Degraded Products in Weathered Polymers

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Synopsis

Styrene–methyl vinyl ketone copolymers, methyl methacrylate–methyl vinyl ketone copolymers, and styrene–methyl vinyl ketone–2,6-di-*t*-butyl-4-acroylaminomethylphenol terpolymers as well as polystyrene and polypropylene have been weathered either by artificial irradiation or by outdoor exposure. The weathered products were analyzed using GC mass spectrometry, liquid chromatography, IR, UV, NMR, and wet analytical methods. Most of the weathered products proved to be low molecular weight polymers with various functional groups, and many low molecular weight compounds were identified. From the degradates of styrene copolymers, acetone, acetic acid, acetophenone, benzoic acid, formic acid, phenol, benzaldehyde, etc., were identified; from the degradates of methyl methacrylate copolymers, acetone, acetic acid, methanol, methyl methacrylate, methyl vinyl ketone, etc., were identified; and from the degradates of polypropylene, aliphatic acids up to propionic were analyzed. In many cases, the most abundant species was acetic acid. From polypropylene weathered outdoors for two years, 1.2 μl/g acetic acid was obtained. The degradates of styrene copolymers were found to contain fluorescent substances.

INTRODUCTION

The burden of accumulating plastic wastes has stimulated the research and development of degradable plastics.[1] Polymers incorporated with small amounts of ketone side groups are considered one of the most promising materials for photodegradable plastics. This has been pursued separately by Guillet[2] and the Research Institute for Polymers and Textiles, Japan.[3,4] This study was undertaken in order to ascertain the nature of the degraded products of photodegradable plastics, mainly of the types of vinyl ketone copolymers, along with the products from commercial polymers.

EXPERIMENTAL

Materials

Styrene–methyl vinyl ketone copolymers (SA and SB), methyl methacrylate–methyl vinyl ketone copolymer (MA), and styrene–methyl vinyl ketone–2,6-di-*t*-butyl-4-acroylaminomethylphenol terpolymer[4] (SC) were prepared by radical polymerization in toluene at 70°C using AIBN as an initiator. Polymers purified by repeated precipitation into methanol were pressed into sheets under pressure of 100 kg/cm^2 at 120°C (St–MVK) and 100°C (MMA–MVK) for 10 min and used in irradiation experiments (Table I).

Polypropylene sample PP-J-300 from Mitsui Petrochemical Co. was stabilized with small amounts of calcium stearate, 2,6-di-*t*-butyl-*p*-cresol, dilauryl thiodipropionate, 1,1,3-tris(2-methyl-4-hydroxy-5-*t*-butylphenyl)butane, etc., and was weathered in the form of 4-mm-thick, 3-mesh nets. Styrene homopolymer PS-MW-1-301 from Denkikagaku Kogyo Co. was pressed into sheets in a similar manner.

Journal of Applied Polymer Science, Vol. 22, 1491–1507 (1978)

0021-8995/78/0022-1491$01.00

TABLE I
Irradiation Conditions and Molecular Weights of Products

Sample no.	Composition polymer–MVK–TBAP	Film thickness, mm	Atmosphere	Irradiation			Molecular weight × 10⁴ [a]
				Source	Time, hr	Energy, kJ/cm²	
SA-0	PSt 70–30–0	—	—	—	—	—	9.0
SA-1	PSt 70–30–0	0.5	air	Hg	1621	—	0.5[b]
SA-2	PSt 70–30–0	0.5	air, in Pyrex	Hg	1450	—	1.2
SA-3	PSt 70–30–0	0.5	Ar, in Pyrex	Hg	1450	—	1.0
SA-4	PSt 70–30–0	0.5	air, in quartz	Xe	240	—	—
SA-5	PSt 70–30–0	0.5	air	W.M.[c]	549	16.3 (UV) 42.6 (Vis)	1.9
SA-8	PSt 70–30–0	0.5	natural[d]	sun	3 days	2.95	3.0
SA-9	PSt 70–30–0	0.5	natural[d]	sun	10 days	12.5	1.9
SA-10	PSt 70–30–0	0.5	natural[d]	sun	1 month	46.3	2.4
SA-11	PSt 70–30–0	0.5	natural[d]	sun	2 months	96.4	1.7
SA-12	PSt 70–30–0	0.5	natural[d]	sun	6 months	250	1.5
SB-0	PSt 90–10–0	—	—	—	—	—	6.0
SB-1	PSt 90–10–0	1.1	air	W.M.	600	—	3.7
SC-0	PSt 89.5–10–0.5	—	—	—	—	—	5.7
SC-1	PSt 89.5–10–0.5	1.0	air	Hg W.M.	250 200	—	3.3
S-0	PSt 100–0–0	—	—	—	—	—	18[e]
S-1	PSt 100–0–0	1.2	air	W.M.	500	15 (UV) 38 (Vis)	12[e]
MA-0	PMMA 75–25–0	—	—	—	—	—	8.0
MA-1	PMMA 75–25–0	0.5	air, in Pyrex	Hg	1500	—	3.0
E-1	PP 100–0–0	4	natural[f]	sun	2 years	909	—
E-2	PP 100–0–0	4	natural[f]	sun	3 years	—	—

[a] Values by GPC.
[b] Value by VPO.
[c] Weather meter.
[d] At Choshi.
[e] Values by viscometry.
[f] At Naha.

Irradiation

The sample sheets were cut into the appropriate sizes and irradiated (Table I) either by a 450-W high-pressure mercury lamp of Ushio Electric Co. (40°C, 15 cm), a 500-W xenon lamp of Ushio Electric Co. (30°C, 15 cm), or by a sunshine weather meter WE-SUN-HC of Toyo Rika Kogyo Co. (40°C). Outdoor exposures were done at Japan Weathering Test Centers at Choshi (35°44′N, 140°45′E) between July 11, 1973 and January 11, 1974 and at Naha (26°13′N, 127°42′E) between July 11, 1973 and July 10, 1976.

Analytical Equipment

The equipment used for the analyses was as follows: infrared spectrophotometers, Hitachi EPI-G3 and DS-402G of Japan Spectroscopic Co., with an attenuated total reflection equipment ATR-7; an ultraviolet spectrophotometer, Hitachi ESP-3T; a fluorescence spectrophotometer, Hitachi MPF-2A; a mass spectrometer, JEOL JMS-07, equipped with a JGC-20 gas chromatograph, PL-723 pyrolyzer, and JEC-6 spectrum computer; nuclear magnetic resonance equipment, Hitachi R-24; a liquid chromatograph, Japan Analytical Ind. Co. LC-08, equipped with 20φ × 600 mm and 8φ × 600 mm columns of Jaigel.

