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STABILITY AND DEGRADATION OF POLYMETHACRYLATES WITH CONTROLLED STRUCTURE

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ABSTRACT

Thermal degradation behaviors for homo- and copolymers of methacrylates prepared by stereospecific living polymerizations as well as radical polymerization were studied. Thermal stability of radically prepared PMMAs can be improved by careful control of end groups and by incorporation of methyl acrylate into the chain. The mechanism of the stabilization was elucidated. Tacticity dependence of thermal stability of PMMAs was examined using isotactic and syndiotactic PMMAs with molecular weights (\bar{M}_n) of 2,500–500,000 under nitrogen. Syndiotactic PMMAs showed higher degradation temperatures than the isotactic PMMAs of the same \bar{M}_n when the \bar{M}_n was lower than 25,000, and *vice versa* for the higher \bar{M}_n . A similar \bar{M}_n and tacticity dependence was observed in degradation in air, and the critical \bar{M}_n was found to be about 10,000. These phenomena are discussed in terms of zip length of degradation and the difference in flexibility between isotactic and syndiotactic PMMA chains. Thermal degradation behavior of polymethacrylates were examined and classified as single-step and two-step degradations. This was related with the structures of the ester group. The glass transition temperatures of stereoregular homo- and copolymers of methacrylates are also discussed in some detail.

INTRODUCTION

Polymethacrylates degrade relatively easily to lower molecular weight compounds or to the monomers by heating or irradiation [1, 2]. This is often noticed on sheet extrusion of poly(methyl methacrylate) (PMMA). The decomposition or stability of methacrylate polymers relates to their structures such as type of ester group and of the end groups, molecular weight and its distribution, stereoregularity, and copolymer composition.

In this paper we describe thermal degradation behaviors for homo- and copolymers of various methacrylates with carefully controlled structures synthesized by stereospecific living polymerizations as well as radical polymerizations. The relationship between the glass transition temperature (T_g) and the structure of polymethacrylate was also studied in some detail. With the knowledge of the stereochemistry of polymer and the techniques for controlling the structure of polymer, we can satisfactorily control the thermal properties of polymethacrylates.

EXPERIMENTAL

Most of the methacrylate monomers were purified in a usual manner, dried over calcium dihydride, and vacuum-distilled just before use. α,α -Dimethylbenzyl methacrylate was purified by recrystallization from petroleum ether.

Anionic polymerization and copolymerization were carried out in glass ampules filled with dry nitrogen. Highly isotactic PMMAs with a narrow molecular weight distribution (MWD) were obtained by the polymerization of MMA with $t\text{-C}_4\text{H}_9\text{MgBr}$ in toluene at -78°C [3, 4]. Highly syndiotactic homo- and copolymers of methacrylates were obtained by polymerization with $t\text{-C}_4\text{H}_9\text{Li}-\text{R}_3\text{Al}$ ($\text{R} = \text{C}_2\text{H}_5-$, $n\text{-C}_4\text{H}_9-$) ($\text{Al/Li} = 3$) in toluene at -78°C [5, 6]. The molecular weights of the polymers were controlled by changing the ratio of initiator to monomer. The reactions were terminated by adding a small amount of methanol containing aqueous HCl. The reaction mixtures were poured into a large amount of precipitant. Hexane was used as the precipitant for PMMAs with molecular weights of $\sim 20,000$ or less: poly(isopropyl methacrylate), poly(cyclopropylmethyl methacrylate), poly(MMA-*co*-butyl methacrylate), and poly(MMA-*co*-benzyl methacrylate). These polymers were collected by filtration, washed with hexane, then with water several times, and dried under vacuum. Methanol was used as the precipitant for PMMAs with molecular weights higher than 20,000: poly(octyl methacrylate), poly(α,α -dimethylbenzyl methacrylate), and poly(α -methylbenzyl methacrylate). These polymers were also collected by filtration, washed with methanol, and dried under vacuum. For other polymers [poly(ethyl methacrylate), poly(butyl methacrylate), poly(isobutyl methacrylate), poly(*t*-butyl methacrylate), and poly(allyl methacrylate)], the reaction mixtures were concentrated under vacuum to dryness, and the residues were dissolved in benzene. The polymers were recovered by freeze-drying of the benzene solutions after the insoluble materials were removed by centrifugation.

Radical polymerization and copolymerization were carried out in glass ampules under nitrogen. The polymers obtained were recovered by precipitation into methanol, washed with methanol, and dried under vacuum at 60°C . Polymers formed in the presence of *t*-butyl mercaptan, whose molecular weights were $\sim 10,000$ or less, were

recovered from the reaction mixture by freeze-drying as mentioned above. PMMA prepared in the presence of cobalt tetraphenylporphyrin was recovered by precipitation into hexane, washed with hexane, and dried under vacuum.

Thermogravimetry (TG) was performed on a RIGAKU TG-8110 apparatus under nitrogen flow (100 mL/min) or in air at a heating rate of 10°C/min. The weight of the samples was ~5 mg. A baseline run without a sample was conducted, and the resulting data were used to correct the observed TG curves for polymer samples. The degradation temperature (T_d) is defined as the temperature at which the weight loss reaches 50% of the total weight loss in each degradation step, and is used throughout this article.

