

Temperature Effects on Positive Electron Resists Irradiated with Electron Beam and Deep-UV Light

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Synopsis

The exposure characteristics of poly(methyl methacrylate) (PMMA) and poly(methyl isopropenyl ketone) (PMIPK) were studied with electron beam and deep-UV light irradiation at different temperatures (20–160°C). The sensitivities and γ (contrast) values for electron beam irradiation show small temperature effects, but those for deep-UV light irradiation reveal relatively large temperature effects. The result in which γ (contrast) values for the electron beam irradiation as a whole are significantly larger than for the deep-UV light irradiation is related to the molecular weight dispersity of irradiated resists. The result in which γ (contrast) for PMMA is larger than that for PMIPK at given development conditions is also related to the molecular weight ratios of the original and irradiated resists. The thickness reduction and negative inversion (crosslinking) compete under a large dose of electron beam irradiation, but the latter is scarcely apparent under deep-UV irradiation. The PMMA sensitivity for deep-UV irradiation diminishes in O₂ gas flow compared with the irradiation in N₂ gas flow, but PMIPK sensitivity is not influenced by O₂. From these results, the different decomposition mechanisms are discussed.

INTRODUCTION

Resists, used for electron beam and X-ray lithography, are important materials for microfabrication. The developmental purposes of those resists are chiefly to raise the sensitivity and resolution and improvement in workability such as dry etching durability.

The factors of positive electron resists affecting the sensitivity and resolution have been studied in detail from the viewpoints of G (scission) and solubility rate with regard to polymer structure¹⁻³ and molecular weight and molecular weight distribution.^{4,5} In the radiation chemistry of polymers, different decomposition mechanisms are known for degradable polymer structures and irradiation sources. The decomposition mechanism influences the molecular parameters of decomposed polymers such as molecular weight distribution. Thus, the effects of these decomposition mechanisms on sensitivity and resolution are expected.

In the present work, positive resists are irradiated with different sources at different temperatures. They are then developed under the same conditions. From these results, the factors affecting the sensitivity and resolution are discussed.

EXPERIMENTAL

Materials

Poly(methyl methacrylate) (PMMA) and poly(methyl isopropenyl ketone) (PMIPK) were chosen as model positive resists. They are well known as electron beam resists^{6,7} and deep-UV resists.^{8,9} The PMMA used was commercially available Elvacite 2041 (du Pont). PMIPK was obtained by radical polymerization. Their molecular weights are shown in Table I.

Deep-UV light and electron beam were used to irradiate resist films on a thermally oxidized silicon wafer. Thin resist films were prepared using the spin-coating technique from a resist solution. In order to release the spinning solvent, they were baked in air for 30 min at a given temperature, shown in Table I.

Film thicknesses, measured by Talystep, were about 0.9 μm after baking for obtaining thickness-dose plots and about 1.6 μm for the GPC measurement of irradiated films.

Electron Beam and Deep-UV Light Irradiation

The silicon wafer that coated the resists was tightly contacted with the temperature-controlled sample stage.

The sample stage for the electron beam irradiation consisted of an insulated and flat copper plate with a Farady cup used for the measurement of electron beam current and a nichrome heater and thermocouple for the temperature control. The stage was equipped with the electron beam exposure system ESM-301 (ELIONIX). The accelerating voltage was 20 kv.

The sample stage for the deep-UV light irradiation also consisted of a flat copper plate in which a heat medium was circulated. The heat medium was maintained at constant temperature by a temperature-controlled bath. The deep-UV light source used was a deuterium spectral lamp D200 (ORIGINAL HANAU). The maximum output was 200 W. The spectral emission range was from 200 to 350 nm, where 220 nm gives the maximum emission intensity. The distance from the lamp to the resist surface was adjusted to 10 cm. The anode current applied was 1.5 A. Under these conditions, the light intensity estimated at the resist surface was 50–60 $\mu\text{W}/\text{cm}^2$. Most of the deep-UV light irradiations were carried out under nitrogen gas flow, except when carried out under oxygen gas flow.

