δ, ppm	assignt[b]	T_1, s
j	0.87	$CH_3 \geq 3$ bonds from -OR, -OCOR, -COR $CH_3 \geq 2$ bonds from C=C	0.79
i	1.16	CH_3 2 bonds from -OR, -OCOR, -COR $CH_2 \geq 3$ bonds from -OCOR, -COR $CH_2 \geq 2$ bonds from -OR, C=C	0.50
	1.23	CH_3CH_2OCOR	1.4
h	1.64	CH_3 1 bond from C=C CH ≥ 3 bonds from -OCOR, -COR CH ≥ 2 bonds from -OR, C=C	1.4
e + g	1.8–2.7	CH_2 2 bonds from 2 -OCOR, -COR CH_2 1 bond from C=C, -COR CH 2 bonds from -OCOR, -COR CH 1 bond from C=C, -COR	0.50
f	2.13	CH_3 1 bond from -COR	1.3
d	3.3	CH_3 or CH_2 1 bond away from -OR	<1.4
c	3.66	CH_3 1 bond from -OCOR	1.4
	3.75	CH_3 1 bond from -OCOC=C	1.4
b	4.04	CH_2 1 bond from -OCOR	0.7
a	4.5–5.0	CH_2=C	~0.7
	5.0–6.0	CHR=C	~0.7

[a] See Figure 1. [b] R denotes alkyl group.

detected in the oil is probably due to incomplete degassing in the combustion analyzer.

^1H NMR. An ^1H NMR spectrum of the plasma-produced oil is shown in Figure 1. With the exception of the spike at 1.23 ppm, all of the peaks are very broad. The absence of any difference in peak width for spectra taken at 100 °C and room temperature suggests that the breadth of these peaks is due to the overlap of many peaks of ordinary line width, which have slightly different chemical shifts.

The assignment of the peaks in regions a through j in Figure 1 are given in Table II along with values of T_1 determined from inversion–recovery experiments. For the assignments to specific functional groups, chemical shift tables[12] were used in combination with the measured values of T_1.[13]

^{13}C NMR. Figure 2 shows a quantitative proton-decoupled ^{13}C NMR spectrum of the plasma-produced oil. To acquire such spectra in a matter of hours, a relaxation agent, $Cr(acac)_3$, was added to a $CDCl_3$ solution of the oil. With a 0.03 M concentration of $Cr(acac)_3$, the values of T_1 for all carbon atoms were reduced to less than 1.4 s. Thus the pulse repetition time of 10.3 s permitted even the most slowly relaxation carbon atoms to recover between pulses to 99.8% of their initial strength. The $Cr(acac)_3$ broadened some of the narrower, well-defined peaks observed in the region between 0 and 50 ppm but did not otherwise alter the spectrum.

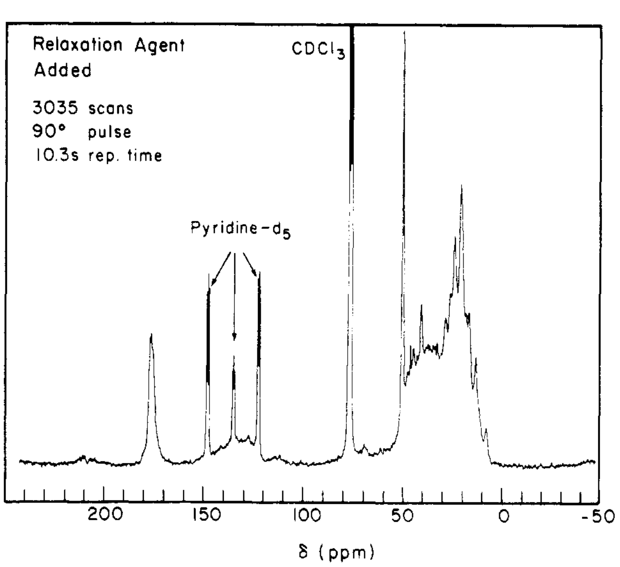

Figure 2. ^{13}C NMR spectrum of the plasma-produced oil. The sample solution contained 0.57 g/mL of oil, 0.035 g/mL of pyridine, and 0.03 M $Cr(acac)_3$, in $CDCl_3$.