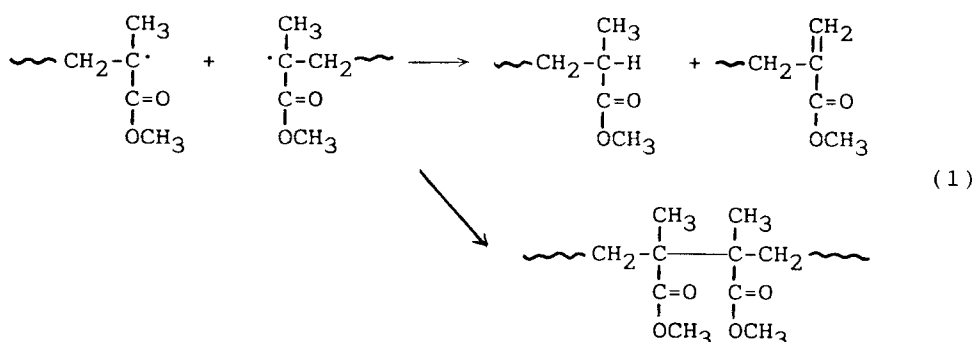
Differential scanning calorimetry (DSC) was performed on a RIGAKU DSC-8230 apparatus under nitrogen flow (100 mL/min) at a heating rate of 20°C/min. The weight of the samples was ~10 mg.

$^1\text{H-NMR}$ spectra were recorded on a JNM GSX-270 or on a JNM GX-500 spectrometer (JEOL) using chloroform- d as the solvent at 55°C.

RESULTS AND DISCUSSION

1. Degradation of Polymers and Copolymers of Methyl Methacrylate (MMA) Prepared by Radical Initiators

In the radical polymerization of MMA, termination reactions could occur through disproportionation and combination reactions of two propagating radicals in the absence of chain transfer reactions (Eq. 1). The disproportionation reaction gives an equal number of polymer chains with vinylidene end groups and those with saturated end groups. A polymer chain formed through a combination reaction contains a head-to-head linkage within the chain.



The unsaturated end groups and the head-to-head linkage have a significant effect on the thermal stability of radically prepared PMMAs [1, 2, 7–10]. The analysis of these linkages could be made by NMR spectroscopy [11, 12]. Figure 1 shows a 270-MHz $^1\text{H-NMR}$ spectrum of the PMMA prepared with AIBN in bulk at 60°C. The peaks at 5.4 and 6.14 ppm have been assigned to the methylene protons of the vinylidene groups at the chain end. The fraction of polymer molecules that contain the vinylidene group at the chain end can be determined from these signals, since the effect of a chain transfer reaction to the monomer can be neglected. Intensity measurements of these signals indicated that 36% of the polymer molecules con-

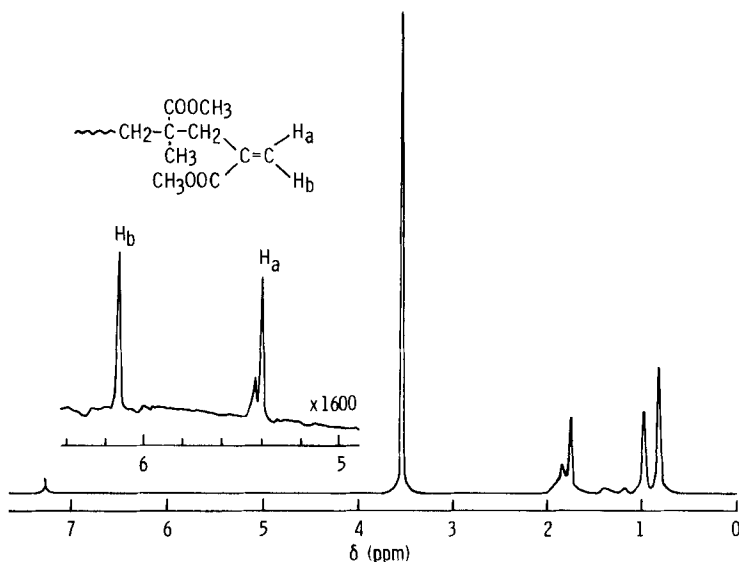


FIG. 1. ^1H -NMR spectrum of radically prepared PMMA measured in CDCl_3 at 55°C and 270 MHz [9]. PMMA: $\bar{M}_n = 44,600$, $\bar{M}_w/\bar{M}_n = 1.67$, $mm:mr:rr = 7.5:33.1:59.4$.

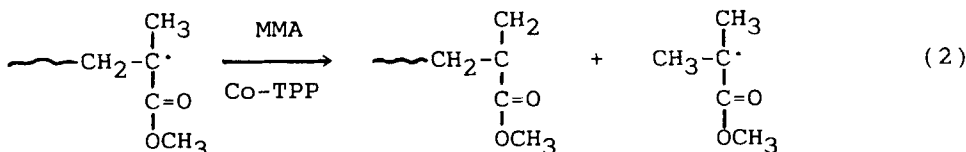
tained a vinylidene double bond at the chain end; 72% of the molecules formed through the disproportionation reaction, and consequently 28% of the molecules formed through the combination reaction, contained a head-to-head linkage in the chain [11]. Direct evidence for the existence of a head-to-head linkage has been provided by the ^{13}C -NMR spectrum of a radically prepared PMMA ($\bar{M}_n = 17,700$); the α -methyl carbon signal of the head-to-head linkage was at 15.0 ppm, and the intensity measurement indicated that 22% of the polymer molecules contain a head-to-head linkage in the chain [12].

Thermal degradation under nitrogen of the radically prepared PMMA proceeds in three steps with weight loss which occur around 165, 270, and 360°C , respectively (Fig. 2). The least stable step is initiated by scissions of the head-to-head linkages, the second step through chain-end initiation from the vinylidene ends, and the most stable step* by random scission within the polymer chain [9].