TABLE I
Positive Resists and Developers

Resist	Molecular weight		Baking temp., ^a °C	Developer ^b
	M_w	M_w/M_n		
Poly(methyl methacrylate) (PMMA)	3.8×10^5	3.2	170	MIBK/IPA = 1/2
Poly(methylisopropenylketone) (PMIPK)	1.2×10^5	2.2	140	EtAc/IPA = 2/1

^a 30 min in air.

^b MIBK = Methyl isobutyl ketone, IPA = isopropyl alcohol, EtAc = ethyl acetate. Development conditions are dipping for 2 min at 20°C.

Development and GPC Measurement

In spite of the electron beam and deep-UV light irradiations, one developer was used for each resist. All developments were accomplished by dipping the sample for 2 min at 20°C in the developer shown in Table I.

The sensitivities for the electron beam irradiation were expressed by the minimum dose giving zero thickness after development. The sensitivities for the deep-UV light irradiation can be defined the same as for electron beam irradiation. However, the irradiation time giving zero thickness was used as the deep-UV sensitivity because the light intensity at the irradiated resist surface was constant during the irradiation.

The resolutions were estimated by γ (contrast), which was obtained from the thickness-dose plot shown in Figure 1.¹⁰

The positive resists used in the present work revealed character as negative resists by use of excess dose of electron beam irradiation. These inverting resists were developed in methyl isobutyl ketone at room temperature for 30 s.

The molecular weights of the resists in Table I and the resists irradiated with deep-UV light and γ -ray were determined by using HLC-802UR gel permeation chromatography (GPC) (TOYO SODA KOGYO) with tetrahydrofuran solvent.

γ -Ray irradiation to the powdery resists sealed in a glass tube under vacuum was carried out at room temperature for 40 days at dose ranging from 2–10 Mrad.

RESULTS AND DISCUSSION

Effects of Temperature on Sensitivity

Figures 2 and 3 show the sensitivities for the electron beam and deep-UV light irradiation as a function of temperature. Though the temperature raise gradually increases the sensitivities, the sensitivities for the electron beam irradiation reveal less dependence on temperature than those for the deep-UV light irradiation.

Polymer degradations which undergo the mechanism of random chain scission and crosslinking can be expressed in terms of the number-average molecular weight of the original polymer (M_n), that of the irradiated polymer (M_n^*), the overall G -value (G), and the dose (Q) as follows¹¹:

$$\frac{1}{M_n^*} = \frac{1}{M_n} + \frac{GQ}{100N_A} \quad (1)$$

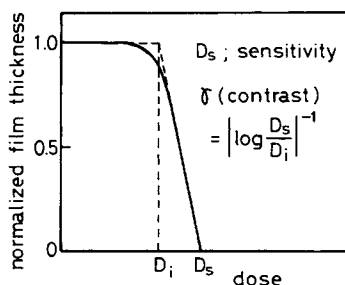


Fig. 1. Definition of the sensitivity and γ (contrast).

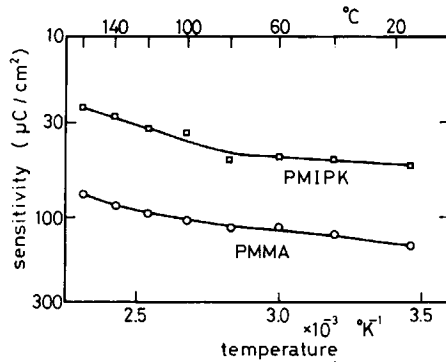


Fig. 2. Temperature effects on the sensitivity for electron beam irradiation.

