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Thermal degradation behavior of gamma-irradiated acetyloxy end-capped poly(oxymethylene)

S. Hasegawa[a,*], H. Takeshita[a], F. Yoshii[a], T. Sasaki[a,1], K. Makuuchi[a], S. Nishimoto[b]

[a]Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, Watanuki, Takasaki, Gunma 370-1292, Japan
[b]Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

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Abstract

The radiation effect on the thermal stability of poly(oxymethylene) diacetate (POMDA) in film has been investigated on irradiation up to 1000 kGy in air with a ^{60}Co gamma-ray source. The gel permeation chromatography (GPC) indicated that the molecular weight of POMDA was lowered in the polydisperse index (M_w/M_n) approaching the ultimate value of 2 as the radiation dose increased. As observed in the differential scanning calorimetry (DSC), the melting temperature of irradiated POMDA decreased progressively with the lowering of the molecular weight, and the thermally less stable components than the original POMDA were produced in increased yields with increasing radiation dose. According to the thermogravimetry (TG), about 55% of higher-dose irradiated POMDA maintained thermal stability comparable or even superior to that of the original POMDA before irradiation, while about 45% had less stability to thermal degradation. The formation of hydroxyl (G(–OH) = 0.5), formyloxy (G(–OCHO) = 0.6) and methoxy (G(–OCH_3) = 0.4) end-groups was identified by the measurement of infrared (IR) dichroism of uniaxially oriented POMDA film after irradiation. The radiation chemical modification of chain-end groups is accounted for by a radical chain reaction mechanism involving random scission of POMDA main-chain as an initiation step. It was concluded that a POM chain possessing at least one hydroxyl end-group is concluded to be thermally less stable than POMDA, while another POM family without bearing any hydroxyl end-group may have thermal stability comparable or superior to the original POMDA. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(oxymethylene); Irradiation; End-groups

1. Introduction

High energy radiation has unusual chemical effects on polymers in the solid state, inducing cross-linking, grafting and chain scission by radical reactions [1]. Cross-linking and grafting have been widely used for improving the chemical and physical properties of polymer materials. However, radiation-induced chain scission results in reduction of molecular weight of polymer materials. The latter radiation effect is in turn useful for polymer recycling. In this regard, we have currently undertaken exploring the application of radiation-induced chain scission to chemical recycling of polymer wastes and have reported interesting results about thermal degradation of polypropylene pre-exposed to ^{60}Co gamma-radiation [2,3].

In the present study we have characterized the effect of pre-irradiation of ^{60}Co gamma-rays on the thermal stability of commercially available poly(oxymethylene) diacetate (POMDA) that is stabilized with acetyloxy end-groups. Poly(oxymethylene) hydrate (POM hydrate) as is produced by conventional polymerization methods possesses thermally labile hydroxyl end-groups and therefore undergoes depolymerization at a low ceiling temperature [4]. For practical purposes stabilization of POM hydrate is achieved by acetylation of the end-groups or by copolymerization [5]. Such a stabilized POM is widely used as an engineering plastic because of its excellent mechanical properties. In the case of POMDA homopolymer stabilized with acetyloxy end-groups, thermal decomposition occurs to negligible extent at temperatures below 300°C. It is expected that induction of main-chain scission by pre-exposure to ionizing radiation might be effective to enhance thermal degradation of such stabilized POMDA. Thus, newly generated chain ends and structures due to radiolysis are potentially reactive sites for initiating depolymerization of POM, so long as they are less stable than the original chain-end groups.

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* Corresponding author. Tel.: +81-27-346-9383; fax: +81-27-346-9687.
E-mail address: hasegawa@takamads.taka.jaeri.go.jp (S. Hasegawa)

[1] Present address: Nuclear Technology and Education Center, Japan Atomic Energy Research Institute, 2-28-49 Hon-Komagome, Bunkyo-ku, Tokyo 113-0021, Japan.

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While a number of studies have been documented so far on the thermal stability of POM-related polymers particularly on the effects of end-groups and atmosphere, there has been less understanding of radiation effect on the thermal stability. Previously, Torikai irradiated POM hydrate in vacuum and in air at room temperature with ^{60}Co gamma-rays, examining the change of the thermal stability [6]. He observed that the viscosity of irradiated POM decreased with increased doses, regardless of whether the irradiation atmosphere was in vacuum or in air. More remarkable was that 80–95% of POM was stabilized during irradiation in vacuum, although irradiation in air failed to cause such a stabilization effect. This may be accounted for by the formation of new end-groups as a result of radiation chemical main-chain scission, although the mechanism of such a stabilization has not yet been experimentally elucidated.

We report herein evidence for the radiation chemical generation of new chain-end structures that could affect significantly the post-thermal degradability of irradiated POMDA. A possible mechanism by which POMDA undergoes radiation-induced main-chain scission into modified end-group structures is proposed to correlate with thermal degradation behavior or irradiated POMDA.

2. Experimental

2.1. Materials

Stabilized POMDA homopolymer (Tenac 3010) [5] bearing acetyloxy end-groups was supplied in pellet by Asahi Chemical Industry Co., Ltd., and was purified to remove stabilizers and other additives by the following procedure. POMDA pellets were dissolved in 1, 1, 1, 3, 3, 3,-hexafluoro-2-propanol (HFIP) (Central Glass Co., Ltd) at 40°C. The resulting HFIP solution was poured into toluene to precipitate POMDA. The POMDA thus precipitated was filtered, followed by drying at room temperature in a vacuum oven.

2.2. Film preparation

The additive-free POMDA in the form of film was used for the irradiation experiments. The purified POMDA in fine powder was heated at 200°C for 3 min, molded with a spacer in 0.5 mm thickness under a pressure of 150 kg/cm^2 for 3 min at the same temperature, and then immediately placed in a cold press and cooled with tap water. This procedure produced sample films of 0.4 mm thickness.

2.3. Irradiation

The POMDA sample films were irradiated with various doses up to 1000 kGy at a dose rate of 10 kGy/h in air at room temperature, using a ^{60}Co gamma-ray source.