*Meisters and his coworkers reported that the least stable step of degradation (165°C), could not be observed by thermogravimetry for the MMA oligomers ($\overline{DP} = 4\text{--}16$) having head-to-head linkage in the middle of the chain which were prepared by the coupling reaction of Br-terminated MMA oligomers [10]. They claimed that the head-to-head oligomers had the similar T_d (270°C) to that for the oligomers having the unsaturated end group (265°C), and suggested that the weight loss at 165°C might be the evolution of occluded MMA monomer. However, the ^1H NMR spectrum shown in FIG. 1 clearly indicates the absence of the monomer. We have reported that the weight loss due to the chain breaking at the head-to-head linkage is strongly suppressed under the action of oxygen [9], and thus careful elimination of oxygen is necessary to observe the weight loss at 165°C . Even in the absence of oxygen, there is some possibility that termination reaction of oligomer radicals formed by scission of the head-to-head linkage causes formation of the oligomer molecules having vinylidene ends, which decompose around 270°C .

The use of chain transfer agents in the radical polymerization of MMA greatly reduces the amount of head-to-head linkage and vinylidene end; and thereby reduces degradation through the least stable and the second steps to stabilize the polymer [9, 11].

Cobalt(II) tetraphenylporphyrin (Co-TPP) is known to promote a chain transfer reaction in the radical polymerization of MMA to give end-unsaturated PMMA with a low molecular weight (Eq. 2) [13].



A PMMA prepared radically in the presence of Co-TPP ($\bar{M}_n = 4830$, number of unsaturated end groups per chain = 0.92) was subjected to thermal degradation under nitrogen. The TG curve showed a weight loss around 270–310°C with a T_d value of 291°C (Fig. 3). The value corresponds to the second step of the degradation observed for the radically prepared PMMA. The result confirms that the second step of degradation occurs at the unsaturated chain end.

Thermal degradation of the radically prepared PMMA in air occurred around 300°C, as shown in Fig. 2. The result indicates that gas-phase oxygen effectively traps polymer radicals originated from chain scissions at the head-to-head linkages, and also traps some of radicals generated by end initiation through the second step. The fact that the temperature for major degradation of PMMA decreased by about 60°C in air as compared with the degradation in nitrogen is explained in the following way. Radicals formed by random scission of the PMMA chain may react with oxygen to form ROO^\bullet , which subsequently abstracts hydrogen to form ROOH . The

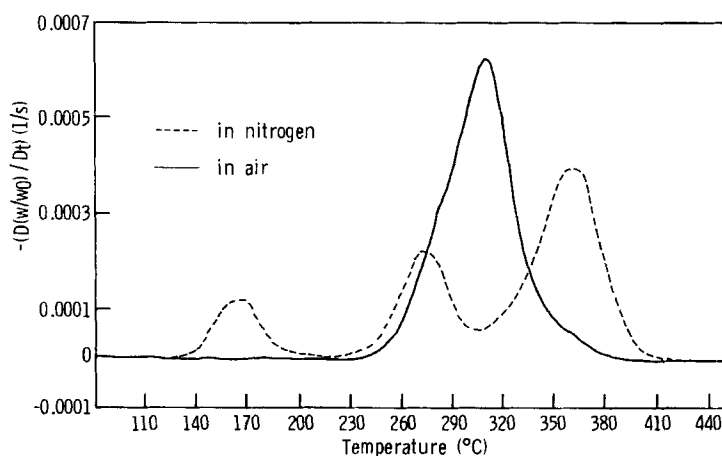


FIG. 2. Derivative thermogravimetric curves for radically prepared PMMA in nitrogen and in air at the heating rate of 2°C/min [9]. PMMA: $\bar{M}_n = 44,600$, $\bar{M}_w/\bar{M}_n = 1.67$, $mm:mr:rr = 7.5:33.1:59.4$.

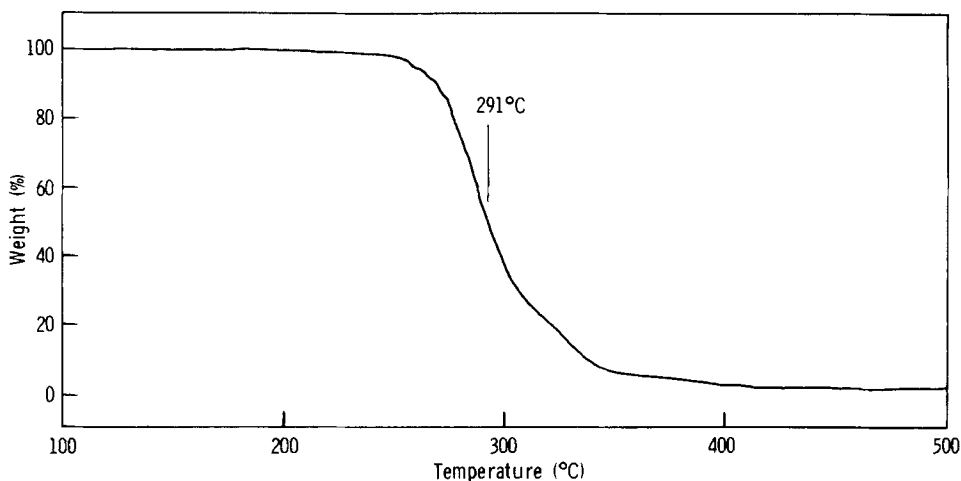


FIG. 3. TG curve of PMMA prepared with AIBN in benzene at 60°C in the presence of cobalt(II) tetraphenylporphyrin. PMMA: $\bar{M}_n = 4830$, number of unsaturated end group per chain = 0.92.

ROOH generates two radicals, RO \cdot and very reactive \cdot OH, that subsequently attack other polymer chains to yield rapid degradation.