where $G = G_s - G_x$ (G_s and G_x are the scission and crosslinking G -values) and N_A is Avogadro's number. If the resist is irradiated at the dose giving the sensitivity, D_s , and its molecular weight is M_{ns}^* , eq. (1) is rewritten as follows:

$$\frac{1}{M_{ns}^*} = \frac{1}{M_n} + \frac{GD_s}{100N_A} \quad (2)$$

On the other hand, the solubility rate ratio S_R of the original and irradiated resist is expressed by their weight-average molecular weight M_w and M_w^* as⁴

$$S_R = \left(\frac{M_w}{M_w^*} \right)^{\alpha_s} \quad (3)$$

where α_s is the developer solvent parameter. If a certain resist is irradiated under different conditions such as different sources and different temperatures followed by development under the same conditions, α_s can be regarded as constant. In this case, as S_R at D_s gives a constant value, the weight-average molecular weight at D_s (M_{ws}^*) must be constant. This is only true with regard to the resist with the same developing conditions. If the molecular weight dispersity and absorption coefficient do not change with progress of irradiations, M_n/M_{ns}^* at D_s gives a constant value, and eq. (2) can be simplified as

$$D_s = \frac{\text{const}}{G} \quad (4)$$

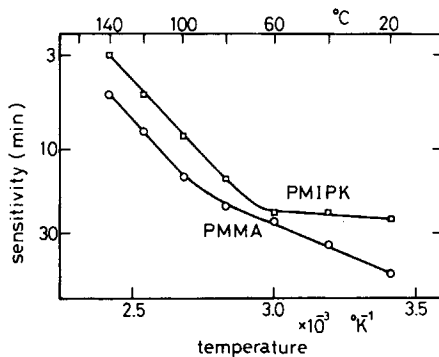


Fig. 3. Temperature effects on the sensitivity for deep-UV light irradiation.

The sensitivity (D_s) for a certain resist obtained under the same developing conditions is, therefore, roughly inversely proportional to $G(\text{scission})$ or the quantum yield for main chain scission.

For electron beam irradiation (Fig. 2), activation energies of the PMMA sensitivity are 1.1 and 1.3 kcal/mol at temperatures of 20–60°C and 80–140°C in which the linear relationships are observed. These values are similar to the PMMA activation energies of $G(\text{scission})$ e.g., about 1 kcal/mol between 0 and 180°C¹² and about 1.5 kcal/mol between –5 and 156°C.¹³ The latter is calculated from the data in the literature. In those data, the T_g is found not to influence the degradation yield and linear relationships between $G(\text{scission})$ and inverse degrees Kelvin are obtained. The results in Figure 2 therefore support eq. (4), and the small deviations from the linear relationship in Figure 2 could be concerned in the development process and variation of molecular weight distribution with electron beam irradiation.

PMIPK also gives small activation energies of 0.6 and 2.6 kcal/mol at temperatures of 20–60°C and 80–140°C, respectively.

Hiraoka¹⁴ has reported that the kind and composition of released gaseous product and generated radicals from PMMA and other polymers are different in UV light and electron beam irradiation and irradiation temperature. Especially a high yield of hydrogen is found in electron beam irradiation. These results suggest that the decomposition mechanism is different in these two irradiation conditions.

The absorption of light and electron beam energy does not generally depend on temperature, at least in the temperature range studied in this work. The temperature effects on the radiation chemical yield of amorphous polymers are caused mainly by a change in molecular mobility which contributes generally to both the main chain scission and the recombination of polymer radicals.

Accelerated electron beam and deep-UV light have energy of several tens of thousand and several electron volts, respectively, and these reactions with polymers are characterized by nonselective and selective reactions, respectively. Thus, the decomposition mechanism of a certain polymer is different under different irradiation sources.

The temperature effects on sensitivity are therefore concerned in both molecular mobility and decomposition mechanism. The differences between PMMA and PMIPK in Figures 2 and 3 depend on the former, and the differences of effects between Figures 2 and 3 depend on the latter. These are discussed later in detail.