2.4. Gel permeation chromatography

The molecular weight distribution of irradiated POMDA samples (1 mg/ml in HFIP) was analyzed at room temperature with a Toso HPLC-8020 GPC instrument, equipped with two separation columns of TSK gel GMH$_{XL}$ (7.8 mm i.d. × 30 cm × 2) (TOSOH Co.) and a differential refractometer. Distilled HFIP was used as an eluent at a flow rate of 1.0 ml/min. Molecular weights were calibrated with standard poly(methyl methacrylate) samples (TOSOH Co.) ranging from 3×10^3 to 1.2×10^6.

2.5. Differential scanning calorimetry

The radiation effects on the melting point and the thermal stability of POMDA samples were analyzed by differential scanning calorimetry (DSC) with a Perkin–Elmer DSC 7 differential scanning calorimeter. Approximately 5 mg of samples were taken from the films and scanned in the temperature range of 50–200°C at a heating/cooling rate of 10°C/min under a nitrogen atmosphere. The temperature and the power response of the calorimeter were calibrated using indium and zinc standards.

2.6. Thermogravimetry

Thermogravimetry (TG) studies of POMDA samples were carried out with a Shimadzu TGA-50 thermobalance controlled by a TA-50 WS digital data acquisition system. Typically samples of about 5 mg were heated under an inert atmosphere of 50 ml/min nitrogen gas stream at a heating rate of 10°C/min.

2.7. FTIR analysis

POMDA thin films of about 15 μm thickness were prepared for the measurements of FTIR spectra on a Shimadzu FTIR 8100A spectrometer at a resolution of 4 cm^{-1}. For quantification of the end-groups of unirradiated and irradiated POMDA, the following compounds in tetrachloromethane were used for convenience as the standards: 2-(2-methoxyethoxy)ethanol ($CH_3O–CH_2CH_2OCH_2CH_2–OH$) for hydroxyl and methoxy groups; ethyl acetate ($CH3COO–CH_2\ CH_3$) and methyl formate ($HCOO–CH_3$) for acetyloxy and formyloxy groups, respectively. For the measurements of IR dichroism, the oriented POMDA film was prepared by stretching a film in a silicon oil bath thermostated at 150°C. The stretching up to 500% elongation resulted in a film of about 15 μm thickness with a sufficient uniaxial orientation of POM main-chains along the direction of stretching.

3. Results and discussion

3.1. Radiation-induced main-chain scission

All irradiated POMDA samples were completely soluble

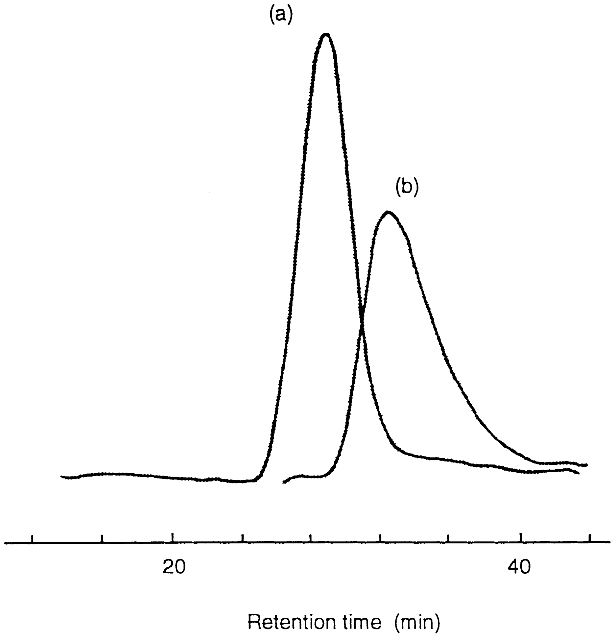


Fig. 1. GPC traces of: (a) unirradiated ($M_w = 1.4 \times 10^5$, $M_w/M_n = 1.09$); and (b) 150 kGy-irradiated ($M_w = 4.8 \times 10^4$, $M_w/M_n = 1.38$) POMDA films dissolved in HFIP solution.

in HFIP. Fig. 1 shows the representative molecular weight distributions (MWD) of unirradiated and 150 kGy-irradiated POMDA, indicating considerable lowering of the molecular weight by irradiation: while unirradiated POMDA has a single-modal narrow MWD ($M_w = 1.4 \times 10^5$, $M_w/M_n = 1.09$), 150 kGy-irradiated POMDA still showed a single modal but broader MWD ($M_w = 4.8 \times 10^4$, $M_w/M_n = 1.38$). Radiation-induced changes in the GPC profile were characteristic of the random scission mechanism that the polydisperse index (M_w/M_n) approached a ultimate value of 2 as the scission proceeds [7].

3.2. Pre-irradiation effects on thermal stability

Fig. 2 shows typical DSC curves for POMDA samples. In the first runs of heating, all irradiated samples but not unirradiated sample showed broad endothermic peaks overlapped with a sharp peak due to ordinary melting of POMDA crystals. Such an overlapping of broad peaks disappeared in the second runs of heating. These observations suggest that part of irradiated POMDA underwent in situ pyrolysis, that is responsible for the broad endothermic peaks, at temperatures near the melting point of POMDA crystals during the DSC analysis. Thus, irradiation of POMDA would produce more labile chain-end structures relative to the original acetyloxy group. It is evident in Fig. 2 that the fraction of such labile structures increases with increased irradiation dose.

The peak melting temperature of POMDA crystals, as evaluated from each of the second heating runs, decreased monotonously with radiation dose (Fig. 3). Previously, Jaffe and Wunderlich reported that irradiation of POM up to 8 kGy at a dose rate of 1 kGy/h in air depressed the melting point by 18°C from an initial value of 182.4°C [8]. Kusy and Turner also reported similar results for samples irradiated in vacuum, in which the melting temperature of irradiated POMDA decreased rapidly by irradiations at lower doses and then showed a uniform depression at rates in the range of 0.154–0.160°C/10 kGy [9]. This rate of melting temperature depression per a given radiation dose seemed to be independent of an irradiation atmosphere whether in vacuum or in air. The extent of the melting temperature depression observed in this work was of the same order as in the previous reports, being attributable to the radiation-induced lowering of molecular weight.