Commercial PMMA usually contains a small amount of acrylate units, presumably to enhance the thermal stability. The small concentrations used have no significant influence on the useful properties of the parent polymer. Grassie and Torrance [14, 15] studied thermal degradation of poly(MMA-co-methyl acrylate) and demonstrated the progressive decrease in the extent of end-initiated degradation (the second step) as the methyl acrylate content of the copolymer increased. They ascribed the stabilization by copolymerized methyl acrylate to the termination of radicals formed by the end-initiated degradation with direct blockage by methyl acrylate units, although some of the methyl acrylate units were depolymerized to give the monomer.

1 H-NMR analysis of poly(MMA-co-methyl acrylate) ($\bar{M}_n = 51,100$, MMA content 88.1%) indicated the amount of the unsaturated end group to be 24% of the chain end. The unsaturated end group of the copolymer has the same structure as that for the end group of PMMA. Thus, the smaller amount of unsaturated end group in the copolymer than in radically prepared PMMA should also be one of the reasons for the increased stability of the copolymer in the temperature range around 270°C.

In the industrial production of PMMA resin, chain transfer agent is also employed to suppress the amount of unsaturated end group. The effect of incorporation of the methyl acrylate unit in the PMMA chain without an unsaturated end group has not been studied. TG analyses were carried out under nitrogen for PMMA ($\bar{M}_n = 10,200$) and poly(MMA-co-methyl acrylate) ($\bar{M}_n = 8840$, MMA content 89.5%) prepared radically in the presence of a chain transfer agent, *t*-butyl mercaptan (*t*-BuSH) (Fig. 4) [16]. Both the PMMA and the copolymer are almost devoid of terminal unsaturation ($\sim 0.2\%$), as evidenced from 500 MHz 1 H-NMR analysis, and did not show a weight loss around 270°C; the latter exhibited a higher T_d (384°C) than did the former (381°C). The results indicate that the increase in

thermal stability by incorporation of a methyl acrylate unit in the chain is small but distinctive in the temperature range of 350–400°C also. To elucidate the mechanism of the stabilization, isothermal degradation of the copolymer was carried out at 310°C for 30 minutes under vacuum, and the volatile degradation products were collected and analyzed by ¹H-NMR spectroscopy. The products consisted of MMA, methyl acrylate, and a small amount of isobutene. The isobutene came from the *t*-BuS— group incorporated at the initiating chain end *via* a chain transfer reaction. The mole ratio of MMA and methyl acrylate in the products was 95.1/4.9, while the MMA/methyl acrylate ratio in the copolymer was 89.5/10.5. The results clearly show that an unzipping reaction along the MMA sequence tends to be terminated at a methyl acrylate unit, as suggested by Grassie and Torrance for end-initiated degradation [14]. The possibility that MMA–methyl acrylate linkage in the copolymer chain is thermally more stable than MMA–MMA linkage for enhancing the thermal stability of the copolymer may be eliminated since the content of methyl acrylate units in the copolymer is only 10.5%.

In a practical sense, the thermal stability in air is more interesting. Figure 5 shows the TG curves for these polymers obtained in air. The poly(MMA-*co*-methyl acrylate) prepared in the presence of *t*-BuSH had a small but distinctively higher T_d than did PMMA prepared under the same conditions. Therefore, methyl acrylate units incorporated in the polymer chain effectively improve the thermal stability of the polymer not only in nitrogen but also in air.

2. Degradation of Anionically Prepared Polymethacrylates with Controlled Structures

As mentioned in the previous section, the presence of abnormal linkages, such as the head-to-head linkage, and the structure of end groups greatly affect the

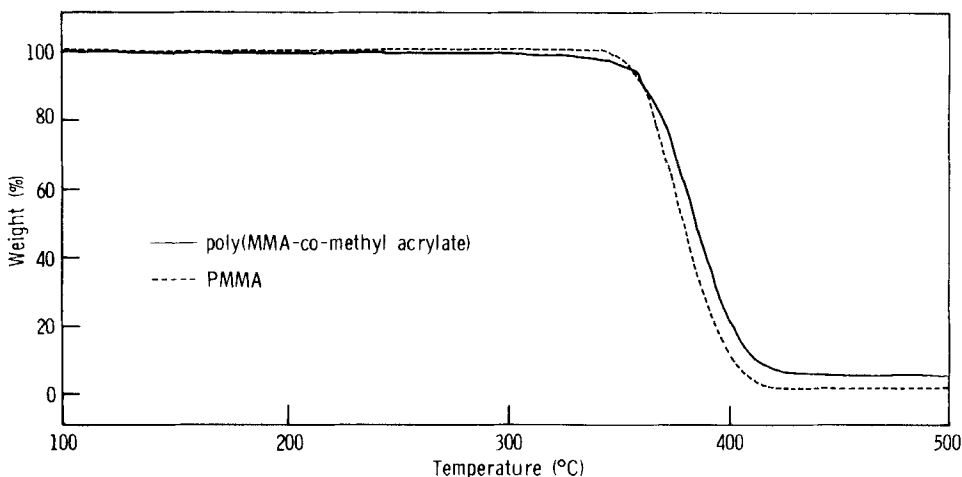


FIG. 4. TG curves measured in nitrogen of PMMA and poly(MMA-*co*-methyl acrylate) prepared with BPO in the presence of *t*-butyl mercaptan (*t*-BuSH) in benzene at 60°C. MMA content of the copolymer: 89.5%. (Heating rate, 10°C/min; nitrogen flow rate, 100 mL/min.)