Relatively large activation energies of 3.3 and 6.9 kcal/mol for PMMA and 0.4

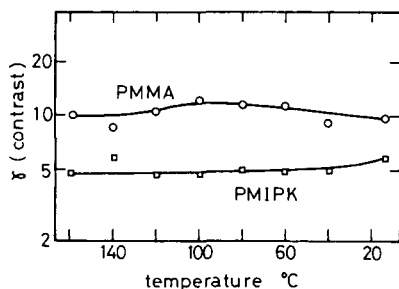


Fig. 4. Temperature effects on $\gamma(\text{contrast})$ for electron beam irradiation.

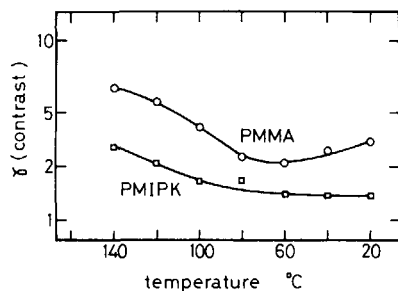


Fig. 5. Temperature effects on γ (contrast) for deep-UV light irradiation.

and 7.8 kcal/mol for PMIPK at the temperature ranges of 20–60°C and 80–140°C are obtained for the deep-UV light irradiation (Fig. 3).

The inflection points in Figure 3 which do not necessarily coincide with their T_g values (T_g PMMA, 105°C; T_g PMIPK, 114°C¹⁵) may correspond to other transitions, e.g., the side group motion associating with the photochemical reaction.

Factors Affecting Resolution

The temperature effects on γ (contrast) for the electron beam irradiation (Fig. 4) are scarcely observed, but these for the deep-UV light irradiation (Fig. 5) are somewhat observed. The remarkable thing in these figures is that γ (contrast) for the electron beam irradiation, as a whole, is significantly larger than that for the deep-UV irradiation.

Figures 6 and 7 show the variation of the molecular weight dispersity (M_w^*/M_n^*) with the decomposition factor M_n^*/M_n . The dose giving the smallest M_n^*/M_n for the deep-UV light irradiation is D_s . The values of M_w^*/M_n^* for PMMA and PMIPK with γ -ray irradiation approaching 2. The results imply that the polymer molecular weight approaches a random distribution. This behavior is well known for polymers that undergo main chain degradation without being crosslinked or branched simultaneously. On the other hand, the values of M_w^*/M_n^* for PMMA and PMIPK with deep-UV light irradiation become larger than that of the original polymer. The spread of the polymer molecular weight distribution after the irradiation must cause the small γ (contrast) from the deep-UV light irradiation (Fig. 5).

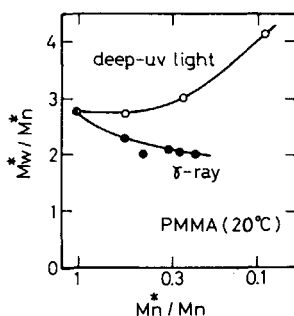


Fig. 6. Changes in PMMA molecular weight dispersity. Asterisk (*) indicates irradiated resists.

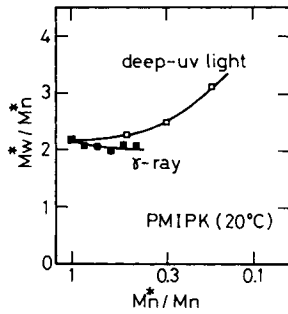


Fig. 7. Changes in PMIPK molecular weight dispersions. Asterisk (*) indicates irradiated resists.

The resolution of positive resists under the given developing conditions is diminished by increasing the overlap of molecular weight distribution between the original and the irradiated resist.