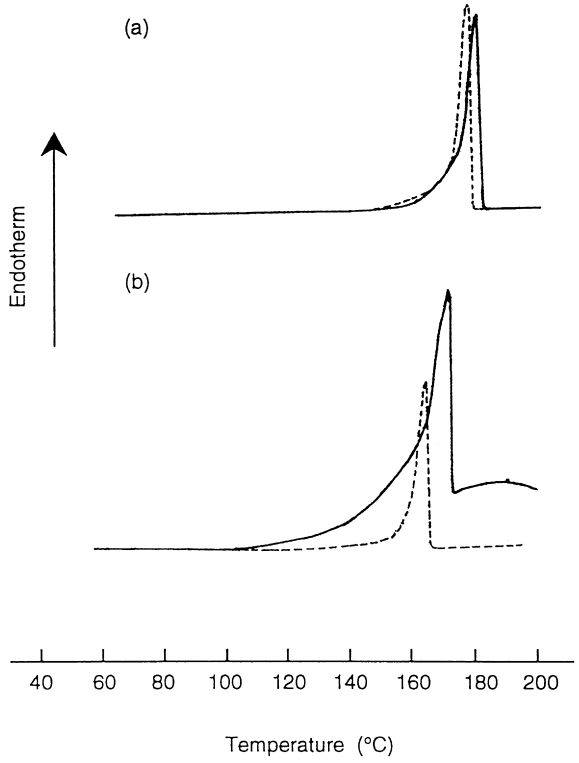


Fig. 2. DSC profiles of: (a) unirradiated; and (b) 220 kGy-irradiated POMDA films upon heating at a rate of 10°C/min under an atmosphere of nitrogen flow: (—) first heating run; (––) second heating run.

Fig. 4(a) shows TG curves of POMDA samples. POMDA bearing acetyloxy end-groups was thermally stable upon heating up to near 300°C, which was much higher than the corresponding melting point (179°C). Thus, the pyrolysis of POMDA leading to weight loss was initiated at 290°C in the molten state and completed at 330°C without giving any solid residue. The radiation treatment of POMDA produced thermally less stable components, thereby lowering the temperature for initiating pyrolysis to considerable extent. The fraction of such thermally unstable components initially increased with increasing dose, and then reached a certain constant value of about 45% at doses above 600 kGy. The remaining fraction had almost the same thermal stability as

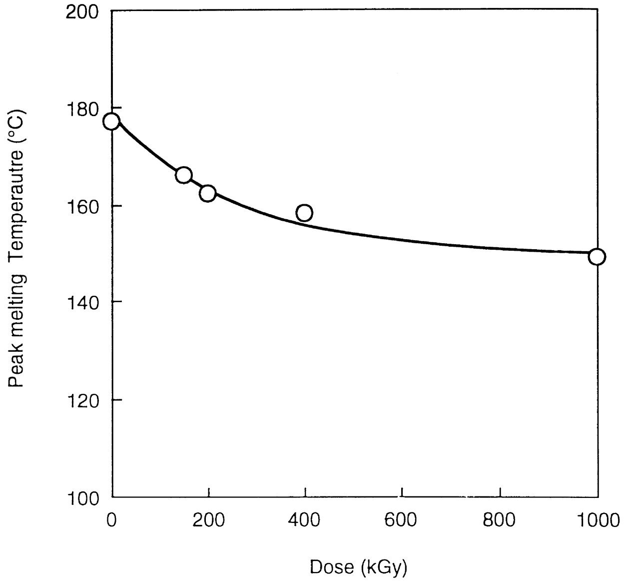


Fig. 3. Dose response of peak melting temperature in the DSC for POMDA films irradiated at varying radiation doses.

the unirradiated POMDA. In the light of DSC data that the crystallinities of POMDA samples used in this study were around 70%, the radiation chemical modification of POMDA to produce thermally less stable forms is thought to occur mainly in the amorphous phase (about 30% in fraction). Such a chemical modification in the crystal phase would be minor, which accounts for the unchanged fraction of thermal stability. Similar to POMDA before irradiation, all the irradiated samples afforded no solid residue such as char and underwent complete gasification upon heating up to 500°C.

Fig. 4(b) specifies the temperatures at which the respective secondary components produced in a given irradiated POMDA samples were pyrolyzed at the maximum rates of weight loss. Evidently the distribution of secondary components that were modified in their thermal reactivity by the pre-irradiation is strongly dependent on the radiation dose. Thus, the lowest temperature of causing pyrolysis of the most unstable component decreased significantly from 250°C in the 60 kGy-irradiated sample to 140°C in the 940 kGy-irradiated sample. In some cases, for example in the 220 kGy-irradiated sample, a slight but a distinct depression in the peak height of pyrolysis rate was observed. In view of the fact that such a dimple in the peak was located in the vicinity of the melting point of unmodified POMDA crystals in the irradiated film, this phenomenon is presumably attributable to the consumption of exothermic heat energy by the endothermic melting of POMDA crystals. In this association, the temperature at which the dimple was observed showed exactly the same dose dependence as the melting peak temperature shown in Fig. 3. Further, the dimple disappeared in the POMDA film irradiated at higher doses in accord with the observation that the influence of endothermic crystal melting became much smaller at higher doses.