The spectrum in Figure 2 exhibits peaks for pyridine-d_5, the solvent used to dissolve the relaxation agent prior to its addition to the oil solution, and for $CDCl_3$, the solvent for the oil. The weak band extending from 204 to 216 ppm and the intense peak at 176 ppm are both due to carbonyl carbons: the former is attributable to ketone groups and the latter to ester groups.[10] Olefinic carbons are responsible for the broad peak extending from 108 to 155 ppm.[10] Carbons that are part of various esters ($-CH_nOCOR$) and ethers ($-CH_nOR$) appear between 70 and 50 ppm. The absence of any absorptions in the region 52.5–55 ppm, characteristic of CH_2 groups in PMMA,[14] indicates that there are few if any linear sequences of MMA in the oil. The strong peak at 50.5 ppm is due to the methoxy carbon of a methyl ester. Between 50 and 0 ppm various CH_n (n = 0, 1, 2, or 3) resonances appear. Protons attached to the carbon atoms that absorb in this region are responsible for the 0–3 ppm region of the ^1H NMR spectrum.

To help identify the peaks in Figure 2, an INEPTR (insensitive nucleus enhancement by polarization transfer with refocusing) experiment was carried out.[11] With this experiment, one can determine for each CH_n (n = 0, 1, 2, or 3) resonance in the spectrum the value of n.[15,16] Four spectra are required, first a normal ^{13}C spectrum and then three INEPTR spectra at refocusing delays of τ_2 = 0.9, 2.0, and 2.7 ms (with τ_1 set at 1.8 ms). Quaternary carbons are distinguished by the fact that they appear in the normal ^{13}C spectrum but not in any of the INEPTR spectra, whereas, all other CH_n give strongly positive peaks in the INEPTR spectrum with τ_2 = 0.9 ms. Only tertiary carbons yield strong positive peaks at both τ_2 = 0.9 and 2.0 ms. Secondary carbons are unique in yielding negative peaks at τ_2 = 2.7 ms. Primary carbons can be distinguished by the fact that while they are strongly positive at both τ_2 = 0.9 and 2.7 ms they are nearly absent in spectra taken with τ_2 = 2.0 ms.

INEPTR spectra of the plasma-produced oil taken with a refocusing delay, τ_2, of 0.9, 2.0, and 2.7 ms are shown in