Sample Preparation for Analyses

Irradiated sheets were examined for IR spectra by the ATR method and then crushed into powders. Some of the powder was subjected to wet chemical analysis, some to liquid chromatography, and the remaining powder was analyzed by a pyrolyzer–GC mass spectrometer. Powdered samples were heated for 3 hr at 100°C under a pressure of 10^{-3} mm Hg, and the liquid collected in a cold trap at liquid nitrogen temperature was analyzed by a GC mass spectrometer.

RESULTS

Styrene–Methyl Vinyl Ketone Copolymers

Effect of Irradiation Time

The weight change and molecular weights by the GPC method for styrene–vinyl methyl ketone copolymers of molar composition 70/30 are shown in Figure 1. The weights of the samples gradually increased by oxidation with irradiation time, but decreased after 30 days due to the destruction of the surface. Molecular weights of the polymers appeared to decrease more rapidly at the early stage of the irradiation.

Irradiated powders were dissolved in ethyl acetate and titrated with 0.1*N* KOH methanol solution using a neutral red–bromthymol blue mixed indicator. Acid values thus obtained and hydroxyl values obtained by the acetylation method[5] are shown in Figure 2. With progress of the irradiation time, acid values increased, while the groups which were reactive to acetic anhydride had a tendency to decrease.

Broad IR absorption was observed at 1700 cm^{-1} when the irradiated sheet was examined by the attenuated total reflection method using KRS-5 at an incident

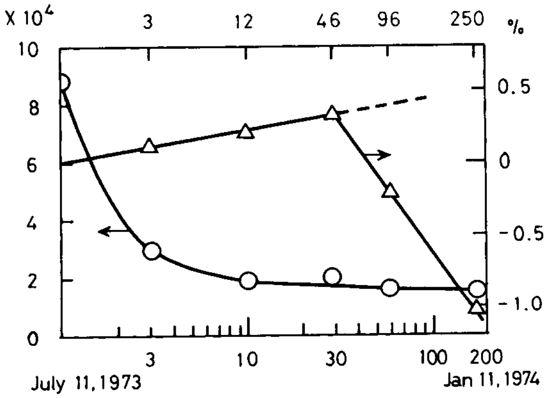


Fig. 1. Weight change and molecular weight vs irradiation time for St–MVK 70/30 copolymers: upper abscissa, irradiated energy (kJ/cm^2); lower abscissa, irradiation time (days); left ordinate, molecular weight; right ordinate, weight change.

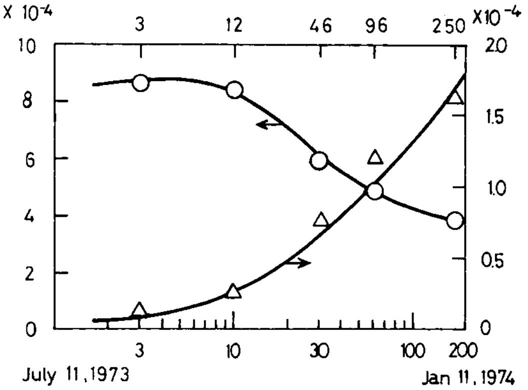


Fig. 2. Acid and hydroxyl values vs irradiation time for St–MVK 70/30 copolymers: upper abscissa, irradiated energy (kJ/cm^2); lower abscissa, irradiation time (days); left ordinate, hydroxyl value (moles/g polymer); right ordinate, acid value (moles/g polymer).

angle of 45° (Fig. 3). The existence of carbonyl and carboxylic compounds was suggested. By extending the absorption curves and comparing the area surrounded by the curves and the straight line (Fig. 3), the increase in the —C=O absorption could be visualized as the absorption ratio at 1700 and 1500 cm^{-1} (Fig. 4).

NMR signals for irradiated and unirradiated samples are shown in Figure 5. In irradiated samples, an additional smaller signal appeared at δ 8.0. This signal was considered attributable to the change in ring current by —COCH$_3$ groups, and the formation of acetophenone groups was suggested.[6] The existence of acetophenone in the irradiated samples was actually confirmed by GC mass spectroscopy of the expelled gases in the pyrolyzer, of the distilled liquid under reduced pressure, and of the fractions separated by liquid chromatography. The amount of acetophenone increased with the irradiation time (Fig. 6), where acetic acid, another irradiation product, is also shown on the right-side ordinate in the scale as the ratio against the remaining solvent, toluene.

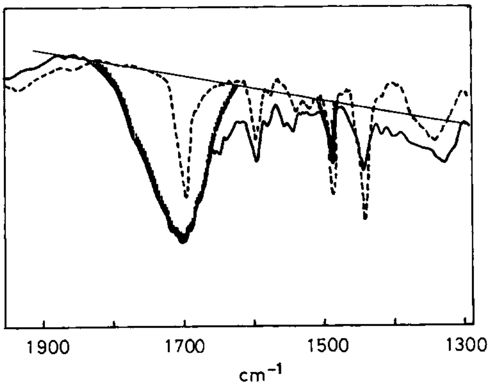


Fig. 3. Infrared spectra for St–MVK 70/30 copolymer by ATR method: (—) after irradiation (SA-5); (- - -) before irradiation (SA-0).

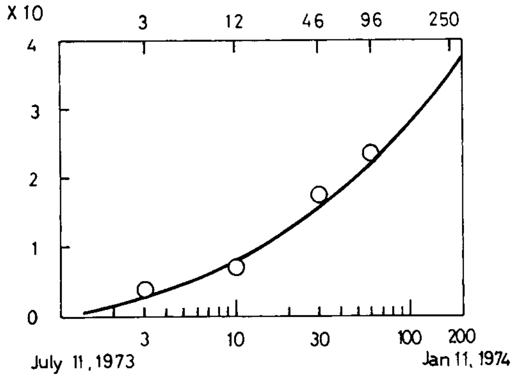


Fig. 4. C=O absorption intensities vs irradiation time for St–MVK 70/30 copolymers: upper abscissa, irradiated energy (kJ/cm^2); lower abscissa, irradiation time (days); ordinate, IR absorption ratio, 1700 cm^{-1}/1500 cm^{-1}.

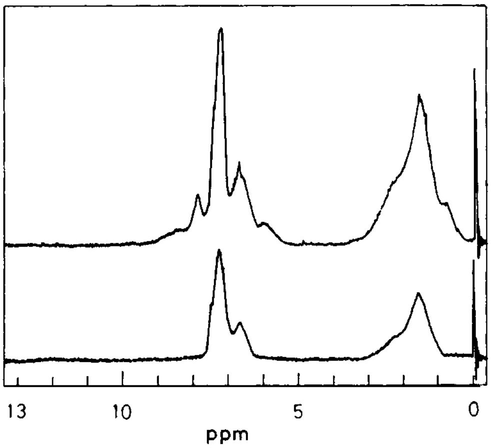


Fig. 5. NMR spectra for St–MVK 70/30 copolymers: upper, after irradiation (SA-2); lower, before irradiation (SA-0).

