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## Effect of Acetylene on the γ-Ray Crosslinking Polymerization of Various Kinds of Acrylic Monomers

Miyuki Hagiwara[a]; Tsukasa Kagiya[a]; Kunio Araki[a]; Tsutomu Kagiya[ab]

[a] Japan Atomic Energy Research Institute Takasaki Radiation Chemistry Research Establishment, Takasakl, Gunma, Japan [b] Faculty of Engineering, Kyoto University, Kyoto, Japan

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# Effect of Acetylene on the γ-Ray Crosslinking Polymerization of Various Kinds of Acrylic Monomers

MIYUKI HAGIWARA, TSUKASA KAGIYA, KUNIO ARAKI, and
TSUTOMU KAGIYA*

Japan Atomic Energy Research Institute
Takasaki Radiation Chemistry Research Establishment
Takasaki, Gunma, Japan

## ABSTRACT

The γ-radiation-induced crosslinking polymerization of methyl
methacrylate (MMA), methacrylic acid (MAA), 2-hydroxyethyl
methacrylate (HEMA), methyl acrylate (MA), and acrylic acid
(AA) was carried out in bulk. The polymerization rates of
AA and HEMA were much larger than those of other monomers.
Acetylene had no influence on the polymerization rate in the
initial stage, and the rate was dependent only on the kinds of
monomers. In the absence of acetylene, gelation took place
in PMA, PAA, and PHEMA obtained at complete conversion,
but not in PMMA and PMAA. By the addition of acetylene,
complete gelation of PMMA was observed, but no gel forma-
tion was observed for PMAA. Volume and weight swelling
ratios were measured for PMA, PAA, PHEMA, and PMMA
with complete gelation. It was found that by the addition of

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*Present address: Faculty of Engineering, Kyoto University,
Sakyo-ku, Kyoto, Japan.

acetylene the molar concentration of crosslinks increased as
much as about twice for PMA and PHEMA, and over about one
hundred times for PMMA AND PAA. The relation between
volume $S_v$ and weight swelling ratio $S_w$ was studied theoreti-
cally. $S_v$ was expressed by the the equation, $S_v = (\rho_p/\rho_s)S_w$
$+ (1 - \rho_p/\rho_s)$, as a function of $S_w$ and the densities of pure
polymer $(\rho_p)$ and solvent $(\rho_s)$ in swollen polymer.

# INTRODUCTION

Many studies on the $\gamma$-ray-induced polymerization of various kinds
of acrylic monomers have been published [1-4]. The recent effort
in the study of the $\gamma$-ray-induced crosslinking polymerization was
concerned with copolymerization by bifunctional monomers [5]. In
a previous paper, it was reported that network formation takes place
in the polymerization of MMA by the addition of acetylenic com-
pounds [6].
The purpose of this paper is to show the characteristic features
of the $\gamma$-ray crosslinking polymerization of various kinds of acrylic
monomers in the absence or presence of acetylene in bulk and to
discuss the effect of acetylene on the crosslinking polymerization.

# EXPERIMENTAL

## Reagents

Commercially available methyl methacrylate (MMA) and methyl
acrylate (MA) were treated with sodium hydroxide to remove inhibitor,
then purified by vacuum distillation under dry nitrogen. Methacrylic
acid (MAA), acrylic acid (AA), and 2-hydroxyethyl methacrylate
(HEMA) were purified by vacuum distillation under dry nitrogen
before use. Commercially available acetylene was used with only
deaeration.

## Polymerization Procedure

A portion of liquid acrylic monomer (2 ml) and gaseous acetylene
(16 ml) were introduced into a glass ampoule of 16 ml capacity. The

ampoule was sealed off at $10^{-4}$ Torr after removal of air by the alternate freezing and thawing technique with liquid nitrogen bath. Then, the ampoule was exposed to $\gamma$-ray from a cobalt-60 source at a dose rate of $6.3 \times 10^3$ rad/hr and at a temperature of $20 \pm 2°C$. The unreacted monomer was removed by evaporation under reduced pressure or by precipitating polymer with ethyl alcohol. The resulting polymer was then dried under vacuum and weighed.