Figure 3. Starting at the right end of the spectrum, it is seen that the 0–30 ppm region almost nulls at 2.0 ms and then returns positive at 2.7 ms. All the individual spikes in this region are observed at both 0.9 and 2.7 ms and in the ordinary ^{13}C spectrum (quaternary carbons do not occur in the 0 to 30 ppm region[10]). Consequently, it is concluded that most of this region contains CH_3 groups, although it may contain a small fraction of CH_2 groups. It is possible that a small fraction of CH groups also appears in this region, but most CH groups appear at >30 ppm.[10] In the 30–50 ppm region, several spikes appear in the ordinary ^{13}C spectrum that do not appear in the INEPTR spectrum using τ_2 = 0.9 ms. These spikes are therefore quaternary carbons and occur at 48.0, 46.5, 45.0, 43.1, and 41.1 ppm. This region shows less absorption at τ_2 = 0.9 ms than at 2.0 ms. At 2.7 ms it is somewhat negative; however, complete inversion is not achieved. Consequently, this region must contain (besides quaternary carbons) both CH and CH_2 groups and probably more of the latter than the former. The methyl ester methoxy spike at 50.5 ppm varies with τ_2 as expected. There is a series of small peaks in the 52–70 ppm region due to ethers and higher esters. All of these peaks are negative at 2.7 ms except the 57.5 ppm peak, which is positive. Therefore these negative peaks are CH_2 carbons. The 57.5 ppm peak is almost null at τ_2 = 2.0 ms, so it is due to a CH_3 group. From their chemical shifts these peaks have been assigned as follows. The CH_3 at 57.5 ppm is probably an ether, $\mathit{C}H_3OR$, since these occur at about +5 ppm relative to the CH_3 of methyl esters,[10] and the methyl ester appears at 50.5 ppm. The presence of an α-carbon produces about a +9 ppm shift, and therefore the CH_2 at 64.1 ppm has been assigned to $CH_3\mathit{C}H_2OR$ and the CH_2 at 59.5 ppm to $CH_3\mathit{C}H_2OCOR$. A β-carbon also produces about a +9 ppm shift, and therefore the CH_2 at 69.5 ppm has been assigned to $CH_3CH_2\mathit{C}H_2OCOR$. The broad olefinic hump from 108 to 120 ppm appears negative at τ_2 = 2.7 ms and therefore has been assigned to $C{=}\mathit{C}H_2$. The olefinic hump from 120 to 135 ppm appears even stronger at τ_2 = 2.0 ms than at 0.9 ms and therefore has been assigned to $C{=}\mathit{C}HR$. Additional olefinic absorbance occurs in the ordinary ^{13}C spectrum in the 135–155 ppm region, which does not appear in the INEPTR spectra. Consequently, this absorption has been attributed to $C{=}\mathit{C}R_1R_2$ groups. These assignments for the olefinic carbons are consistent with the fact that more highly substituted olefins generally appear at higher ppm.[10]

The assignments for all of the ^{13}C NMR peaks are given in Table III. The mole fraction of carbon in various environments was determined with these assignments and the spectrum shown in Figure 2. Peak areas were measured with a planimeter after expanding different portions of the spectrum by known amounts. Solvent peaks were subtracted out. The results are listed in Table IV. Since all oxygen-containing environments have been specifically identified, the results of Table IV can be checked for consistency against the elemental analysis results previously cited. The O/C ratio computed from Table IV is 0.184, in excellent agreement with the value of 0.185 obtained by elemental analysis on this batch of oil. The assignments of the olefinic peaks in Table IV can be checked against the ^1H NMR results on the same batch of plasma-produced oil (see Figure 1). The fraction of hydrogen atoms that are part of olefinic groups is computed from Table III by first evaluating the ratio of olefinic hydrogen atoms to total carbon atoms. This ratio is then divided by the overall H/C ratio, determined by elemental analysis, to obtain the fraction of hydrogen atoms that are