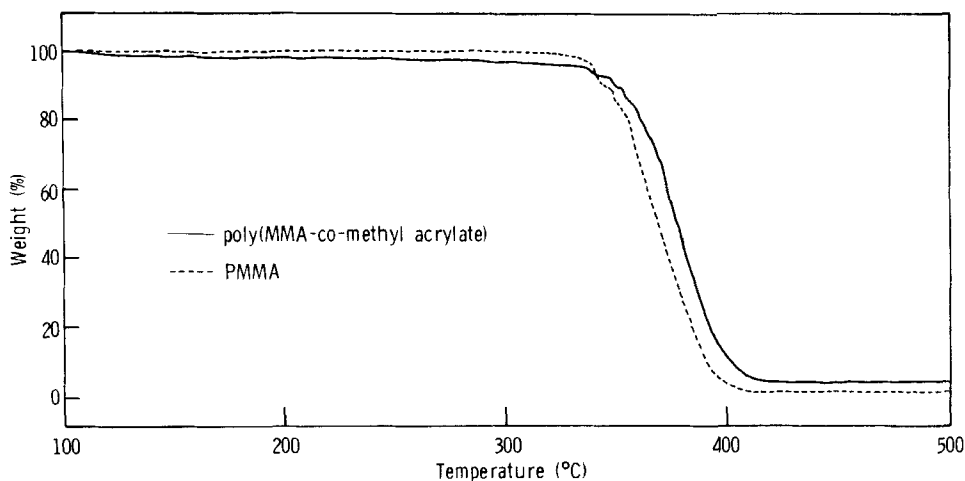


FIG. 5. TG curves measured in air of PMMA and poly(MMA-co-methyl acrylate) prepared with BPO in the presence of *t*-BuSH in benzene at 60°C. MMA content of the copolymer: 89.5%. (Heating rate, 10°C/min; nitrogen flow rate, 100 mL/min.)

thermal stability of radically prepared polymers and copolymers of MMA. Therefore, polymethacrylate samples with the same chemical structure but different properties (molecular weight, tacticity, etc.) are highly desirable for understanding the relationship between thermal stability and polymer structure.

Recently, we found that polymerizations of MMA in toluene at low temperatures with *t*-C₄H₉MgBr [3, 4] and with *t*-C₄H₉Li-R₃Al (Al/Li ≥ 3) [5, 6], both of which contain the *t*-C₄H₉- group at one end of the chain and the methine proton at the other end, gave highly isotactic and syndiotactic PMMAs with narrow MWDs, respectively. The molecular weights of the polymers can be easily controlled by changing the ratio of initiator to monomer. Living polymerization, particularly of the latter, can also be applied to the preparation of stereoregular polymers of methacrylates other than MMA. Therefore, these polymer samples meet the above-mentioned requirement for the study of thermal stability of polymethacrylates. In this section, studies on the thermal degradation of polymethacrylates with controlled structures prepared with these stereospecific living polymerizations are described.

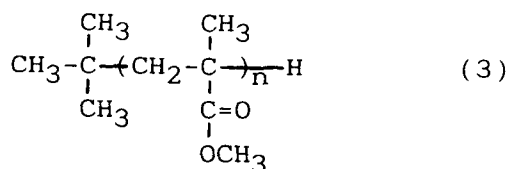
2.1. Effect of Tacticity and Molecular Weight on the Degradation of PMMA

The stereochemical structure of a polymer is one of the important factors affecting its properties [17]. The thermal stability of poly(vinyl chloride) is reported to depend on its tacticity [18–22]. The degradation of isotactic and syndiotactic PMMAs was studied by kinetic analysis of monomer formation [23]; the isotactic polymer showed higher degradation rates over a range of temperatures from 300 to 400°C, but the overall energies of activation were similar for both polymers. Chiantore and Guaita [24, 25] reported TG curves for isotactic and syndiotactic PMMAs whose end-group structures were different. Although the TG curves re-

ported were slightly different, the difference was not clear enough to show which PMMA is more stable, and the authors did not mention the effect of tacticity on degradation via main-chain scission.

In a previous communication we reported the higher degradation temperature of syndiotactic PMMA as compared with isotactic PMMA when using PMMAs with \bar{M}_n s from 4,700 to 22,000 [26].

The anionically prepared PMMAs ($\bar{M}_n = \sim 5000$) having the structure depicted in Eq. (3) decomposed through a single reaction step, as shown in Fig. 6 [27].



The isotactic PMMA started to decompose at a lower temperature than did the syndiotactic one when the \bar{M}_n s were similar. Figures 7 and 8 show the T_d s of isotactic and syndiotactic PMMAs with different \bar{M}_n s in nitrogen and in air, respectively [27]. The T_d s depended on the \bar{M}_n of the PMMAs, and decreased with increasing \bar{M}_n . This molecular weight dependence of the degradation temperature indicates that the degradation of the PMMAs around 300–400°C is caused by random scission followed by unzipping.

The molecular weight dependence of the degradation temperature also indicates that studies on the tacticity dependence of degradation temperatures should be made for polymers with almost the same \bar{M}_n . Figure 6 also indicates that