## Gel Measurement

The resulting polymer was placed in a stainless steel basket and then extracted with boiling acetone (PMMA, PMA), ethyl alcohol (PHEMA), or water (PAA, PMAA) for 20 hr to remove the soluble part of the polymer. The gel fraction was determined as the percentage weight fraction of the residue.

## Swelling Ratio

The volume $(S_V)$ and weight $(S_w)$ swelling ratios were obtained from Eqs. (1) and (2):

$$S_V = V/V_0 \tag{1}$$

$$S_w = W/W_0 \tag{2}$$

where $V_0$ and $W_0$ are the volume and weight, respectively, of the original sample (about 5 mm $\times$ 5 mm $\times$ 5 mm). V and W are the volume and weight of the swollen sample after immersion in solvent for 20 hr at its boiling temperature.

## RESULTS AND DISCUSSION

## Polymerization Rate

The polymerization of various kinds of acrylic monomers was carried out in the absence or presence of acetylene as shown in Fig. 1. The conversion of monomer to polymer is proportional to irradiation time at the initial stage in all cases. The polymerization rate is dependent only on the kind of acrylic monomer; acetylene has no influence on the polymerization rate.
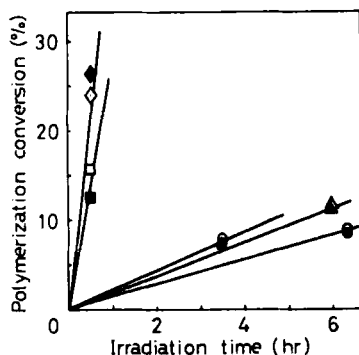
FIG. 1. Polymerization conversion-irradiation time curves for
the crosslinking polymerization of various acrylic monomers: ( o )
MMA; ( ● ) MMA-Ac; ( △ ) MA; ( ▲ ) MA-Ac; ( ◊ ) MAA; ( ◆ ) MAA-Ac;
( ◊ ) AA; ( ◆ ) AA-Ac; ( □ ) HEMA; ( ■ ) HEMA-Ac. Ac indicates that
the polymerization was carried out in the presence of acetylene.
Conditions: dose rate, $6.3 \times 10^3$ rad/hr; temperature, $20 \pm 2°$C.

    The order of polymerization rate is as follows: AA, 50%/hr;
HEMA, 29%/hr; MAA, 2.2%/hr; MA, 1.9%/hr; MMA, 1.5%/hr. It is
apparent that the polymerization rates of monomers having a car-
boxy or hydroxy group (AA, MAA, HEMA) as substituent are larger
than those of monomers having a methyl ester group (MA, MMA).
    On the other hand, as can be seen in Table 1, gelation by cross-
linking is observed even in the absence of acetylene at the initial
stage below 10% conversion in the polymerization of AA and HEMA,
while this is not the case with MMA, MA, and MAA. These results
suggest that the higher rate of polymerization of AA and HEMA
may be caused by the Trommsdorff effect due to gelation.

Crosslinking and Gelation

    The degree of gelation and swelling ratio of the polymer obtained
in the absence of acetylene at complete conversion are shown in
Table 2. Acrylic polymers such as PMA and PAA give 100% gel
fraction, while methacrylic polymers such as PMMA and PMAA do
not give any gel fraction except PHEMA.
    It is known that in the polymerization of MA and AA, the growing
chain radical abstracts the α-hydrogen, $-CH_2-CH(COOR)-$, of the

TABLE 1. Gel Fraction of Polymers Obtained in the Initial Stage below 10% Conversion[a]

| Polymer | Without acetylene | | With acetylene | |
|---|---|---|---|---|
| | Conversion (%) | Gel fraction (%) | Conversion (%) | Gel fraction (%) |
| PMMA | 10 | 0 | 9 | 0 |
| PMAA | 10 | 0 | 10 | 0 |
| PHEMA | 10 | 100 | 10 | 100 |
| PMA | 9 | 2 | 8 | 1 |
| PAA | 10 | 32 | 9 | 30 |

[a]Dose rate, $6.3 \times 10^3$ rad/hr; temperature, $20 \pm 2°$ C.