Two reasons are considered for the spread of polymer molecular weight distribution under deep-UV light irradiation. One of them is the light intensity nonuniformity in the cross section of the resist film and in the all-irradiated surface. However, the former can be neglected because of the small absorption coefficient under the deep-UV light.¹⁶ The latter is not measured but it may be estimated to be small from the structure of the present irradiation system. The other reason is the difference in degradation mechanism between the deep-UV and γ -ray irradiation. The most probable difference is the large contribution of unzipping to the degradation under deep-UV light irradiation.

Figures 8 and 9 show the molecular weight variations for PMMA and PMIPK irradiated with deep-UV light at 20°C. The longest irradiation time for each resist gives D_s . The degradation ratio (M_w/M_{ws}^*) for PMMA at D_s is larger than that for PMIPK; $M_w/M_{ws}^* = 9.3$ for PMMA and 4.1 for PMIPK. This is mainly responsible for the smaller γ (contrast) of PMIPK ($\gamma = 1.4$) than that of PMMA ($\gamma = 2.7$) with regard only to the developing conditions used, which is recognized from eq. (3).

Table II shows the correlations between γ (contrast) and the molecular weight dispersity (M_{ws}^*/M_{ns}^*) irradiated with deep-UV light at different conditions. Each irradiation time gives D_s . These values are plotted in Figure 10. A linear

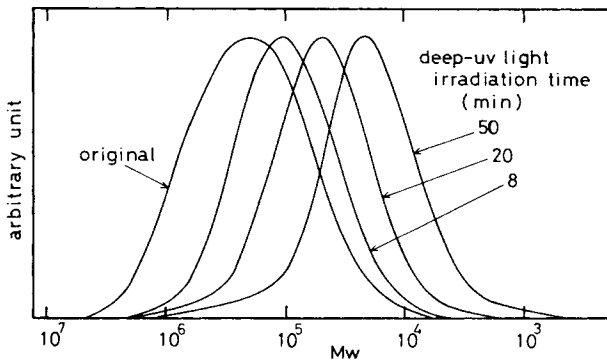


Fig. 8. Change in PMMA molecular weight distribution.

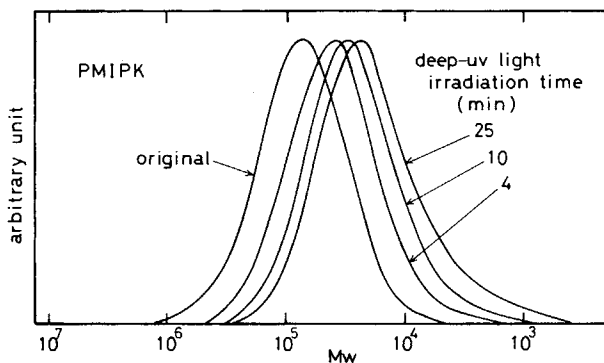


Fig. 9. Change in PMIPK molecular weight distribution.

relationship between γ (contrast) and M_{ws}^*/M_{ns}^* is recognized in each resist. The small slope for PMIPK could be caused by the small value of M_w/M_{ws}^* because the molecular weight overlap of the original and irradiated resists from small M_w/M_{ws}^* decreases less by decreasing the molecular weight dispersion than that from large M_w/M_{ws}^* .

It has become apparent that the resolution of positive resists is governed dominantly by both M_{ws}^*/M_{ns}^* (the molecular weight dispersity at D_s) and M_w/M_{ws}^* (the weight-average molecular weight ratio between original and irradiated resists at D_s).

Thickness Reduction and Negative Inversion

At an excess dose of electron beam irradiation, PMMA and PMIPK show thickness reduction without solvent development. As shown in Figures 11 and 12, both phenomena compete mutually. The thickness reduction for PMIPK at 20°C was very small. In contrast, at excess dose of deep-UV irradiation, negative inversion is scarcely observed, as shown in Figure 13. The thickness reduction is caused by the production of volatile fragments in the degradation process. For PMMA, fragments such as H_2 , CO , $CH_3 \cdot + CH_4$, and CO_2 were detected under electron beam irradiation.¹⁴ With a certain polymer such as poly(olefin sulfone), unzipping occurred upon electron beam irradiation, which has been termed vapor development.¹⁷ Negative inversion is caused by the crosslinking of polymer chains.