Low Molecular Weight Degradates and the Effect of Oxygen

Styrene–methyl vinyl ketone copolymers of molar composition 70/30 were irradiated either in atmospheric conditions or in a Pyrex or a quartz vessel filled with argon. Degraded products were analyzed by GC mass spectrometer using a Tenax column (3 mm ϕ × 1 m, 100°–200°C). The degradates were either charged in the pyrolyzer to be heated at 100°–130°C or subjected to distillation at 100°C and 10^{-3} mm Hg to obtain the liquid which was later injected into the chromatographic column. A number of total ion current curves were obtained by GC mass spectroscopy (Fig. 7). The sample irradiated under atmospheric conditions (SA-5) was confirmed to contain water, carbon dioxide, acetic acid, acetophenone, and benzoic acid as main low molecular weight products. Formic acid, acetone, propionic acid, benzene, toluene, phenol, benzaldehyde, and benzyl alcohol were found in smaller contents.

The main products were also separated and identified by liquid chromatography (Fig. 8). In the figure, the solid line indicates UV absorption and the

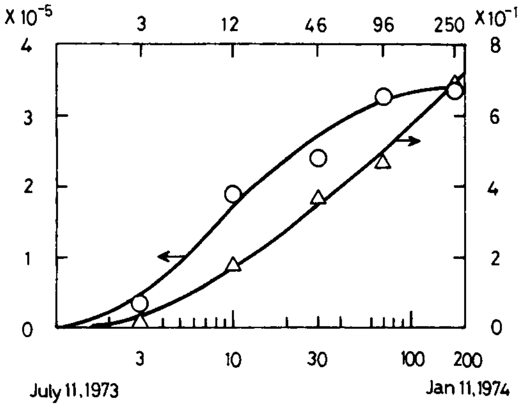


Fig. 6. Yields of acetophenone and acetic acid vs irradiation time for St–MVK 70/30 copolymers: upper abscissa, irradiated energy (kJ/cm^2); lower abscissa, irradiation time (days); left ordinate, acetophenone (moles/g polymer); right ordinate, acetic acid (relative value).

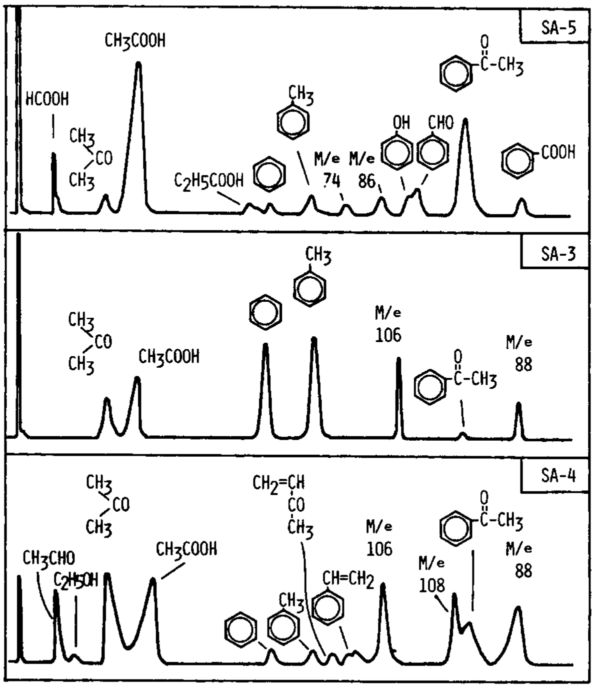


Fig. 7. Total ion current curves for degraded products from St–MVK 70/30 copolymers; Tenax GC column, 100°–200°C: SA-5 and SA-3, liquid condensed in a cold trap; SA-4, gas expelled at 130°C in pyrolyzer.

broken line, the refractive index. The former half of the RI curve has been omitted since it was almost identical to the UV curve. Here, A is a degraded polymer with a molecular weight of ca. 20,000, and D is acetophenone; E is benzoic acid and F, benzoic acid and toluene. In G, toluene and phenol were found by GC mass spectroscopic analysis of the concentrate of the fraction. H, I, and J in the RI curve are, respectively, acetic acid, ethanol, and water. Materials in B and C were nonvolatile, and their molecular weights would be close to 320 and

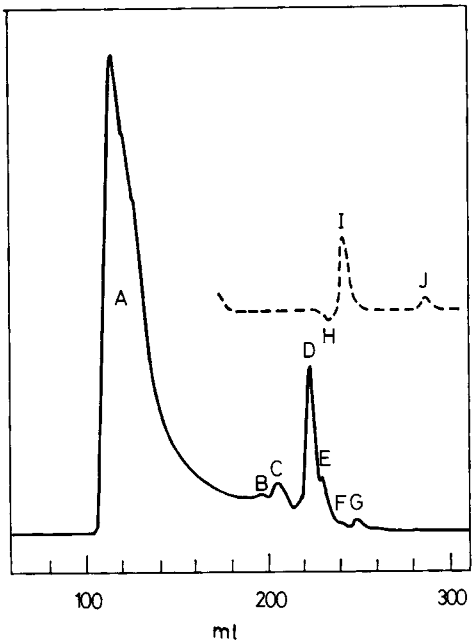


Fig. 8. Liquid chromatogram for the degradates from St–MVK 70/30 copolymer; SA-5 3% $CHCl_3$ solution, 2 ml/min, Jaigel column: (—) UV; (- - -) RI.

250, respectively. The peaks B through G were observed only in the UV curve.