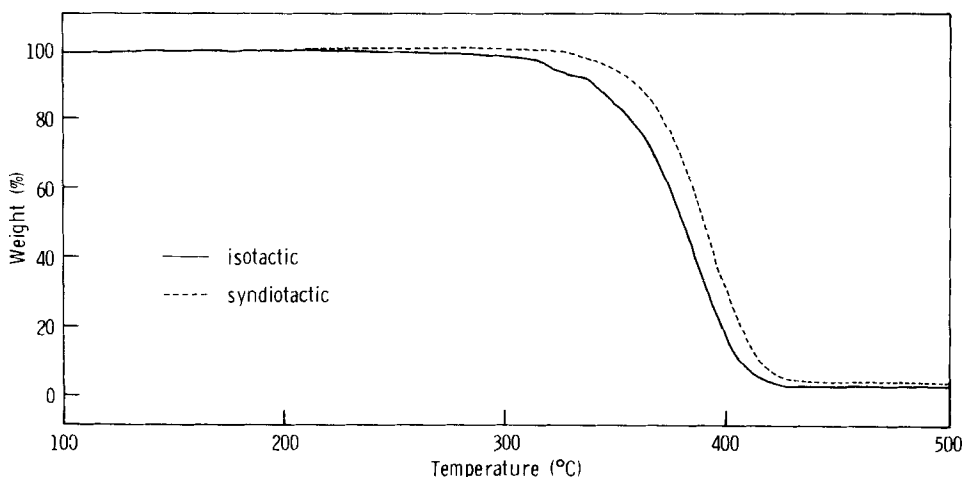


FIG. 6. TG curves obtained in nitrogen is isotactic and syndiotactic PMMAs prepared by $t\text{-C}_4\text{H}_9\text{MgBr}$ and $t\text{-C}_4\text{H}_9\text{Li}-(n\text{-C}_4\text{H}_9)_3\text{Al}(1/3)$ in toluene at -78°C . Isotactic PMMA: $\bar{M}_n = 5400$, $\bar{M}_w/\bar{M}_n = 1.10$, $mm:mr:rr = 97:2:1$. Syndiotactic PMMA: $\bar{M}_n = 5700$, $\bar{M}_w/\bar{M}_n = 1.11$, $mm:mr:rr = 1:9:90$. (Heating rate, $10^\circ\text{C}/\text{min}$; nitrogen flow rate, $100\text{ mL}/\text{min}$.)

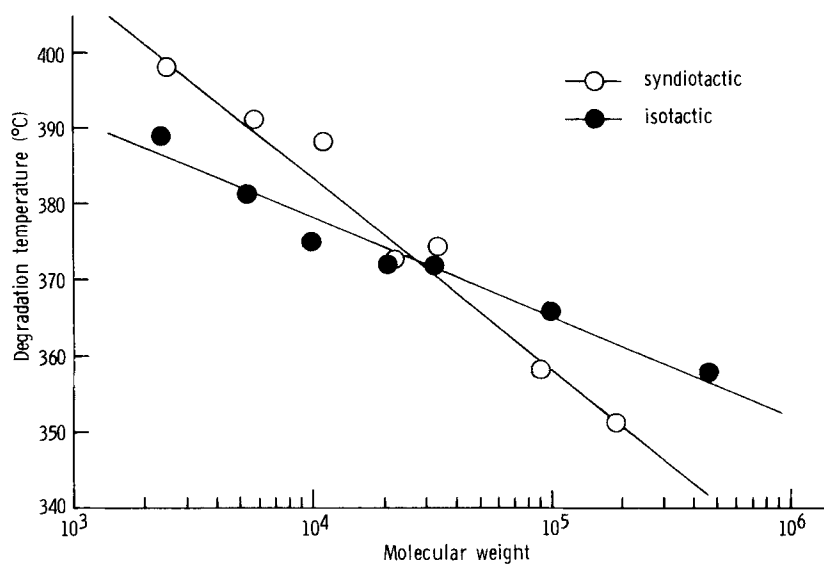


FIG. 7. Thermal degradation in nitrogen of isotactic and syndiotactic PMMAs with different molecular weights.

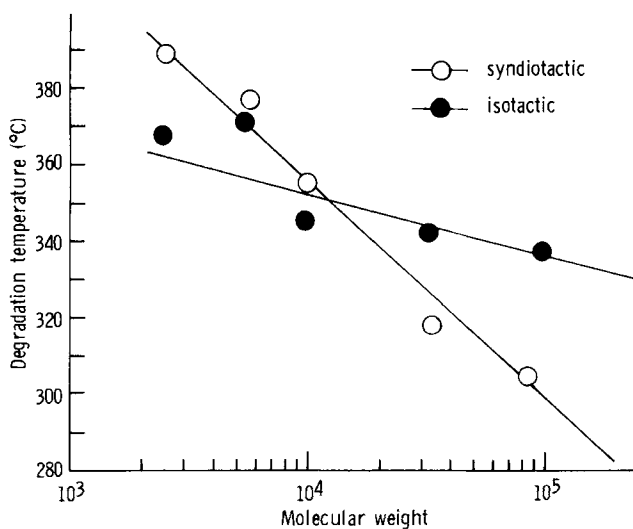
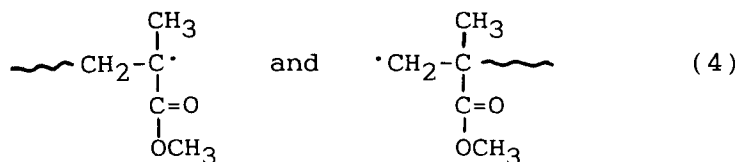


FIG. 8. Thermal degradation in air of isotactic and syndiotactic PMMAs with different molecular weights.

the syndiotactic PMMAs have higher degradation temperatures than do isotactic PMMAs in nitrogen when the molecular weights are lower than 25,000 and *vice versa* for higher molecular weight polymers. This finding is quite new and very interesting when compared with our previous results [26]. Chiantore *et al.* [28] estimated the average zip lengths* from Monte Carlo simulation to be 550 and 250 for two types of PMMA radicals formed concomitantly by main chain scission (Eq. 4):



When the degree of polymerization (\overline{DP}) of PMMA is smaller than the zip length, the scission of one bond in the main chain is enough for the polymer chain to degrade completely. Under this circumstance, the stability of the main-chain bonds is the only factor that determines the thermal stability of the polymer. The lower thermal stability of isotactic PMMAs in the lower molecular weight region can be ascribed to the lower stability of the polymer molecules; this may be due to their higher chain mobility, as mentioned later. As the \overline{DP} increases, the termination reaction between polymer radicals undergoing unzipping becomes important. The reactivity of the chain-end function is affected by the tacticity; for example, isotactic PMMA macromonomer exhibits a higher reactivity than does the syndiotactic one [29]. We thus assume that in the higher molecular weight region in Fig. 7, the greater segmental mobility of isotactic PMMA radicals may provide more opportunities for the radicals to undergo a termination reaction, and thus the isotactic PMMAs exhibit higher thermal stability than do the syndiotactic PMMAs in this molecular weight region.