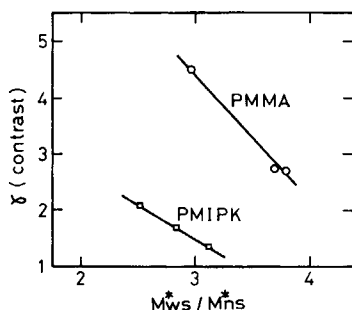


Fig. 10. Relation between γ (contrast) and molecular weight dispersion after deep-UV irradiation.

TABLE II
Molecular Weight Dispersions after Deep-UV irradiation under Different Conditions

Resist	Irradiation condition		γ (contrast)	Molecular weight of irradiated resist	
	Temp., °C	Time, min		$M_{us}^* \times 10^{-5}$	M_{us}^*/M_{rs}^*
PMMA	20	N ₂ gas flow	2.7	4.1	3.7
	20	O ₂ gas flow	2.7	4.0	3.8
	120	N ₂ gas flow	4.5	3.6	3.0
PMIPK	20	N ₂ gas flow	1.4	2.9	3.1
	20	O ₂ gas flow	1.7	2.9	2.8
	120	N ₂ gas flow	2.1	2.8	2.6

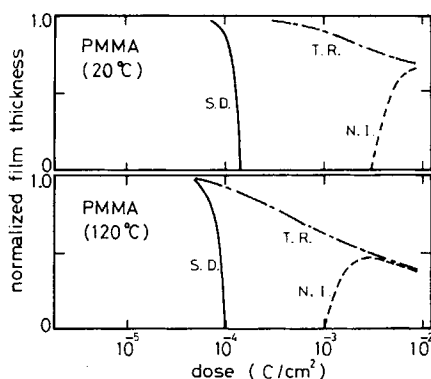
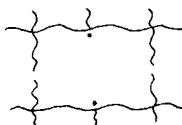
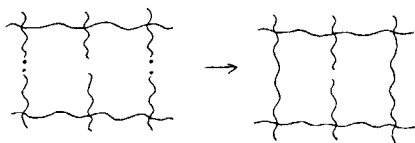


Fig. 11. Thickness reduction (T.R.), negative inversion (N.I.), and solvent development (S.D.) curves of PMMA for electron beam irradiation at different temperatures.

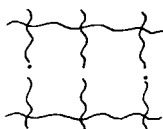
It has been reported that the PMMA decomposition under UV light irradiation proceeds as main chain scission induced by the ester group elimination.^{14,18} The polymer radicals formed by the elimination could scarcely recombine mutually because of the steric hindrance by side chains, as follows:



On the other hand, the high yield of hydrogen under electron beam irradiation¹⁴ suggests the formation of side chain radicals in the primary process of decomposition, even if a polymer radical induced by the ester group elimination is formed.¹⁹ The probability in which side chain radicals are face to face becomes very large accordingly to the increase in the amount of side chain radicals. These radicals could be easily combined at a rate faster than that required to decompose the main chain as follows:



However, at D_s , small amounts of side chain radicals are induced and the probability of crosslinking is very small. Thus, negative inversion near D_s could scarcely occur:



In addition to the amount of side chain radicals, the probability to recombine

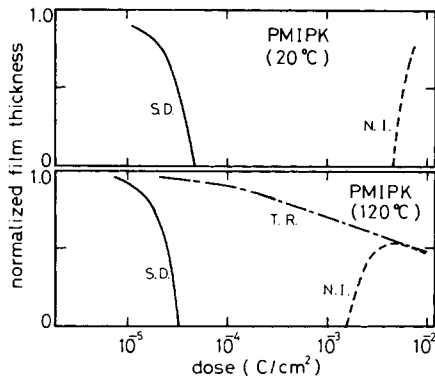


Fig. 12. Thickness reduction (T.R.), negative inversion (N.I.), and solvent development (S.D.) curves of PMIPK for electron beam irradiation at different temperatures.

the side chain radicals between polymer chains depends on the polymer motion.³ The polymer motion of PMIPK must be small compared with that of PMMA because PMIPK has a short side chain and a high T_g . The small difference in the sensitivity for the negative inversion between PMMA and PMIPK is considered to be caused by the polymer motion.