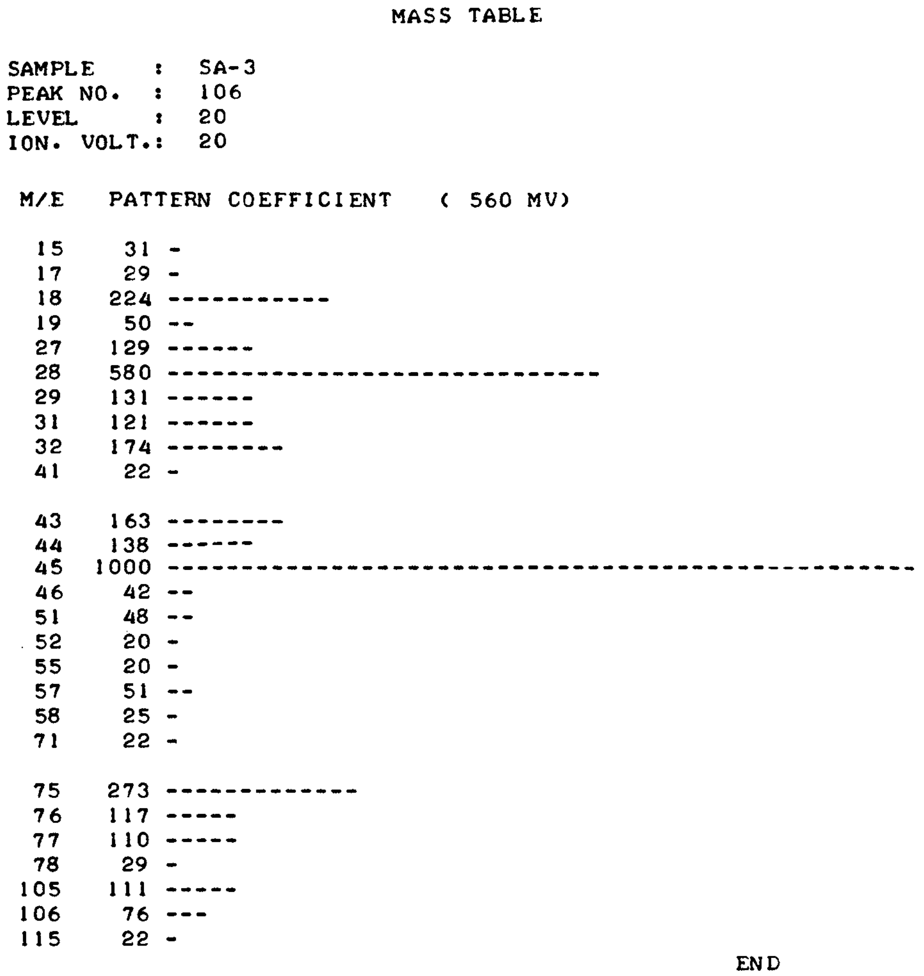
The formation of acetic acid and acetophenone was slight in SA-3 where irradiation was done in argon (Fig. 7). Some nonoxidative products, of which parent peaks were 106 and 88, were found (Figs. 9 and 10). Toluene and benzene were found in all samples. Since they were found in unirradiated sample SA-0 (Fig. 11), it can be said that the solvents for the preparation of the polymers still remained.

Effect of Methyl Vinyl Ketone Content

The content of methyl vinyl ketone in practical photodegradable plastics should be only a few percent. Therefore, styrene–methyl vinyl ketone copolymers of lower methyl vinyl ketone content (90/10) were also analyzed in the same way. The amount of the produced acetic acid was 0.17 μl/g for 90/10 copolymer SB-1, much less than 1.3 μl/g for 70/30 copolymer SA-5. The species of the low molecular weight compounds, however, were almost the same regardless of the methyl vinyl ketone content.

Fluorescent Compounds in the Degradates

Photodegraded copolymers of styrene and methyl vinyl ketone showed slight fluorescence. To separate the fluorescent compounds, powders of SA-1 were dissolved in benzene, applied on 20 × 20 cm thin-layer chromatographic plates of Wako Gel B-5 (silica gel), and developed with a benzene–dioxane (1:15) mixed



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                         MASS TABLE

SAMPLE     :  SA-3
PEAK NO.   :  106
LEVEL      :  20
ION. VOLT.:   20

 M/E   PATTERN COEFFICIENT    ( 560 MV)

  15     31 -
  17     29 -
  18    224 -----------
  19     50 --
  27    129 ------
  28    580 -----------------------------
  29    131 ------
  31    121 ------
  32    174 --------
  41     22 -

  43    163 --------
  44    138 ------
  45   1000 -----------------------------------------------------
  46     42 --
  51     48 --
  52     20 -
  55     20 -
  57     51 --
  58     25 -
  71     22 -

  75    273 -------------
  76    117 -----
  77    110 -----
  78     29 -
 105    111 -----
 106     76 ---
 115     22 -
                                                END
```

Fig. 9. Fragmentation pattern for the substances in $m/e = 106$ peak for St–MVK 70/30 copolymer SA-3.

solution. Four spots were obtained at the R_f values of 0.3, 0.4, 0.45, and 0.7 in addition to the substance remaining at the original point. The substance at each spot was scratched off and collected from 18 plates. The substances at $R_f = 0.4$ and $R_f = 0.45$ were combined as the separation was insufficient. Four fractions thus obtained were dissolved in acetone–methanol 10:1 solution, filtered, concentrated to dryness, and measured for fluorescence in 0.5% dioxane solution. Complicated fluorescence curves were obtained; the simplest ones for the substance remaining at the original point are shown in Figure 12.

Ternary Copolymers of Styrene–Methyl Vinyl Ketone–2,6-Di-*t*-butyl-4-acroylaminomethylphenol

The incorporation of 2,6-di-*t*-butyl-4-acroylaminomethylphenol (TBAP) is known to control the degradation velocity of vinyl ketone copolymers.[4] In this

```
                          MASS TABLE

SAMPLE     :  SA-3
PEAK NO.   :  88
LEVEL      :  20
ION. VOLT.:   20

 M/E    PATTERN COEFFICIENT    ( 270 MV)

  15     41 --
  16     39 -
  17     59 --
  18    303 ---------------
  27     23 -
  28   1000 --------------------------------------------------
  29     74 ---
  31     33 -
  32    435 ---------------------
  40     35 -

  41     30 -
  42     35 -
  43    942 -----------------------------------------------
  44    278 -------------
  45    594 -----------------------------
  55     33 -
  57     93 ----
  58     96 ----
  69     35 -
  71     36 -

  73     36 -
  75     91 ----
  77     36 -
  87    359 -----------------
  88     91 ----
  95     23 -
 115     33 -
 118     25 -
                                                END
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Fig. 10. Fragmentation pattern for the substances in *m/e* = 88 peak for St–MVK 70/30 copolymer SA-3.

respect, ternary copolymers of the molar composition PSt 89.5–MVK 10–TBAP 0.5 were irradiated and analyzed in the same way. The products of the irradiation were almost identical with those of the binary copolymers, except that isobutene was found by GC mass spectrometry (Fig. 11, SC-1).

Methyl Methacrylate–Methyl Vinyl Ketone Copolymers

Copolymers of methyl methacrylate and methyl vinyl ketone with molar composition 75/25 were irradiated and analyzed using the same method as styrene copolymers. The number of the low molecular weight compounds found in the degradates was small compared with those found in styrene copolymers. The MA-1 main products were acetic acid and methyl methacrylate monomer (Fig. 13). A broad peak, suggestive of the decomposition of the sample in the chromatographic column, was observed. The mass-spectroscopic fragmentation patterns for this peak are given in Figure 14.