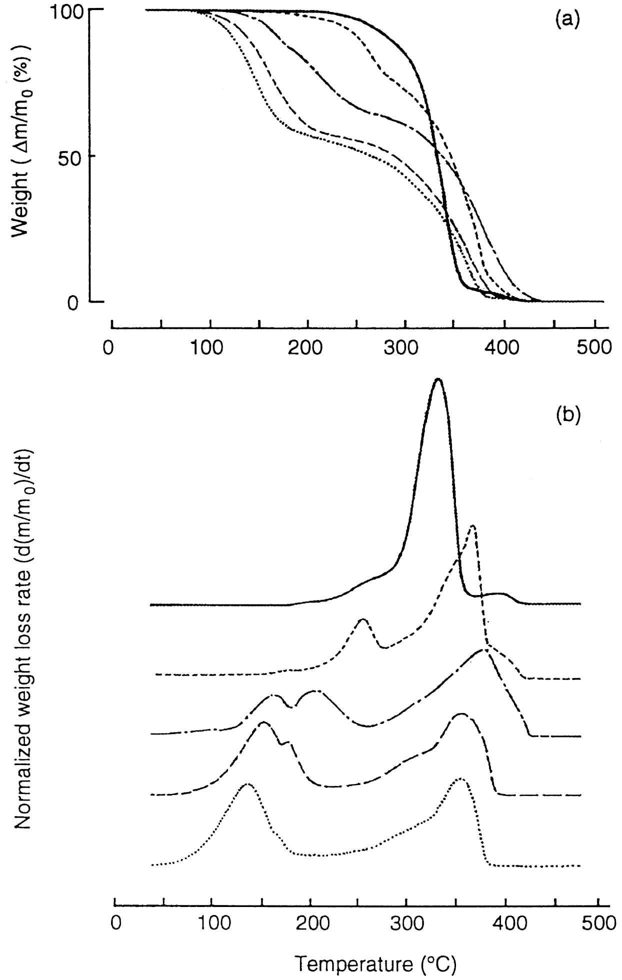


Fig. 4. (a) TG and (b) DTG profiles of POMDA films upon heating at a rate of 10°C/min under an atmosphere of nitrogen flow: (—) unirradiated; (––) 60 kGy-irradiated; (– - –) 220 kGy-irradiated; (– – –) 600 kGy-irradiated; (·····) 940 kGy-irradiated.

As mentioned earlier, about half the part of irradiated POMDA maintained stability comparable or even superior to that of the original unirradiated POMDA, whereas the rest became susceptible to thermal degradation. In contrast, the previous study [6] showed that aerobic irradiation did not lead to a stabilization effect. This disagreement may result partly from a difference in the dose rate: we irradiated at a dose rate of 10 kGy/h, which is eight-times higher than the rate (1.25 kGy/h) employed previously [6].

Such radiated chemically stabilized components showed higher DTG peak temperatures 40–60°C than the original POMDA prior to irradiation. From the complicated peak profile there would be more than two stabilized components after irradiation. It is also noteworthy that the pyrolysis temperatures of stabilized components seemed to be of radiation-dose independence. This implies that the radiated chemically stabilized components may possess some well-defined chemical structures.

Not only less stable components, which undergo pyrolysis more readily to initiate successive depolymerization at

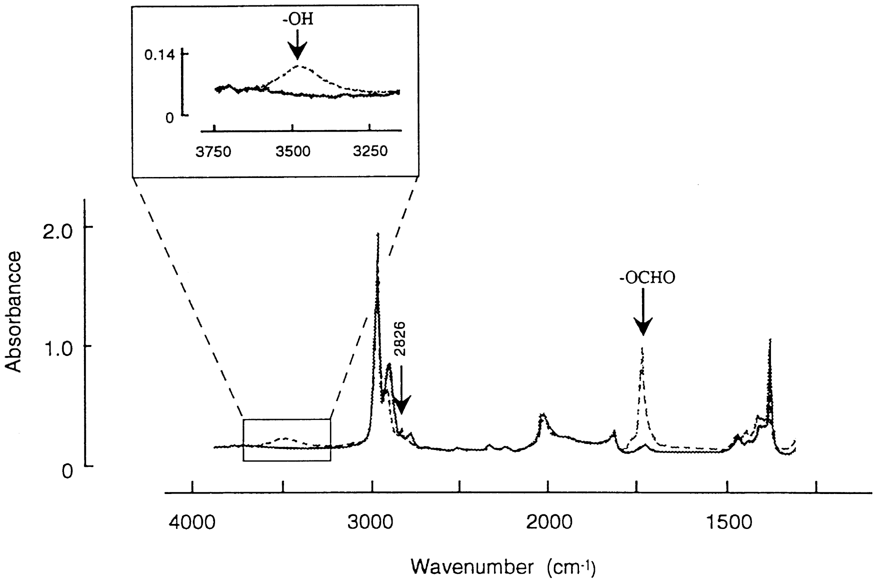


Fig. 5. FTIR spectra for uniaxially oriented POMDA film (—) before and (– –) after 800 kGy-irradiation, as recorded with polarized IR beam parallel to the orientation.

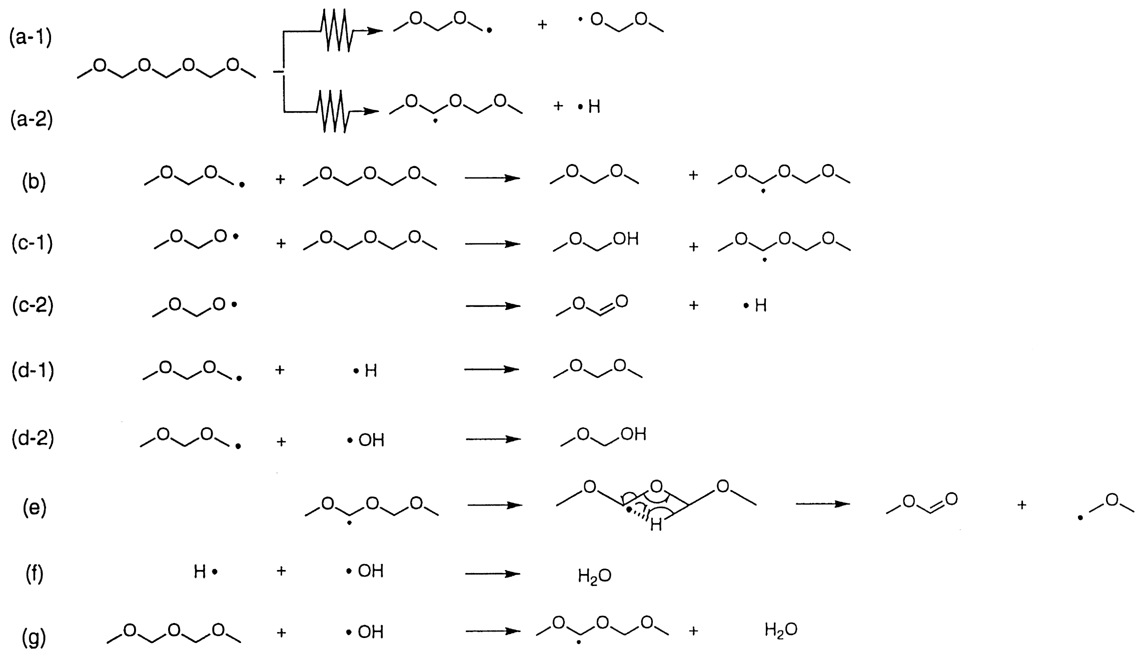
lower temperature, but also more stable components would be produced by way of radiation-induced main-chain scission of POMDA as a primary step. It is widely accepted that the crystal region in the polymer solid is practically more stable to radiation, resulting in a lower amount of damage fixations relative to the amorphous region. As discussed earlier, about 30% of the POMDA samples corresponding to the amorphous region are expected to undergo degradation more readily upon irradiation. This may be roughly parallel to the ultimate value (about 45%) of less stable fraction in the higher-dose irradiated POMDA samples that were pyrolyzed at lower temperatures than the original POMDA (see Fig. 4(a)). The GPC analysis of the irradiated POMDA, however, clearly shows that main-chain scission proceeded homogeneously during irradiation. It is presumable that the modification of polymer chain-ends may occur predominantly in the amorphous phase, while POM main-chain scissions proceed both in the amorphous and crystal phases.