Similar results were observed in the thermal degradation of isotactic and syndiotactic PMMAs in air except for the fact that the molecular weight for the intersecting point of the two straight lines was lower than that for degradation in nitrogen (Fig. 8). As mentioned previously, gas-phase oxygen effectively traps macroradicals generated in degradation [9], and this decreases the zip length as compared with degradation in nitrogen.

Thermal degradation of isotactic and syndiotactic polymers of MMA- d_8 ($\overline{M}_n = 4730$ and 4630) prepared with $t\text{-C}_4\text{H}_9\text{MgBr}$ and $t\text{-C}_4\text{H}_9\text{Li}-(\text{C}_2\text{H}_5)_3\text{Al}$, respectively, was examined. The T_d of the syndiotactic poly(MMA- d_8) was higher than that of the isotactic polymer, confirming the tacticity dependence of degradation temperature in the lower molecular weight range. Both of the isotactic and syndiotactic poly(MMA- d_8)s had 5–10°C higher degradation temperatures than did the corresponding undeuterated PMMAs with a similar \overline{M}_n and MWD. This might be explained by the smaller volume of deuterium compared with hydrogen; i.e., there is a smaller steric repulsion between the substituents along the PMMA chain [26].

*The average number of monomer units successively released by depolymerization along the chain.

The sensitivity of PMMA as an electron-beam resist depends on the tacticity; isotactic PMMA is more sensitive than syndiotactic PMMA. That is, the former degrades into lower molecular weight polymers more easily than the latter under irradiation by an electron beam [30]. A similar phenomenon was also reported for poly(α,α -dimethylbenzyl methacrylate)s [31, 32]. Therefore, isotactic PMMA is more labile than syndiotactic PMMA both in thermal degradation in a limited range of \bar{M}_n and in radiation-induced degradation processes, even though the mechanisms of degradation in these processes may be different.

It has been shown in NMR relaxation experiments that isotactic PMMA chains have higher segmental mobility than do syndiotactic chains both in solution [33–38] and in the solid state [39, 40]. The higher flexibility of the isotactic polymer chains is also reflected in their lower T_g s than those of syndiotactic PMMAs (see Section 3). The difference in segmental mobility is likely to be one of the factors causing the difference in thermal stability between isotactic and syndiotactic PMMAs.

2.2. Thermal Degradation of Isotactic and Syndiotactic Polymethacrylates

The thermal stability of polymethacrylates depends on the structure of monomeric units as well as on the tacticity and \bar{M}_n . The T_d s of various polymethacrylates with various tacticities were examined in nitrogen and are shown in Tables 1 and 2 [41]. The polymethacrylates can be classified into two categories. The one consists of the polymers that degrade through a single step around 300–400°C (Table 1), and the other of the polymers that decompose through two reaction steps (Table 2). The first group includes the polymers of methyl, ethyl, *n*-butyl, *n*-octyl, cyclopropylmethyl, and isobutyl methacrylates. The T_d s for the syndiotactic polymers of the first group with similar \bar{M}_n s are shown in Table 1 together with the T_g s of the

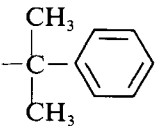
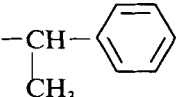
TABLE 1. Thermal Degradation Temperatures (T_d s) of Syndiotactic Polymethacrylates Which Undergo Single-Step Degradation

Ester group	T_d , °C	T_g , °C	\overline{DP}^a	$\frac{\bar{M}_w}{\bar{M}_n}^a$	Tacticity, % ^b		
					<i>mm</i>	<i>mr</i>	<i>rr</i>
—CH ₃	388	122	109	1.17	0	11	89
—CH ₂ CH ₃	374	55	101	1.10	2	9	89
—CH ₂ CH ₂ CH ₂ CH ₃	362	22	103	1.11	0	9	91
—(CH ₂) ₇ CH ₃	348	—35	82	1.14	2	7	91
—CH ₂ CH $\begin{cases} \text{CH}_2 \\ \\ \text{CH}_2 \\ \text{CH}_3 \end{cases}$	369	44	71	1.20	1	10	89
—CH ₂ CH $\begin{cases} \text{CH}_3 \\ \\ \text{CH}_3 \end{cases}$	346	51	108	1.10	0	7	93

^aDetermined by GPC.

^bDetermined by ¹H NMR.