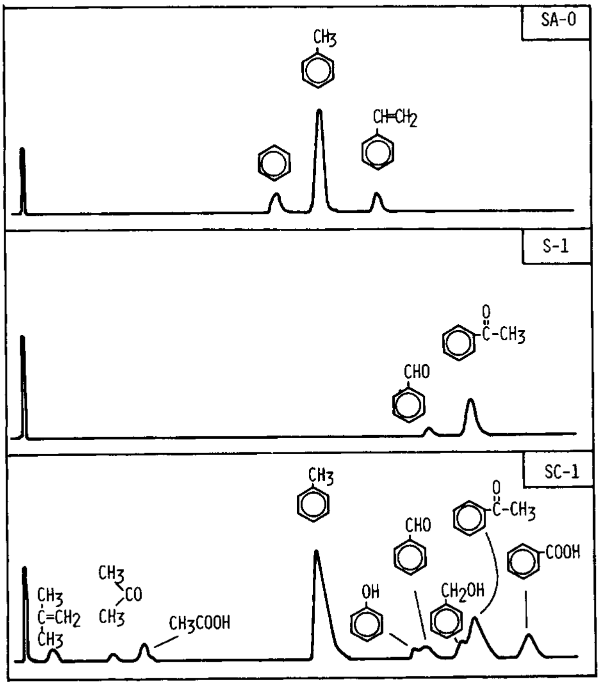


Fig. 11. Total ion current curves for unirradiated St–MVK 70/30 copolymer (SA-0), irradiated polystyrene (S-1), and irradiated St–MVK–TBAP terpolymer (SC-1). Tenax GC column, 100°–200°C, gases expelled at 110°C in the pyrolyzer.

Propylene Homopolymers

Polypropylene samples, after two and three years of outdoor weathering at Naha, became brittle and emitted an irritating odor. Vacuum distillation of these samples for 3 hr at 100°C at 10^{-3} mm Hg gave 4.9 μl/g (E-1) and 12 μl/g (E-2) liquid in a trap cooled to liquid nitrogen temperature. The liquid discolored to a dark brown upon standing. The liquid was confirmed to contain water and carboxylic acids up to propionic by GC mass spectroscopy (Fig. 13, E-1). The amount of the produced acetic acid, the most abundant species except water from E-1, was 1.2 μl/g. The liquid from E-2 (Fig. 15) gave nearly the same total ion current curves except that it showed additional peaks for tetrahydrofuran and 1-hydroxy-2-propanone. NMR signals for the neat liquid from E-2 were at δ 2.45 (*s*), 1.60 (*q*), and 8.92 (*s*) (intensities of the latter two signals were less than a tenth of the former), in addition to a very strong one at 5.40 which was assigned to the proton of water. The signals at δ 2.45 and 8.92 were assigned respectively to methyl protons of acetic acid and the formyl proton of formic acid. The IR spectra for the liquid from E-2 are shown in Figure 15. The —C=O stretching absorptions between 1700 and 1800 cm^{-1} showed two peaks. When the sample was treated with $LiAlH_4$ for 1.5 hr at the boiling temperature of tetrahydrofuran, the peak at 1770 cm^{-1} disappeared and the absorption at 1710 cm^{-1} decreased.

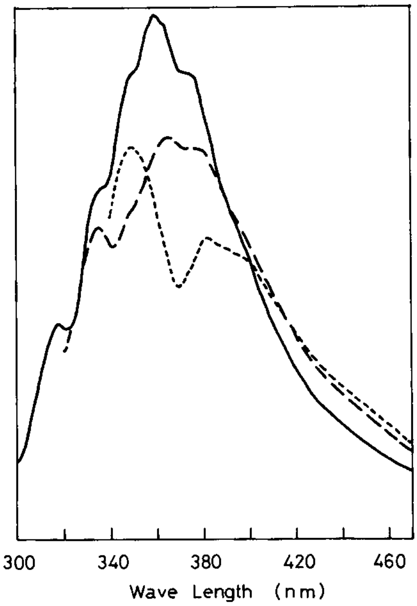


Fig. 12. Fluorescence for the degradates from St–MVK 70/30 copolymer (SA-1): (—) excitation 300 nm; (– – – –) excitation 320 nm; (- - -) excitation 340 nm; abscissa, wavelength (nm).

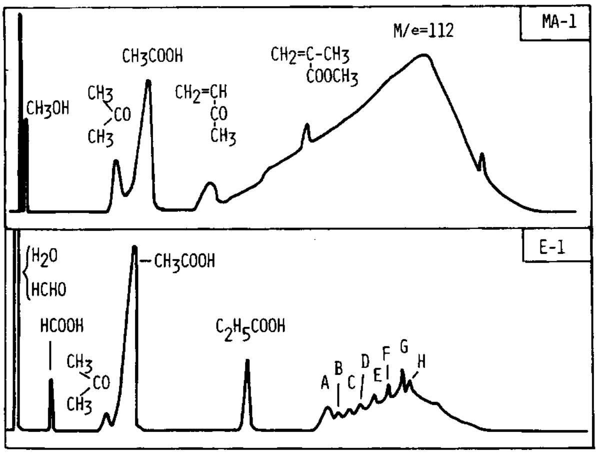
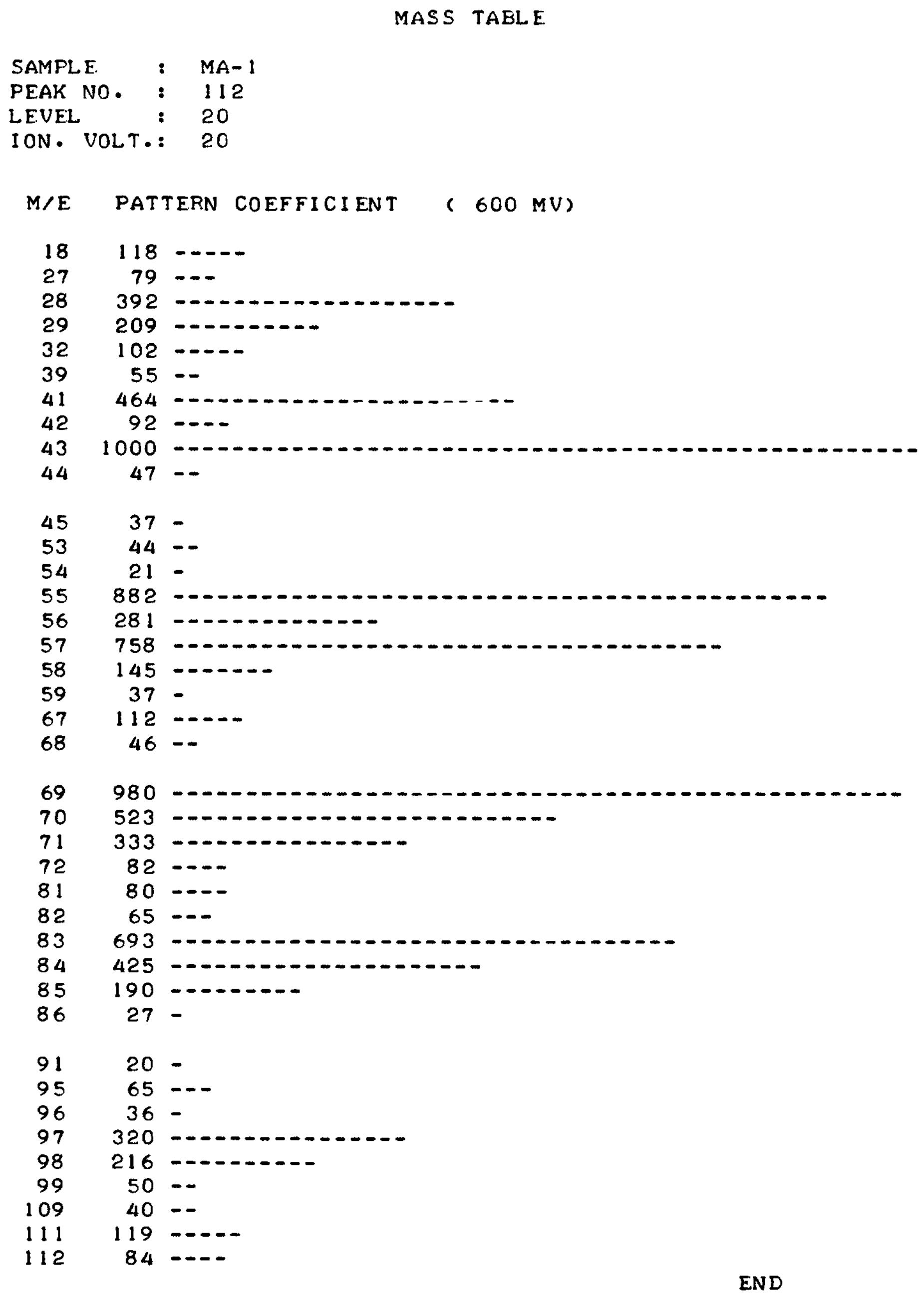