There has been a general conclusion that the introduction of cross-links into linear polymer chains can improve the thermal stability in the solid state. Fischer et al. suggested the formation of cross-links upon irradiation of POM, according to their NMR studies [10]. In the present study, however, all the irradiated POMDA samples could be completely soluble in HFIP at room temperature without any gel formation due to radiation cross-linking. Further, the molecular-weight distribution profiles of the irradiated POMDA samples (see Fig. 1) did not indicate the formation of a precursor for cross-linking. Therefore, the formation of large amount of stable components in higher-dose irradiated POMDA samples cannot be explained in terms of radiation cross-linking.

The thermal stability of POM family is known to depend strongly on the chemical structure of polymer end-groups. For example, POM hydrate bearing hydroxyl end-groups, as a product by conventional polymerization process, is quite labile to thermal degradation [11]. Commercially available POM is therefore stabilized by substitution of the hydroxyl end-groups with acetyloxy groups. Dudina et al. investigated in detail the effect of the chemical nature of end-groups, such as hydroxyl, acetyloxy and methoxy groups, on the thermal degradation reactivity of POM main chain [12]. They concluded that thermal degradation proceeds by a common depolymerization mechanism, being initiated either by bond dissociation at the chain end for POM hydrate or by random main-chain scissions for end-capped POM (stabilized POM). According to this conclusion, the methoxy end-group provides higher thermal stability than the acetyloxy end-group.

3.3. IR Spectroscopic characterization of radiation-modified chain-end-groups

Thermal stability of POM hydrate in the solid state is modified by irradiation in vacuum, as reported previously [6]. Formyloxy and methoxy end-groups were assumed to be formed by disproportionation of radicals as generated primarily by radiation-induced main-chain scissions, thus leading to the modification of thermal stability. In the previous study, however, the IR spectroscopic detection of such end-groups in the POM hydrate irradiated up to 2000 kGy was not successful. For better understanding of a mechanism by which POMDA undergoes radiation chemical modification of the thermal stability, further effort was made to identify the formation of new end-groups by measuring IR dichroism for a uniaxially oriented sample film.



Scheme 1. Radical reactions involved in the radiation-induced degradation of POMDA.

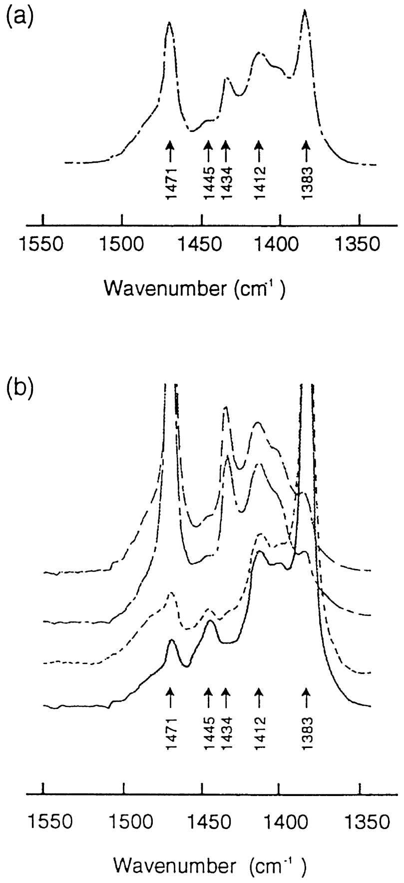


Fig. 6. (a) Conventional FTIR spectra for uniaxially oriented POMDA film before irradiation. (b) The corresponding IR dichroism as recorded with polarized IR beam parallel to the orientation: (– – –) unirradiated; (– - –) 640 kGy-irradiated, and perpendicular to the orientation: (- - -) unirradiated; (—) 640 kGy-irradiated.

Fig. 5 compares the IR absorbances ($A_{/\!/}$) of the uniaxially oriented POMDA film of 15 μm thickness before and after 800 kGy-irradiation, as recorded with polarized IR beam ($I_{/\!/}$) being parallel to the direction of POMDA orientation. As reported previously [5], the carbonyl (C=O) groups in the acetyloxy-capped chain-ends of POMDA are characterized by an IR absorption at 1755 cm^{-1}. Such acetyloxy C=O groups in the oriented POMDA film turned out to show an IR dichroism. Thus, there was no absorption ($A_{/\!/}[1755] \approx 0$) at 1755 cm^{-1} in the uniaxially oriented film before irradiation (Fig. 5: the absorption at 1728 cm^{-1} may be attributed to contamination during stretching in a silicon oil bath at 150°C), while clear absorption ($A_{\perp}[1755] = 0.04$) could be observed using perpendicularly polarized IR beam ($I_{\perp}$). This dichroism suggests that the acetyloxy C=O groups as the primary end-caps may be located perpendicularly to the uniaxially oriented POM main-chains in the stretched POMDA film prior to irradiation. More interesting was that the acetyloxy C=O band at 1755 cm^{-1} emerged ($A_{/\!/}[1755] > 0$) along with intense new absorption bands at 3459 and 1736 cm^{-1} upon irradiation of the oriented POMDA film (Fig. 5). It is likely that the acetyloxy C=O groups produced secondarily by irradiation is no longer perpendicular to the uniaxially oriented POM main-chains. The new bands appeared at 3459 and 1736 cm^{-1} are accounted for by radiation chemical formation of hydroxyl (–OH) and carbonyl (C=O) groups, respectively. The latter band may be assigned to formyloxy C=O groups by reference to the IR spectrum of methyl formate standard in tetrachloromethane involving absorption at 1736 cm^{1}. These characteristic absorption bands were more intensified with increasing radiation dose. Particularly, the significant enhancement of absorbance at 1736 cm^{-1}