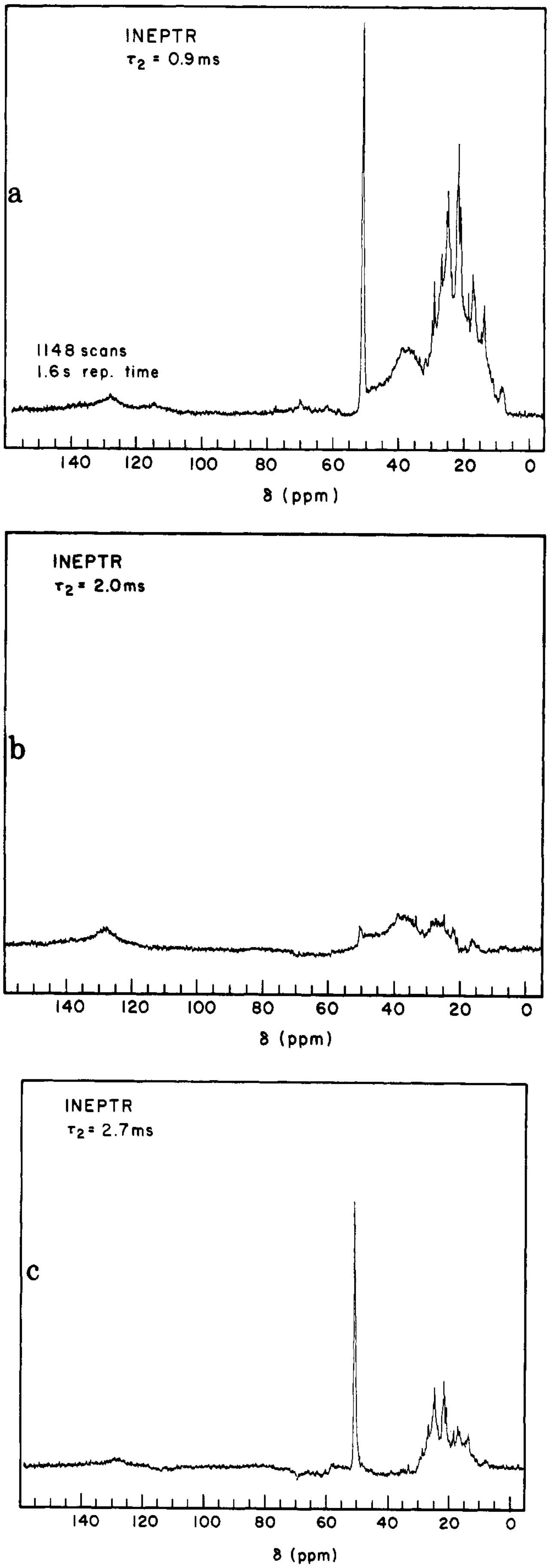

Figure 3. INEPTR ^{13}C NMR spectra of the plasma-produced oil in $CDCl_3$ (0.73 g/mL): (a) τ_2 = 0.9 ms; (b) τ_2 = 2.0 ms; (c) τ_2 = 2.7 ms.

Table III
^{13}C NMR Peak Assignments for the Plasma-Produced Oil[a]

δ, ppm	assignt	δ, ppm	assignt
204–216	$-\mathrm{COR}$	57.5	$\mathrm{\mathit{C}H_3OR}$
176	$-\mathrm{COOR}$	50.5	$\mathrm{\mathit{C}H_3OCOR}$
167.1	$\mathrm{CH_2{=}C(CH_3)(\mathit{C}OOCH_3)}$	30–49	alkyl $-\overset{\mid}{\underset{\mid}{\mathrm{C}}}-, -\overset{\mid}{\underset{\mid}{\mathrm{C}}}\mathrm{H}-, -\mathrm{CH_2}-$
135–155	$\mathrm{C{=}\mathit{C}(R_1)(R_2)}$	48.0, 46.5, 45.0, 43.1, 41.1 }	$-\overset{\mid}{\underset{\mid}{\mathrm{C}}}-$
120–135	$\mathrm{C{=}\mathit{C}H(R)}$		
135.7	$\mathrm{CH_2{=}\mathit{C}(CH_3)(COOCH_3)}$		
124.9	$\mathrm{\mathit{C}H_2{=}C(CH_3)(COOCH_3)}$	0–30	alkyl $-\mathrm{CH_2}-, \mathrm{CH_3}-$
108–120	$\mathrm{C{=}\mathit{C}H_2}$	17.8	$\mathrm{CH_2{=}C(\mathit{C}H_3)(COOCH_3)}$
69.5	$\mathrm{CH_3CH_2\mathit{C}H_2OCOR}$	13.4	$\mathrm{\mathit{C}H_3CH{=}CH}-$ or $\mathrm{\mathit{C}H_3(CH_2)}_n-$, $n \geq 3$
64.1	$\mathrm{CH_3\mathit{C}H_2OR}$	7.7	$\mathrm{\mathit{C}H_3CH_2COR}$
59.5	$\mathrm{CH_3\mathit{C}H_2OCOR}$		

[a] R denotes alkyl group.