Fig. 13. Total ion current curves for degraded products from MMA–MVK 75/25 copolymer (MA-1) and polypropylene (E-1); Tenax GC column, 100°–250°C: MA-1, gas expelled at 110°C in pyrolyzer; E-1, liquid condensed in a cold trap.



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                        MASS TABLE

SAMPLE     :  MA-1
PEAK NO.   :  112
LEVEL      :  20
ION. VOLT.:   20

 M/E   PATTERN COEFFICIENT   ( 600 MV)

  18    118 -----
  27     79 ---
  28    392 -------------------
  29    209 ----------
  32    102 -----
  39     55 --
  41    464 -----------------------
  42     92 ----
  43   1000 --------------------------------------------------
  44     47 --

  45     37 -
  53     44 --
  54     21 -
  55    882 --------------------------------------------
  56    281 --------------
  57    758 -------------------------------------
  58    145 -------
  59     37 -
  67    112 -----
  68     46 --

  69    980 -------------------------------------------------
  70    523 --------------------------
  71    333 ----------------
  72     82 ----
  81     80 ----
  82     65 ---
  83    693 ----------------------------------
  84    425 ---------------------
  85    190 ---------
  86     27 -

  91     20 -
  95     65 ---
  96     36 -
  97    320 ----------------
  98    216 ----------
  99     50 --
 109     40 --
 111    119 -----
 112     84 ----
                                                   END
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Fig. 14. Fragmentation pattern for the substances in $m/e = 112$ peak for MMA–MVK 75/25 copolymer MA-1.

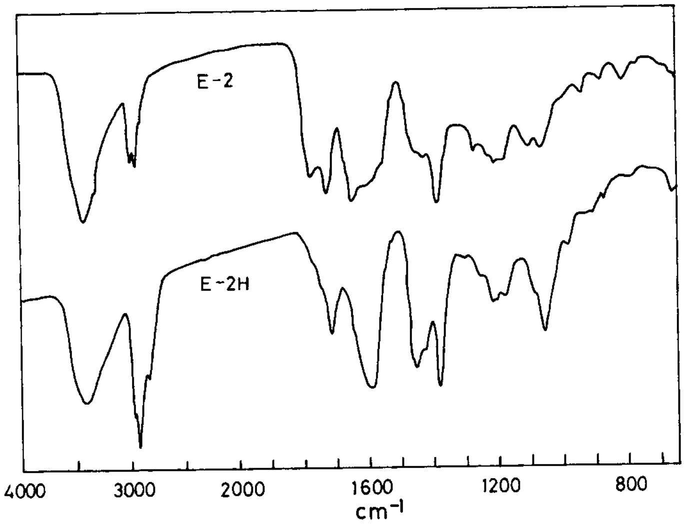
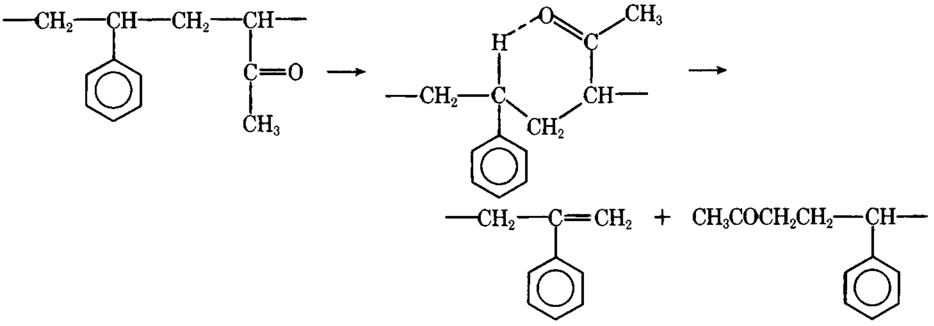


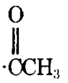
Fig. 15. Infrared spectra for the liquid obtained from degraded polypropylene E-2: E-2, original; E-2H, after treatment with $LiAlH_4$ for 1.5 hr.

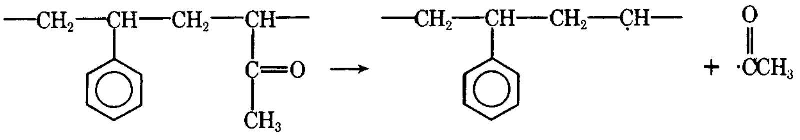
DISCUSSION

The polymers with methyl ketone side groups degrade by irradiation according to a Norrish Type II reaction:

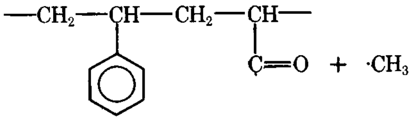


In addition, the Norrish Type I reaction also proceeds to give

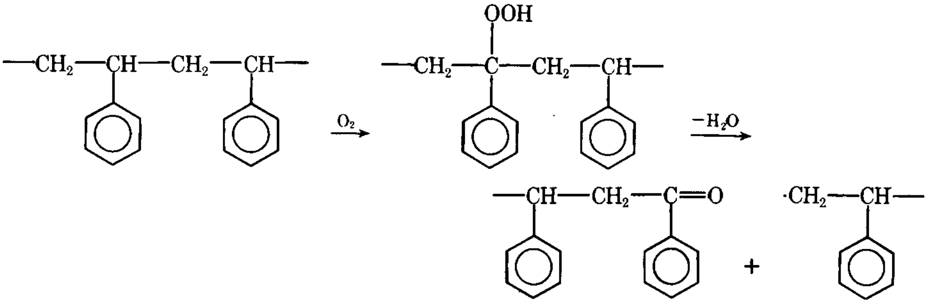

$\cdot\overset{O}{\overset{\|}{C}}CH_3$ and $\cdot CH_3$ radicals,



or

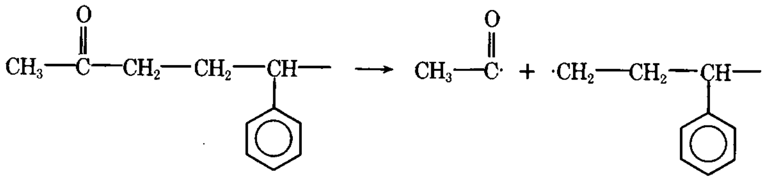


Under atmospheric conditions, formation of hydroperoxide on tertiary carbon atoms is inevitable and leads to the scission of polymer chains:

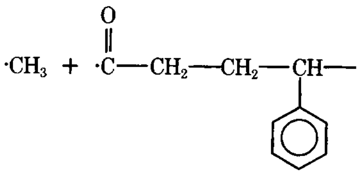


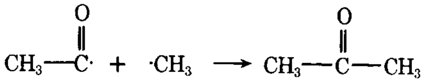
The photodegraded polymers are therefore considered low molecular weight polymers with broad molecular weight distribution which have hydroperoxide, hydroxyl, carboxyl, carbonyl groups, etc., and olefinic double bonds. Some of these functional groups have been quantitatively analyzed by wet chemical methods as well as by IR. With progress of irradiation, low molecular weight polymers are further degraded and oxidized to acetic acid, acetophenone, benzoic acid, etc.

Acetone was obtained more from copolymers with large molar composition of methyl vinyl ketone and less by the irradiation under atmospheric conditions rather than in argon. Hence, the degradation process to acetone is considered attributable to the combination of methyl and acetoxy radicals produced by either the Norrish Type I reaction or by the products from the following reactions:



or

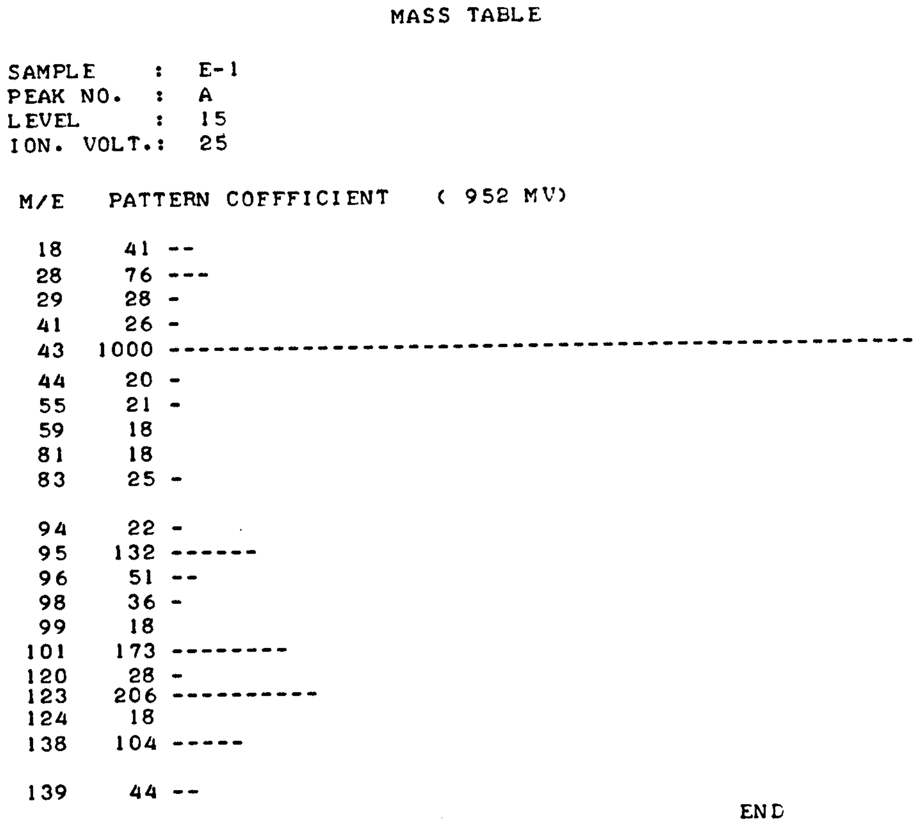




$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}\cdot + \cdot CH_3 \longrightarrow CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

Under atmospheric conditions, acetone is further oxidized to acetic acid.

Acetophenone-type endgroups have been reported in homopolystyrene,[6] and acetophenone was observed by pyrolytic GC mass spectrometry of the irradiated surface of homopolystyrene (Fig. 11, S-1). The acetophenone found in every styrene–methyl vinyl ketone copolymer is, therefore, brought about both from the methyl vinyl ketone component and via hydroperoxides. The formation of benzoic acid and partly oxidized products, benzaldehyde and benzyl alcohol,



```
                              MASS TABLE

SAMPLE      :  E-1
PEAK NO.    :  A
LEVEL       :  15
ION. VOLT.:    25

 M/E    PATTERN COFFFICIENT    ( 952 MV)

  18     41 --
  28     76 ---
  29     28 -
  41     26 -
  43   1000 --------------------------------------------------
  44     20 -
  55     21 -
  59     18
  81     18
  83     25 -

  94     22 -
  95    132 ------
  96     51 --
  98     36 -
  99     18
 101    173 --------
 120     28 -
 123    206 ----------
 124     18
 138    104 -----

 139     44 --
                                                    END
```