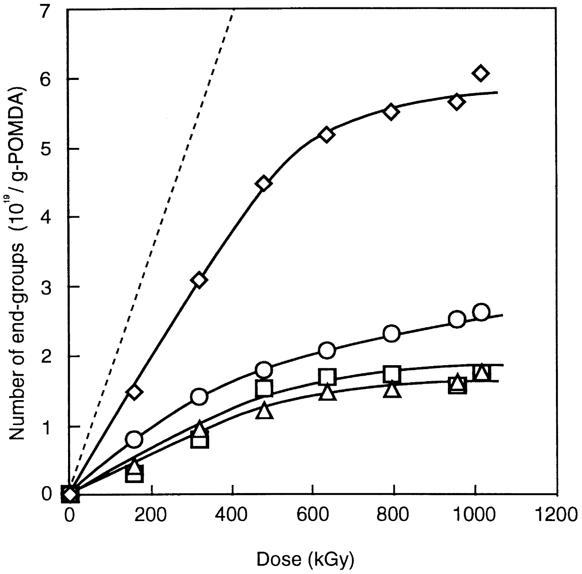


Fig. 7. Dose response of the numbers of end-groups produced upon irradiation, as evaluated by IR spectrometry: (□) hydroxyl group; (○) formyl group; (△) methoxy group; (◇) sum of the above three functional groups. Also shown is (– –) the total number of chain ends estimated from the GPC data for 150 kGy-irradiated POMDA film.

indicates high yield of formyloxy groups by irradiation, in accord with a mechanistic consideration on radiation degradation of POMDA as mentioned later (see Scheme 1).

However, methoxy groups are expected to show IR absorption at near 1447 cm^{-1} by reference to 2-(2-methoxyethoxy)ethanol standard in tetrachloromethane. In the case of POMDA bearing methoxy end-groups, however, the IR absorption by the methoxy groups was overlapped with the intense absorption bands due to the methylene ($-CH_2-$) groups in the POM main-chain. Using the uniaxially oriented POMDA film as mentioned above, therefore, attempt was made to measure a dichroism in the IR spectra for detecting the absorption by methoxy groups. Fig. 6(b) shows appreciably different IR spectra of 640 kGy-irradiated film recorded with a polarizer successively oriented parallel and perpendicular to the direction of POMDA orientation, in comparison with the conventional IR spectrum as in Fig. 6(a). It is obvious in Fig. 6(b) that the absorption bands at 1471 cm^{-1} and 1434 cm^{-1} assigned to $-CH_2-$ groups exhibited a perpendicular-to-chain dichroism. Thus, the spectra of unirradiated and 640 kGy-irradiated films corresponding to IR polarization parallel to the uniaxially oriented POM main-chains revealed absorbance at 1445 cm^{-1} due to increased formation of methoxy groups by irradiation. In accord with this assignment, the C–H stretching vibration band specific to the methoxy groups appeared at 2826 cm^{-1} on irradiation (Fig. 5).

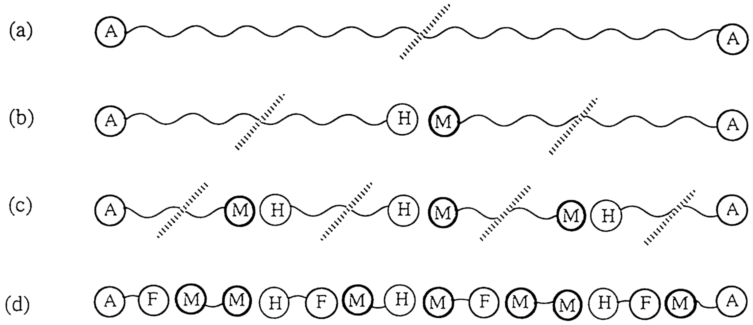
In measurements of IR spectral dichroism for the uniaxially oriented POMDA films after irradiation, it was noted that all the absorbances of the methoxy band at 1445 cm^{-1}, the hydroxyl band at 3459 cm^{-1} and the formyloxy band at 1736 cm^{-1} are almost independent of the angle between the directions of IR polarization and the POMDA orientation. Thus, it is most likely that these functional groups are produced at the untied and flexible chain-ends, but not at the highly oriented and less flexible POM main-chains. In view of the solid-state reaction of POMDA with high crystallinity, the formation of new end-groups by radiation-induced main-chain scission appears to occur mainly in the amorphous and crystal-amorphous interfacial regions.

Radiation chemical yields of hydroxyl, formyloxy and methoxy groups produced by irradiation of POMDA film in air were estimated from the FTIR data, by reference to standard compounds such as 2-(2-methoxyethoxy)ethanol and methylformate. For quantitative analysis of formyloxy groups, the increment in absorbance at 1736 cm^{-1} as observed by irradiation (see Fig. 5) was assumed to result exclusively from the formation of formyloxy groups. Fig. 7 shows the dose response of the respective functional groups in the radiation chemical formation, indicating that irradiation of POMDA in air may produce hydroxyl, formyloxy and methoxy groups in almost equivalent yields: the yield increased linearly with increasing radiation dose up to 480 kGy and then gradually approached a constant value on further irradiations. The slope of the linear portion in the dose–response relationship gave the corresponding G-value (the number of functional groups produced per 100 eV of radiation energy absorbed by POMDA) in the aerobic irradiation: $G(-OH) = 0.5$; $G(-OCHO) = 0.6$; $G(-OCH_3) = 0.4$. As discussed earlier, these structures may be attributed to the chain-end groups.