TABLE 2. Gel Fraction and Swelling Ratios of the Polymers Obtained in the Absence of Acetylene at Complete Conversion

| Polymer | Gel fraction (%) | Swelling ratio[a] | |
|---|---|---|---|
| | | $S_v$ | $S_w$ |
| PMMA | 0 | — | — |
| PMAA | 0 | — | — |
| PHEMA | 100 | 1.93 | 1.97 |
| PMA | 100 | 7.59 | 5.63 |
| PAA | 100 | 21 | 14.97 |

[a]— denotes soluble in solvent; $S_v$ = volume swelling ratio; $S_w$ = weight swelling ratio.

resulting polymer to form a side-chain radical, $-CH_2-\overset{\cdot}{C}(COOR)-$ [7].
The grafting of monomer to the side-chain polymer radical is con-
sidered to lead to crosslinking by recombination. It is easy to under-
stand in the case of PHEMA that the hydrogen $+ CH_2-C(CH_3)-$
$(COO-CH_2-CH_2-OH)+$ at the $\alpha$- and $\beta$-position with respect to the
hydroxy group plays the same role as the $\alpha$-hydrogen of MA and
AA [8].

   When the $\alpha$-hydrogen of MA or AA is replaced by a methyl group
as in MMA and MAA, no gel formation is observed; however, on
addition of acetylene, complete gelation takes place in the polymeriza-
tion of MMA (Table 3). On the other hand, in the polymerization of
MAA, gelation is not observed even in the presence of acetylene.
Therefore, the methoxy group in the ester residue is also considered
to play an important role in gel formation.

## Crosslinking and Swelling Ratio

   The degree of swelling ratio of the polymer obtained at complete
gelation are also shown in Tables 2 and 3. The volume and weight
swelling ratios of PAA, PMA, and PHEMA obtained in the presence
of acetylene (Table 3) are smaller than those without acetylene
(Table 2).

   In order to study quantitatively the effect of acetylene on the degree
of crosslinking of these polymers, the molar concentration of cross-
links was evaluated (Table 4) according to the relation (3) between
swelling and the degree of crosslinks [9, 10].

TABLE 3.  Gel Fraction and Swelling Ratios of Polymers Obtained in
the Presence of Acetylene at Complete Conversion

| Polymer | Gel fraction (%) | Swelling ratio | |
|---------|------------------|----------------|----------------|
|         |                  | $S_v$          | $S_w$          |
| PMMA    | 100              | 3.17           | 2.67           |
| PMAA    | 2.2              | —              | —              |
| PHEMA   | 100              | 1.53           | 1.89           |
| PMA     | 100              | 6.22           | 4.25           |
| PAA     | 100              | 6.25           | 4.22           |

TABLE 4. Molar Concentration of Crosslinks of the Polymers Obtained in the Absence or Presence of Acetylene[a]

| Polymer | Additive[b] | $S_v$ | $1/S_v$ | $\chi$ | $v_1$ | $\phi \times 10^5$ (mole/ml) |
|---------|-------------|-------|---------|--------|-------|------------------------------|
| PMMA    | –           | ∞     | 0       | 0.48   | 73.9  | 0     |
|         | Ac          | 3.17  | 0.316   | 0.48   | 73.9  | 41.1  |
| PHEMA   | –           | 1.93  | 0.518   | 0.46   | 58.6  | 277.5 |
|         | Ac          | 1.53  | 0.653   | 0.46   | 58.6  | 661.8 |
| PMA     | –           | 7.59  | 0.133   | 0.50   | 73.9  | 2.7   |
|         | Ac          | 6.22  | 0.161   | 0.50   | 73.9  | 4.3   |
| PAA     | –           | ~21   | 0.047   | 0.50   | 18.1  | 0.25  |
|         | Ac          | 6.25  | 0.160   | 0.50   | 18.1  | 26.3  |

[a]Polymer-solvent systems: PMMA-acetone [12]; PHEMA-ethyl alcohol [11]; PMA-acetone [3]; PAA-water.
[b] –, in the absence of acetylene; Ac, in the presence of acetylene.

$$\ln(1 - v_2) + v_2 + \chi v_2^2 + (v_2^{1/2} - v_2/2)(\nu_e/V_0)v_1 = 0 \qquad (3)$$

Here $v_2$ is the volume fraction of the polymer in the swollen state and is equal to the reciprocal of the volume swelling ratio $(1/S_v)$,