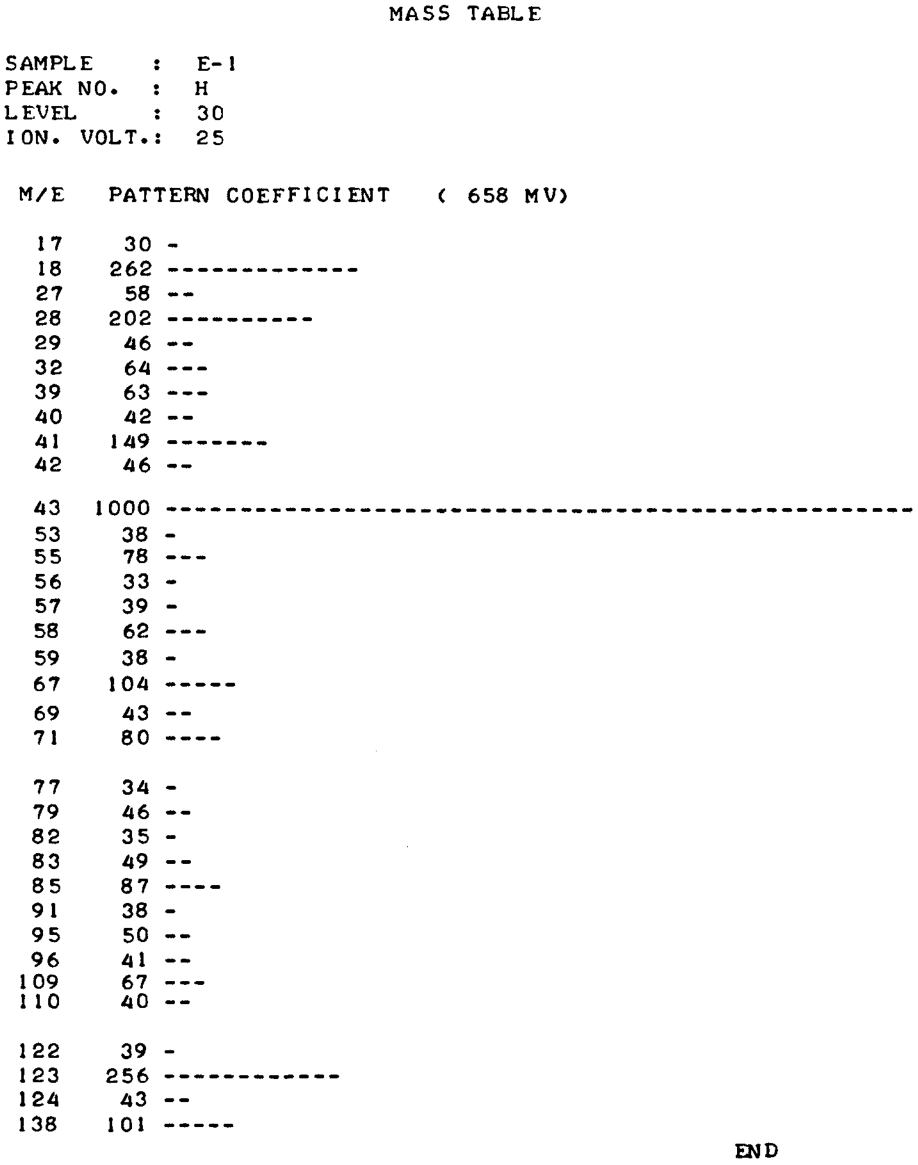
Fig. 16. Fragmentation pattern for the substances in peak A for polypropylene E-1.

is understandable, but the formation of phenol is obscure. Hydroxyl radicals, as the result of the decomposition of hydroperoxides, may attack the phenyl radical from polystyrene. As cyclopentadienone derivatives are produced by dehydration cyclization of poly(methyl vinyl ketone),[7] the conversion of these compounds to phenol cannot be eliminated.

From the degradates of terpolymer incorporated with 2,6-di-*t*-butyl-4-acroylaminomethylphenol (TBAP), substituted phenol was not detected, but isobutene, a scission product at the *t*-butyl group, was detected (Fig. 11, SC-1).

Fluorescent compounds isolated from the degradates of styrene–methyl vinyl ketone copolymers were only found in trace amounts, and further analysis of these compounds was impossible. The fluorescence curves (Fig. 12) were entirely different from the curves for the substances B and C in liquid chromatogram (Fig. 8).

The degradation of polypropylene initiates from the carbonyl groups introduced by the decomposition of hydroperoxides, which have been produced by the air oxidation during polymerization or processing,[8] and is considered to proceed in a similar manner as in styrene copolymer. Contrary to polystyrene and poly(methyl methacrylate), polypropylene has a tendency to crosslink and become brittle when it is irradiated. During the course of this crosslinking, however, various kinds of low molecular weight compounds are produced (Fig.



```
                          MASS TABLE

SAMPLE     :  E-1
PEAK NO.   :  H
LEVEL      :  30
ION. VOLT.:   25

 M/E   PATTERN COEFFICIENT   ( 658 MV)

  17     30 -
  18    262 -------------
  27     58 --
  28    202 ----------
  29     46 --
  32     64 ---
  39     63 ---
  40     42 --
  41    149 -------
  42     46 --

  43   1000 --------------------------------------------------
  53     38 -
  55     78 ---
  56     33 -
  57     39 -
  58     62 ---
  59     38 -
  67    104 -----
  69     43 --
  71     80 ----

  77     34 -
  79     46 --
  82     35 -
  83     49 --
  85     87 ----
  91     38 -
  95     50 --
  96     41 --
 109     67 ---
 110     40 --

 122     39 -
 123    256 ------------
 124     43 --
 138    101 -----
                                                    END
```

Fig. 17. Fragmentation pattern for the substances in peak H for polypropylene E-1.

13, E-1). Main products are aliphatic acids; the most abundant one is acetic acid. GC mass-spectroscopic analysis of the liquid degradates showed some other substances. Identification is still in progress.

The total ion current became larger after separating the propionic acid. It is evident that the small peaks A through H overlap with big broad peaks (Fig. 13, E-1). The fragmentation pattern of this big peak showed a strong base peak at *m*/*e* = 43 (Figs. 16 and 17). From the analysis of the fragmentation patterns and from the fact that C═O absorption was observed in both the original extracts and the sample treated with $LiAlH_4$ for 1.5 hr, it is presumed that some complexes or precursors of compounds with terminal acetyl group(s) exist most likely in the liquid from degraded polypropylene. The $CH_3C{=}O$ fragment is generated slowly in the Tenax column. The peaks A, B, C, and F (Fig. 13, E-1) were tentatively assigned as unsaturated ketone $C_9H_{14}O$, methyl propenyl ketone, a mixture of mesityl oxide and acetyl acetone, and 2,5-hexadione, respectively.

CONCLUSIONS

Photodegraded products of styrene–methyl vinyl ketone copolymers, methyl methacrylate–methyl vinyl ketone copolymers, and terpolymers of styrene series have been analyzed along with the degradates of the styrene and propylene homopolymers. Most of the photodegraded products are low molecular weight polymers with various functional groups. More than ten low molecular weight compounds were identified from the degradates. In many cases, the most abundant species was acetic acid. The degradates of polystyrene copolymers were found to include fluorescent substances. The degradates from styrene–methyl vinyl ketone–TBAP terpolymers and propylene homopolymer were sent to the Nomura Research Institute at Kamakura for the evaluation of toxicity, and no harmful results have been obtained.[9]

The authors wish to thank Mr. T. Shirota for arranging research facilities, to Dr. M. Kato for discussing the results, to Mr. M. Yamazaki of Japan Zeon Co. and Mr. T. Yamamoto of Mitsubishi-Monsanto Chem. Co. for their cooperation in the preparation of a portion of the samples, to Mr. Y. Yoshikawa for the weather-meter experiment, and to Miss A. Shigehisa, Mrs. K. Naomi, and Mr. K. Nakamura for their aid in the analyses.

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Received October 29, 1976