3.4. Mechanism of radiation modification of chain-end groups

Assuming that a family of POM has a linear and unbranched polymer chain with specific functional groups at both chain-ends in a formal structure of $E^1-(CH_2O)_n-E^2$, and that it undergoes main-chain scission upon irradiation to produce similar structures of reduced molecular weights with modified end-groups, the total number of end-groups quantified by the IR spectrometry may be correlated to that of POM chain-ends evaluated from the GPC data. As plotted in Fig. 7, although there was discrepancy to some extent, a fair agreement seemed to be obtained between the chain-end numbers derived from the FTIR and GPC measurements of a given POMDA film irradiated up to 480 kGy. This indicates validity of the aforementioned assumption, further leading to a conclusion that the main-chain scission of POMDA by irradiation results mainly in three types of modified chain-end structures.

Formation of radicals produced in POM by irradiation has been extensively studied. Yoshida and Rånby characterized three types of radical structures, $-O-CH_2\cdot$, $-CH_2-O\cdot$, and $-O-\cdot CH-O-$, in the irradiated POM by means of ESR spectroscopy [13]. Carbon–oxygen bond cleavage in the main-chain $-CH_2-O-$ may occur in the primary step to produce the radical $-O-CH_2\cdot$ and $-CH_2-O\cdot$ Most part



Scheme 2. Progressive scissions of POMDA main-chains followed by the formation of various combinations of end-groups: (Ⓐ); acetyloxy, (Ⓕ); formyloxy, (Ⓗ); hyroxyl, (Ⓜ); methoxy end-groups.

of the radicals $-\mathrm{O}-\cdot\mathrm{CH}-\mathrm{O}-$ is considered as a product of the secondary reaction of the primary radicals $-\mathrm{O}-\mathrm{CH}_2\cdot$ and/or $-\mathrm{CH}_2-\mathrm{O}\cdot$. On the basis of the primary free radicals observed by the ESR studies, the reaction steps leading to three types of end-group structures are outlined as in Scheme 1. In view of the fact that there was little oxygen effect under the present conditions of irradiation, possible reaction steps involving oxygen are conveniently omitted in Scheme 1. The hydroxyl and methoxy end-groups are produced by hydrogen abstractions of $-\mathrm{CH}_2\mathrm{O}\cdot$ and $-\mathrm{O}-\mathrm{CH}_2\cdot$ from $-\mathrm{CH}_2-$ groups in the main chain as in reaction steps (c-1) and (d-1), respectively, accompanied by the formation of secondary radicals $-\mathrm{O}-\cdot\mathrm{CH}-\mathrm{O}-$. The formyloxy end-groups are produced by β-scission of $-\mathrm{O}-\ \cdot\mathrm{CH}-$, as in reaction step (e-1), which generates the radicals $-\mathrm{O}-\mathrm{CH}_2\cdot$. It is obvious in Scheme 1 that the molecular weight decreases successively with the increased yields of three types of end-groups.

Scheme 2 illustrates progressive scissions of POMDA main-chains due to direct action of radiation and hydrogen abstraction followed by β-scission, resulting in several combinations of end-groups among the original acetyloxy and the newly produced structures. Table 1 shows all the possible combinations of end-groups for POM chains. In the light of thermal degradation behavior of POM hydrate, it may be reasonable to assume that the POM chains possessing hydroxyl end-groups at either one chain-end or both chain-ends are thermally less stable than the unirradiated POMDA. There are four different combinations of chain-end structures for such a hydroxylated POM family: HH (POM hydrate), HA, HF, and HM as shown in Table 1. However, another POM family including AA (POMDA), AM, AF, FM, FF, and MM in Table 1 would be thermally more stable than the hydroxylated POM, while these might be classified into some sub-classes depending on the relative thermal stability of the respective end-groups.

Table 1
Combinations of various end-groups produced by gamma irradiation of POMDA

	Ⓐ	Ⓗ	Ⓕ	Ⓜ
Ⓐ	**A A**	H A	**F A**	**M A**
Ⓗ	A H	H H	F H	M H
Ⓕ	**A F**	H F	**F F**	**M F**
Ⓜ	**A M**	H M	**F M**	**M M**

3.5. *Correlation of pyrolysis reactivity with radiation-modified chain-end groups*

A group of radiation chemical products, possibly hydroxylated POM family, at a given radiation dose that are thermally less stable than POMDA seems to show a single-modal DTG pattern, taking into account the dimple phenomenon (see Fig. 4(b)). Such a single-modal DTG pattern implies that the hydroxylated POM family shows a common temperature profile of pyrolysis into gasification, irrespective of whether the opposite chain-end of hydroxylated POM bears non-hydroxyl groups. It follows that the chain-end hydroxyl group(s) in the hydroxylated POM family should determine the characteristic pyrolysis temperature at which the chain-end(s) undergo pyrolysis to initiate depolymerization of POM by a radical chain reaction mechanism. Thus, the overall pyrolysis rate of hydroxylated POM would be proportional to the number of hydroxyl end-groups, which may increase progressively with lowering of the molecular weight by irradiation.

Fig. 8 shows that the DTG peak temperature, at which pyrolytic weight loss proceeded at a maximum rate, for the hydroxylated POM family decreased significantly and approached a constant value near the ceiling temperature of 119°C for POM hydrate [4] with increasing radiation doses. It is also remarkable that the pyrolysis of hydroxylated POM family occurred even in the lower temperature region at which the crystal of irradiated POMDA still remained without melting. In view of the above prediction that the POM hydrates will be produced almost exclusively in the amorphous region, the corresponding hydroxylated chain-ends with higher mobility could be pyrolyzed at considerably lower temperatures independent of the melting