Table IV
Mole Percent of Various Carbon Environments in the Plasma-Produced Oil

carbon environment	mol %
$-\mathrm{COR}$	1.2
$-\mathrm{COOR}$	8.2
$\mathrm{C{=}\mathit{C}(R_1)(R_2)}$	2.3
$\mathrm{C{=}\mathit{C}H(R)}$	3.2
$\mathrm{C{=}\mathit{C}H_2}$	0.9
$\mathrm{CH_3CH_2\mathit{C}H_2OCOR}$	0.3
$\mathrm{CH_3\mathit{C}H_2OR}$	0.1
$\mathrm{CH_3\mathit{C}H_2OCOR}$	0.1
$\mathrm{\mathit{C}H_3OR}$	0.1
$\mathrm{\mathit{C}H_3OCOR}$	8.5
alkyl $-\overset{\mid}{\underset{\mid}{\mathrm{C}}}-, -\overset{\mid}{\mathrm{C}}\mathrm{H}-, -\mathrm{CH_2}-$ (30–50 ppm region)	30.5[a]
alkyl $-\mathrm{CH_2}-, \mathrm{CH_3}-$ (0–30 ppm region)	44.6[a]
	$\sum = 100.0$

[a] See Table V for further details.

part of olefinic groups. This same ratio is computed from the ^{1}H NMR spectrum in Figure 1 by dividing area a in this figure by the total area. The latter result is 0.025, which is in excellent agreement with the value of 0.027 obtained from Table IV.

In Table IV the concentrations of CH_n ($n = 0, 1, 2$, or 3) groups exhibiting peaks in the region 0–50 ppm are not completely differentiated according to the value of n. A further refinement of the functional group distribution can be achieved by taking advantage of the INEPTR data. This is done by using quantitative relationships for peak strength as a function of τ_1, τ_2, and $J_{\mathrm{C\text{-}H}}$.[17] Details of this procedure are given in ref 13. The resulting distribution of CH_n groups is given in Table V.

Carbon environments given in Table V absorb in the 0–50 ppm region of the ^{13}C NMR spectrum. The hydrogens attached to these carbons appear in the 0–3 ppm region of the ^{1}H NMR spectrum. With the mole percent of CH, $\mathrm{CH_2}$, and $\mathrm{CH_3}$ in this region given in Table V, the ^{1}H NMR peak assignments listed in Table II, and the areas of these peaks as measured from Figure 1, the possible composition range of each ^{1}H NMR peak assigned to more than one CH_n group was calculated. This range and the average over each range is listed in Table VI. These peak compositions are quite reasonable. The large percentage of $\mathrm{CH_2}$ in the 1.8–2.7 ppm region is consistent with the rapid relaxation observed for this region. The large percentage of $\mathrm{CH_3}$ assigned to the 1.64 ppm peak is accommodated if one of every two nonprotonated olefinic carbon sites, listed in Table IV, is occupied by a $\mathrm{CH_3}$ group. The local environments for the various CH_n groups (n = 1, 2, or 3) in Table V (which are listed to the right of the mole percent of each group in this table) were computed from the average ^{1}H NMR peak compositions in Table VI and peak assignments for the other ^{1}H NMR peaks listed in Table II.

As a further check of the accuracy of the functional group distributions presented in Tables IV and V, a comparison was made between the number of end groups and the number of branch points. This was done as follows. From previous measurements[7] it is known that the average molecular weight of the nonvolatile plasma products is about 500. The average molecular weight of the carbon