$\chi$ is the polymer–solvent interaction parameter [11, 12], $V_0$ is the volume of the unswollen polymer, $v_1$ is the molar volume of the solvent, and $(\nu_e/V_0)$ is the number of moles of crosslinked units per unit volume (molar concentration of crosslinks). The value of the molar concentration of crosslinks was calculated from the swelling data (Tables 2 and 3) by the use of Eq. (4).

$$\phi = (\nu_e/V_0) = \frac{1}{v_1} \frac{-[\ln(1 - 1/S_v) + (1/S_v) + \chi(1/S_v)^2]}{[(1/S_v)^{1/3} - (1/S_v)/2]} \qquad (4)$$

The molar concentrations of crosslinks of the polymer obtained without acetylene $\phi_0$ and that $(\phi_a)$ with acetylene are shown in Table 5.

TABLE 5. Molar Concentrations of Crosslinks of Polymer Obtained
in the Presence and Absence of Acetylene

| Polymer | $\phi_0 \times 10^5$ | $\phi_a \times 10^5$ |
|---|---|---|
| PHEMA | 277.5 | 661.8 |
| PMA | 2.7 | 4.3 |
| PAA | 0.25 | 26.3 |
| PMMA | 0 | 41.1 |
| PMAA | 0 | 0 |

Hence, the magnification ratios $(\phi_a/\phi_0)$ of the molar concentration of
crosslinks are obtained as follows: PMMA, $\infty$; PAA, 105.2; PHEMA,
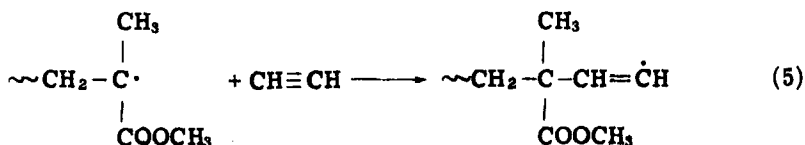2.4; PMA, 1.6; PMAA, 0.
    It is clear that the molar concentration of crosslinks increased
only about twice in PMA and PHEMA, however, over one hundred
fold in PMMA and PAA by the addition of acetylene.

## Mechanism of Crosslinking Polymerization

    As described above, hydrogen abstraction from the methoxy group
in PMA and from the hydroxyethyl group in PHEMA by the growing
radical may lead to crosslinking through the recombination of grafted
side chain radicals. Furthermore, it can also be estimated that in
the polymerization of MA and HEMA the rate of hydrogen abstrac-
tion by the growing chain-end radical and the successive recombina-
tion reaction are larger than those of the reactions in which acetylene
participates. Hence, acetylene has a small effect on the crosslinking
of these polymerization.
    On the other hand, from consideration of the fact that acetylene
markedly increased the concentration of crosslinks in PMMA but not
in PMAA, the crosslinking of PMMA is estimated to take place by
the mechanism shown in Eqs. (5)-(13).
Addition of acetylene:

$$\begin{array}{c} CH_3 \\ | \\ \sim CH_2-C\cdot \\ | \\ COOCH_3 \end{array} + CH\equiv CH \longrightarrow \begin{array}{c} CH_3 \\ | \\ \sim CH_2-C-CH=\overset{\cdot}{C}H \\ | \\ COOCH_3 \end{array} \qquad (5)$$

$$\sim CH_2-\underset{\underset{\{}{|}}{\overset{\overset{CH_3}{|}}{C}}-COO\dot{C}H_2 \ + \ CH\equiv CH \longrightarrow \ \sim CH_2-\underset{\underset{\{}{|}}{\overset{\overset{CH_3}{|}}{C}}-COOCH_2-CH=\dot{C}H \tag{6}$$
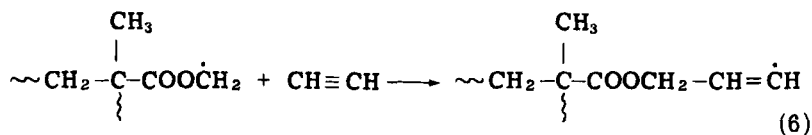
Hydrogen abstraction by vinyl radical from ester residue:

$$\sim CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH=\dot{C}H \ + \ H-CH_2OOC-\underset{\underset{\{}{\}}}{\overset{\overset{CH_3}{|}}{C}}-CH_2 \sim \longrightarrow$$

$$\sim CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH=CH_2 \ + \ \dot{C}H_2OOC-\underset{\underset{\}}{\overset{\overset{CH_3}{|}}{C}}-CH_2 \tag{7}$$

$$\sim CH_2-\underset{\underset{\}}{\overset{\overset{CH_3}{|}}{C}}-COOCH_2-CH=\dot{C}H \ + \ H-CH_2OOC-\underset{\underset{\}}{\overset{\overset{CH_3}{|}}{C}}-CH_2 \sim \longrightarrow$$

$$\sim CH_2-\underset{\underset{\}}{\overset{\overset{CH_3}{|}}{C}}-COOCH_2-CH=CH_2 \ + \ \dot{C}H_2OOC-\underset{\underset{\}}{\overset{\overset{CH_3}{|}}{C}}-CH_2 \sim \tag{8}$$
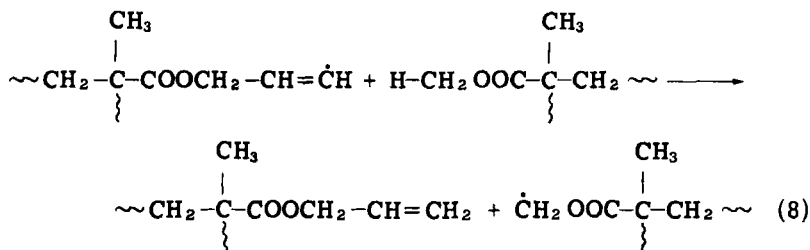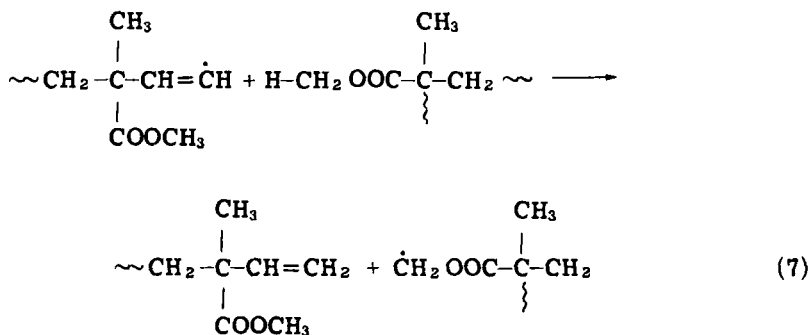
Grafting to side-chain radical:

$$\sim CH_2-\underset{\underset{\}}{\overset{\overset{CH_3}{|}}{C}}-COO\dot{C}H_2 \ + \ n(CH_2=\overset{\overset{CH_3}{|}}{C}-COOCH_3) \longrightarrow$$

$$\sim CH_2-\underset{\underset{\}}{\overset{\overset{CH_3}{|}}{C}}-COOCH_2-\left(CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\right)_{n-1}CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\cdot \tag{9}$$

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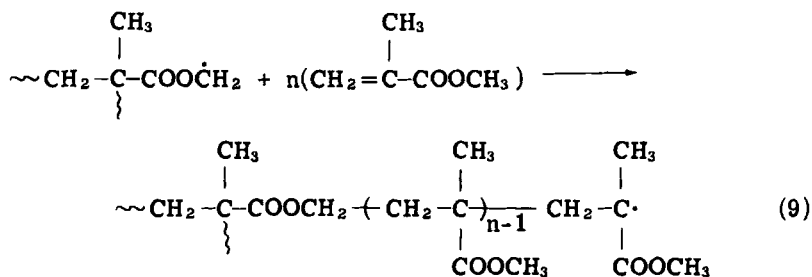
Long-chain formation leads to crosslinking:

$$\sim CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH=CH_2 \;+\; \dot{C}H_2\,OOC-\underset{\underset{\{}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2 \sim \longrightarrow$$

$$\sim CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\dot{C}H-CH_2-CH_2\,OOC-\underset{\underset{\{}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2 \sim \qquad (10)$$