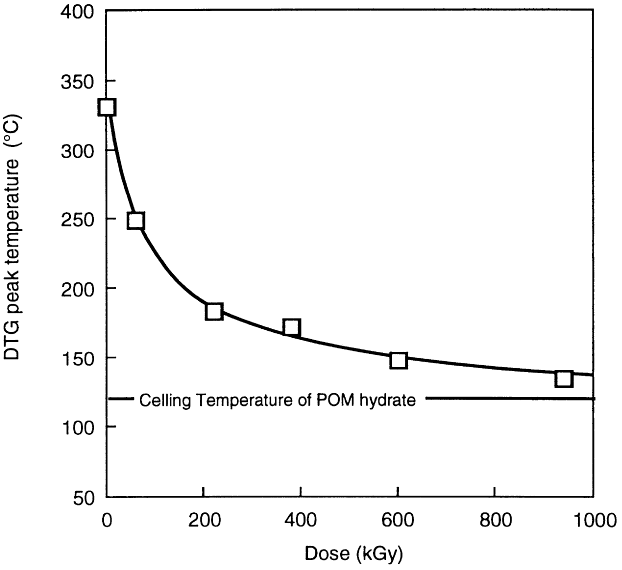


Fig. 8. Dose response of the DTG peak temperature for the thermally less stable hydroxylated POM family.

of POMDA crystals. The succeeding depolymerization from the resulting POM radicals may depend on their mobility related to molecular weights and the heating temperature. As a result of this dependency, the maximum rate of weight loss would decrease with increasing radiation dose, as shown in Fig. 8.

Fig. 4(b) also indicates that the DTG peak temperatures for the thermally stable POM family remained at similar level to unirradiated POMDA, independent of the radiation dose. In this case, the temperatures corresponding to the progressive weight loss were much higher than the ceiling temperature of POM hydrate. Presumably, the bond cleavage at neither the POM main chain nor the non-hydroxyl end-groups may occur at melting points of irradiated POMDA that are higher than the ceiling temperature of POM hydrate, but in the further heated molten state. In view of the evidence that some radiation chemical products with modified chain-end structures would be more thermally stable than the original POMDA, pyrolysis of the modified end-groups occurring at a DTG peak temperature appears to be a rate-determining step for initiating depolymerization of POM main chain. Thus, the carbon–oxygen bond in the POM main chain would be sufficiently stable upon heating. Under such conditions, it follows that the thermal degradation rate may be independent of molecular weight and therefore radiation dose. The DTG analysis of non-hydroxylated POM family also provided a profile that there were more than two sub-components with different thermal stability. This is not surprising, because pre-irradiation treatment generates six possible combinations of the chain-end structural modification to give varying bond cleaving reactivity.

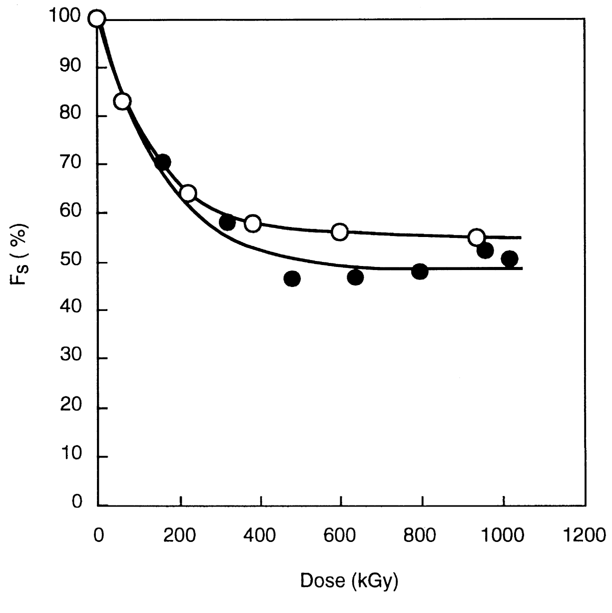


Fig. 9. Dose response of the fraction of thermally stable POM family, as evaluated from (○) TG and (●) FTIR data.

If the fraction of hydroxyl modification at a POM chain end in the POMDA irradiated at a given dose is represented as f_H, then the fraction of the thermally stable POM family (F_S) bearing hydroxyl groups at neither chain end is given as follows:

$$F_S = (1 - f_H)^2.$$

According to this relationship, not only the weight fraction of stabilized POM chains as evaluated by the TG analysis (see Fig. 4, but also the fraction of non-hydroxyl end-groups introduced to both POM chain ends as derived from the FTIR spectrometry (see Fig. 5) could lead to evaluation of the F_S value. Fig. 9 shows the variation of the F_S value thus evaluated as a function of radiation dose where the F_S values based on the thermal and spectroscopic analyses are in fair agreement with each other. It is also seen from Fig. 9 that the fraction of the thermally stable POM family including the original POMDA decreased rapidly with increasing radiation dose up to 400 kGy, then approaching a constant value (about 55 and 50% from the TG and IR data, respectively) on further irradiation. Thus, the POM family with at least one hydroxyl end-group would become an ultimate fraction in the range from 45 to 50% on high-dose irradiation of the POMDA.

4. Conclusions

1. Random scissions of main-chain carbon–oxygen bonds proceeded effectively upon irradiation of POMDA film in air, in accord with the GPC analysis that the molecular weight was lowered progressively with the polydisperse index (M_w/M_n) approaching to the ultimate value of 2 as the radiation dose increased.
2. Depression of the melting temperature of irradiated POMDA as observed in the DSC analysis is attributable to the radiation-induced lowering of molecular weight.

The DSC analysis also indicated radiation chemical formation of thermally less stable components than the original POMDA bearing acetyloxy end-groups, the yield of which increased with increased irradiation dose.

3. According to the TG data, about 55% of higher-dose irradiated POMDA maintained thermal stability comparable or even superior to that of the original POMDA, while about 45% had less stability to thermal degradation. The formation of large amount of more stable components in the higher-dose irradiated POMDA films could neither be explained in terms of crystallinity nor in terms of radiation cross-linking.
4. Radiation chemical modification of the thermal stability of POMDA is correlated to the main-chain scission followed by the formation of hydroxyl ($G(\text{–OH}) = 0.5$), formyloxy ($G(\text{–OCHO}) = 0.6$) and methoxy ($G(\text{–OCH}_3) = 0.4$) end-groups, as identified by measuring IR dichroism of uniaxially oriented POMDA film. Among various combinations of three newly generated end-groups along with the original acethyloxy end-group, a POM chain possessing at least one hydroxyl end-group is concluded to be thermally less stable than POMDA with modification of neither of the acetyloxy end-groups. Another part of POM family without bearing any hydroxyl end-group may have thermal stability comparable or superior to the original POMDA.

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