Table V
Estimated Mole Percent of Various CH_n Appearing in the 0–50 ppm Region of the ^{13}C NMR Spectrum of the Plasma-Produced Oil

mol % CH_n[a]	% CH_n with environ[b]
15.3 $-\overset{\mid}{\underset{\mid}{\mathrm{C}}}-$	
3.8 $-\overset{\mid}{\mathrm{C}}\mathrm{H}-$	53 ≥ 3 bonds from –COR, –OCOR, and ≥ 2 bonds from –OR, C=C
	47 2 bonds from –COR, –OCOR, or 1 bond from –COR, C=C
20.4 $-\mathrm{CH_2}-$	50 ≥ 3 bonds from –OCOR, –COR, and ≥ 2 bonds from C=C, –OR
	50 2 bonds from 2 –COR, –OCOR, or 1 bond from –COR, C=C
35.7 $-\mathrm{CH_3}$	51 ≥ 3 bonds from –OR, –COR, –OCOR, and ≥ 2 bonds from C=C
	33 2 bonds from –OR, –COR, –OCOR
	12 1 bond from C=C
	4 1 bond from –COR

[a] Based on the total moles of carbon in the plasma-produced oil. [b] Represents the percentage of the particular CH_n group with the described environment. These percentages were calculated from the average compositions assigned to the ^{1}H NMR peaks (see Tables II and VI).

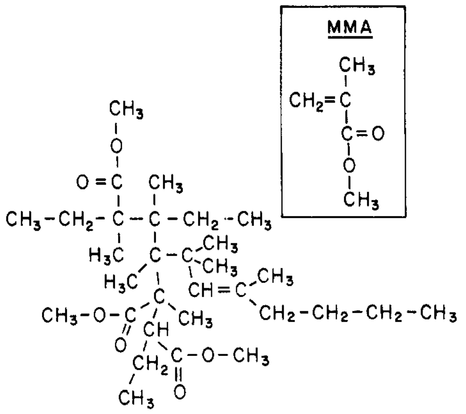

Figure 4. Prototypical structure of a plasma-produced oil molecule.

Table VI
Estimated CH_n Compositions of Some ^1H NMR Peaks of the Plasma-Produced Oil

area[a]	δ, ppm	composn range, mol %	av composn, mol %
i	1.16	$27 \le CH_2 \le 60$	44 CH_2
		$40 \le CH_3 \le 73$	56 CH_3
h	1.64	$0 \le CH \le 56$	28 CH
		$44 \le CH_3 \le 100$	72 CH_3
e + g	1.8–2.7	$0 \le CH \le 32$	16 CH
		$68 \le CH_2 \le 100$	84 CH_2

[a] Absorption areas shown in Figure 1.

environments is about 17 (based on Tables IV and V). Thus there are about $500/17 \simeq 29$ carbon atoms per molecule. There is one branch point for each non-protonated olefinic carbon and tertiary carbon and two for each quaternary carbon. From Tables IV and V it is seen that their are 36.7 branch points per 100 carbon atoms or $(36.7)(29/100) = 10.6$ per molecule. The end groups are $-C{=}CH_2$, CH_3O-, CH_3OCO-, and $-CH_3$. There are 45.2 of these groups per 100 carbon atoms or 13.1 per molecule. However, each molecule must have two more end groups than branch points to allow for chain ends. Subtracting these out, we see that the number of branch points, 10.6, agrees satisfactorily with the number of end groups minus chain ends, 11.1.

Structure of Plasma-Produced Oil. A prototypical structure for an oil molecule can be developed with the aid of the functional group distributions presented in Tables IV and V. One such structure is shown in Figure 4. Except for the methyl ester groups, the structure bears little resemblance to MMA. This is a consequence of the variety of reactions that occur in organic plasmas.[18]

Summary

The oily substance produced by passage of MMA vapor through an rf plasma has a complex structure quite different from that of PMMA oligomers. ^1H and ^{13}C NMR spectra reveal that the oil contains about 6% olefinic carbon and about half the oxygen of MMA, most of it in the form of methyl ester groups. A prototypical structure for the oil can be developed with the functional group composition determined from NMR spectroscopy and elemental analysis. The various functional groups present exist in an enormous variety of chemical environments due to the diversity of chemical reactions that take place in the rf plasma.

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