$$\sim CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH=CH_2 \;+\; \cdot\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2 \sim \longrightarrow$$

$$\sim CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\dot{C}H-CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2 \sim \qquad (11)$$

$$\sim CH_2-\underset{\underset{COOCH_2-CH=CH_2}{|}}{\overset{\overset{CH_3}{|}}{C}}\sim \quad + \;\cdot\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2 \sim \longrightarrow$$

$$\sim CH_2-\underset{\underset{COOCH_2-\dot{C}H-CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2 \sim}{|}}{\overset{\overset{CH_3}{|}}{C}}\sim \qquad (12)$$

$$CH_3$$
$$|$$
$$\sim CH_2-C\sim \qquad\qquad + \ \overset{\cdot}{C}H_2\ OOC-\underset{\displaystyle\S}{\overset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}}-CH_2\sim \ \longrightarrow$$
$$|$$
$$COOCH_2-CH=CH_2$$

$$CH_3$$
$$|$$
$$\sim CH_2-C\sim \qquad\qquad\qquad\qquad CH_3$$
$$| \qquad\qquad\qquad\qquad\qquad |$$
$$COOCH_2-\overset{\cdot}{C}H-CH_2-CH_2\ OOC-\underset{\displaystyle\S}{C}-CH_2\sim \qquad (13)$$
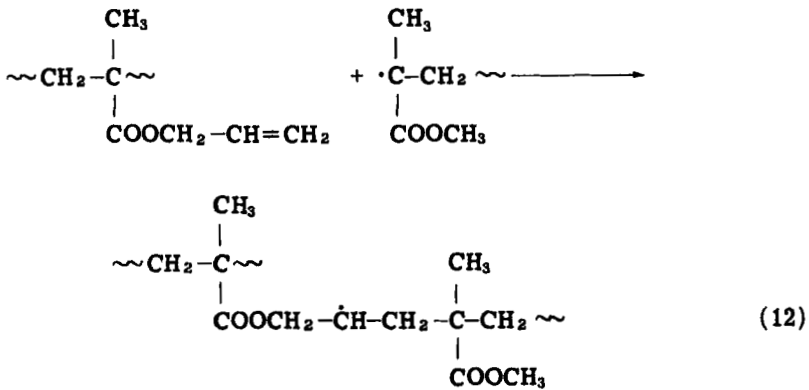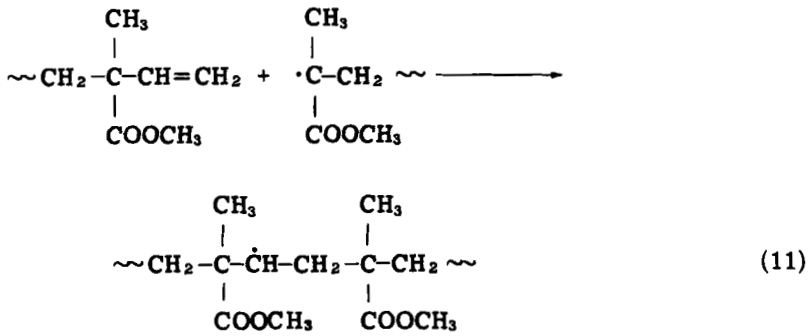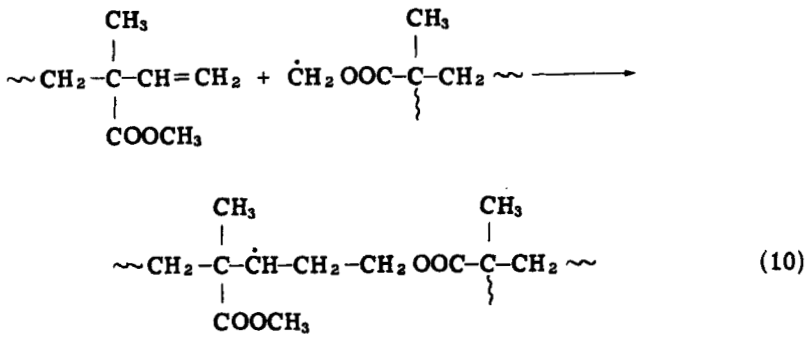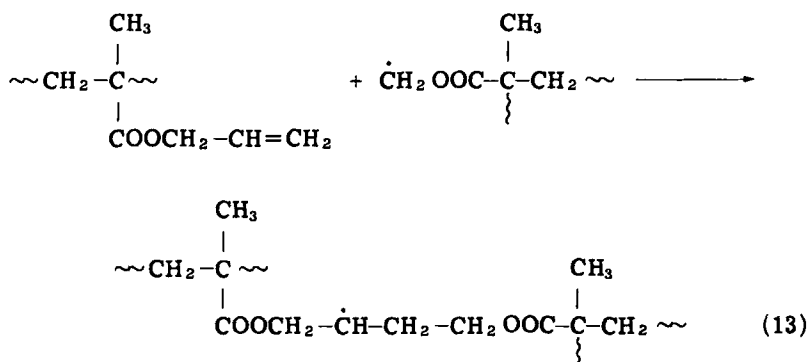
The vinyl radical formed by the addition of acetylene to the main-chain or side-chain radical [reactions (5), (6)] abstracts the hydrogen from the methoxy group on ester residue [reactions (7), (8)]. Then, crosslinking may result from combination between side-chain polymer radicals of various types formed by the reactions (5)-(13) and the addition of these radicals to vinyl unsaturation [reactions (10)-(13)].