In further details of Figures 11 and 12, the sensitivities both of the thickness reduction and the negative inversion increase at high temperature. Thus, using polymers such as PMMA and PMIPK, complete film removal such as the vapor development is very difficult under excess electron beam irradiation, even if the irradiation is performed at high temperature.

Oxygen Effects upon Deep-UV Light Irradiation

Figure 14 shows the thickness–dose plots obtained by the deep-UV light irradiation in O_2 gas flow. The PMMA sensitivity with solvent development decreases remarkably in O_2 gas flow compared with that in N_2 gas flow, but that for PMIPK does not change. The thickness reduction in O_2 gas flow at 120 °C also shows the same tendency. The sensitivity diminution of PMMA with O_2

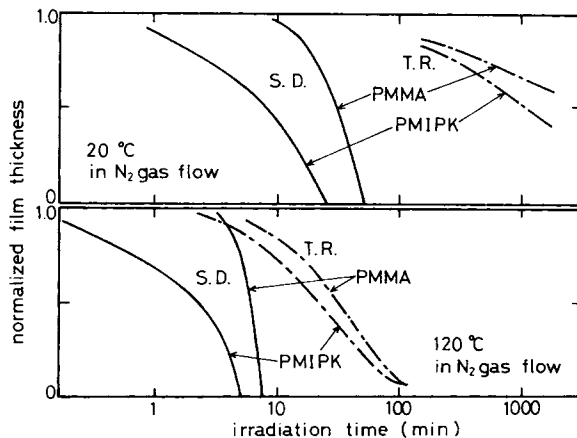


Fig. 13. Thickness reduction (T.R.) and solvent development (S.D.) curves for deep-UV irradiation in N_2 gas flow at different temperatures.

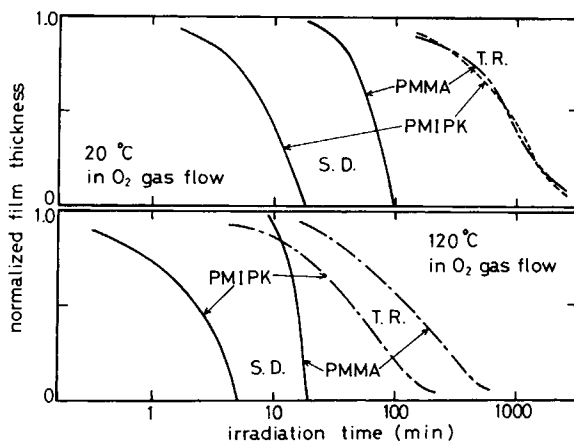


Fig. 14. Thickness reduction (T.R.) and solvent development (S.D.) curves for deep-UV irradiation in O_2 gas flow at different temperatures.

can be explained by the mechanism reported by Grassie et al.,¹⁸ i.e., the predominantly formed polymer radical which has a structure to release the ester side group reacts with oxygen and forms the hydroperoxide. Grassie et al. have inferred that the hydroperoxide is much more stable. Therefore, main chain scission decreases because of the hydroperoxide formation.

On the other hand, it has been reported that PMIPK decomposes photochemically via a seven-membered cyclic transition state in analogy to the Norrish type II process.²⁰ According to this mechanism, the oxygen is not involved in main chain degradation, in a similar manner as the results shown in Figure 14.

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