In the case of PAA, the $\alpha$-hydrogen instead of the hydrogen in the methoxy group of PMMA may be abstracted by the vinyl radical, and crosslinking takes place by similar steps in PMMA. The fact that no crosslinking takes place in PMAA, even in the presence of acetylene, could be attributed to the absence of a hydrogen bonded sufficiently weakly to a carbon atom to be abstracted by vinyl radical.

## Relation Between Two Swelling Ratios

The volume swelling ratio increased with the weight swelling ratio, as shown in Fig. 1. An attempt has been made to obtain the relation between volume and weight swelling ratios as follows. Volume $(S_v)$ and weight $(S_w)$ swelling ratios are defined by Eqs. (14) and (15).

$$S_v = V/V_0 = (V_p + V_s)/V_p = 1 + V_s/V_p \qquad (14)$$

$$S_w = W/W_0 = (W_p + W_s)/W_p = 1 + W_s/W_p \qquad (15)$$

Here $V_p$, $V_s$, denote volumes of polymer and solvent, respectively, in swollen polymer, and $W_p$ and $W_s$ are weight of pure polymer and solvent, respectively. Based on the assumption of the volume additivity of polymer and solvent in the swollen state, Eq. (16) can be derived from Eqs. (14), (15), and the relations $V_p (=W_p/\rho_p)$ and $V_s (=W_s/\rho_s)$, where $\rho_p$ and $\rho_s$ denote densities of pure polymer and solvent, respectively.

$$S_v = (\rho_p/\rho_s)S_w + (1 - \rho_p/\rho_s) \qquad (16)$$

According to Eq. (16), $S_v$ can be predicted from the data of $S_w$. The line in Fig. 2 is a relation obtained from Eq. (16) with the use of the values $\rho_s = 0.79$ g/ml for acetone, $\rho_p = 1.20$ g/ml for PMMA. The theoretical line expresses well the relation between two kinds of swelling ratios observed for PMMA. The observed data for PMA-acetone, PAA-water, and PHEMA-ethyl alcohol also agree with this theoretical line. From these results, it can be concluded that swelling character is not affected by the addition of acetylene.
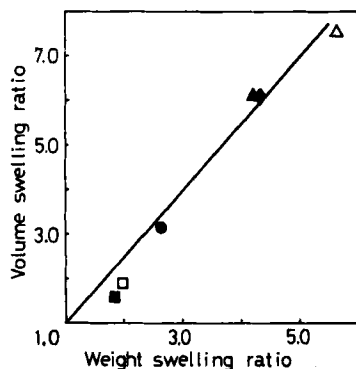


FIG. 2. Relationship between volume swelling ratios of the polymers obtained at complete gelation: ( ● ) PMMA-Ac; ( △ ) PMA; ( ▲ ) PMA-Ac; ( ◆ ) PAA-Ac; ( □ ) PHEMA; ( ■ ) PHEMA-Ac. Ac indicates that the polymer was obtained in the presence of acetylene.

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