TABLE 2. Thermal Degradation of Various Polymethacrylates Which Undergo Two-Step Degradation

Ester group	N_{β}^a	$T_{d1},^b$ °C	$T_{d2},^b$ °C	Weight loss, % ^c		\overline{DP}^d	\overline{M}_w^d \overline{M}_n	Tacticity, % ^e		
				1st	2nd			<i>mm</i>	<i>mr</i>	<i>rr</i>
-C(CH ₃) ₃	9	235	434	46.7 (45.8)	48.6 (54.2)	97	1.40	20	26	54
-C(CH ₃) ₃	9	192	422	46.5 (45.8)	44.9 (54.2)	247	1.61	100	0	0
-CH(CH ₃) ₂	6	330	440	49.8 (39.8)	37.8 (60.2)	103	1.13	0	8	92
-CH(CH ₃) ₂	6	300	400	62.3 (39.8)	21.4 (60.2)	101	2.27	43	20	37
	6	203	442	61.6 (62.3)	35.1 (37.7)	1263	2.13	10	47	43
	3	305	425	64.4 (59.5)	28.4 (40.5)	853	2.28	0	19	81
-CH ₂ -CH=CH ₂	1	287	417	24.3 (38.9)	71.7 (61.1)	94	1.11	0	8	92

^aNumber of β -hydrogen.

^b T_{d1} and T_{d2} are the degradation temperatures for the first step and the second step, respectively.

^cWeight loss during the decomposition at the first step or the second step. The figures in parentheses represent the weight losses calculated for the formation of poly(methacrylic anhydride) and its decomposition, respectively.

^dDetermined by GPC.

^eDetermined by ¹H NMR.

polymers. The T_{d2} s decreased linearly with decreasing T_g of the polymers except for the poly(isobutyl methacrylate) (Fig. 9). This indicates that the thermal stability of the polymer decreases with increasing segmental mobility of the chain. The reason for the lower T_d of poly(isobutyl methacrylate) is not clear. The possibility of involvement of side chain degradation is under investigation.

The second group includes the polymers of *t*-butyl, isopropyl, α,α -dimethylbenzyl, α -methylbenzyl, and allyl methacrylates. The T_{d2} s for the first (T_{d1}) and the second (T_{d2}) decomposition steps are summarized in Table 2. Figure 10 shows the TG curves for the isotactic and syndiotactic poly(*t*-butyl methacrylate)s as a typical example of the polymers in this group. It was reported that radically prepared poly(*t*-butyl methacrylate) decomposed into poly(methacrylic anhydride) via poly(methacrylic acid) and isobutene around 200°C [42-44]. So the decomposition at 192 and 235°C in Fig. 9 might be due to this ester decomposition. The weight losses

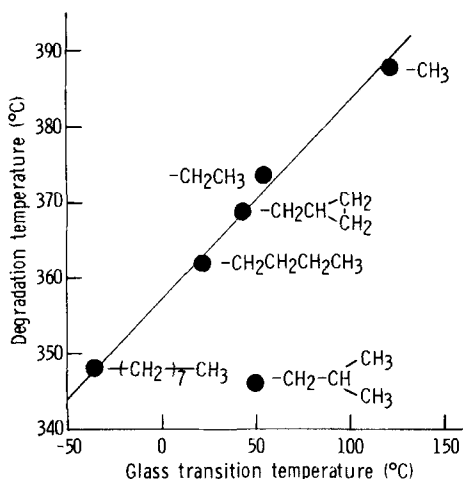
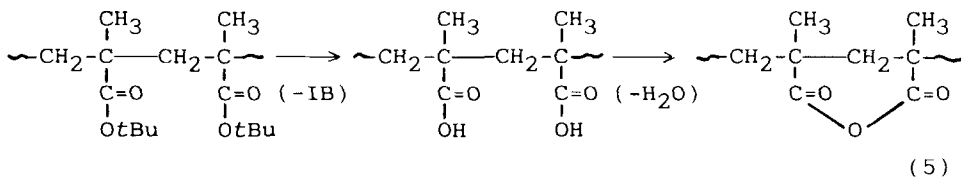


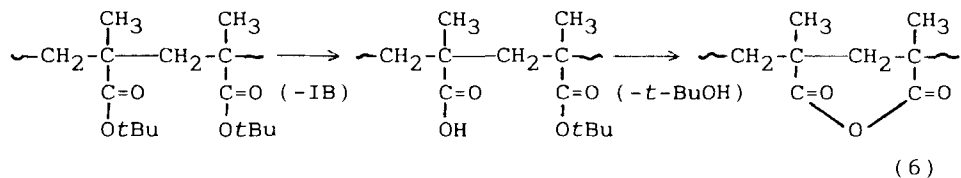
FIG. 9. Relationship between glass transition temperature and degradation temperature of syndiotactic poly(alkyl methacrylate)s which undergo single-step degradation.

of 46.5 and 46.7% for the isotactic and syndiotactic polymers correspond to the formation of poly(methacrylic anhydride) (45.8% (calc.)).

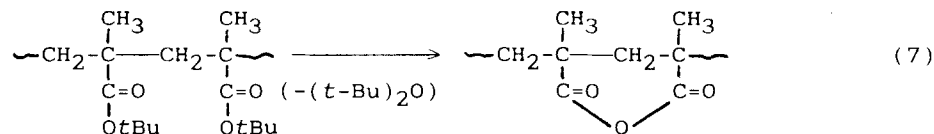
Type I



Type II



Type III

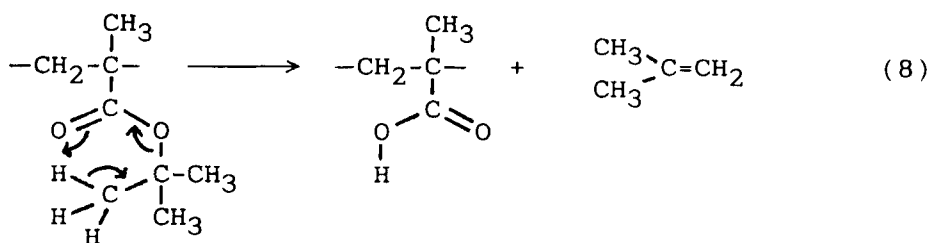


When the polymer was heated at 200°C under high vacuum, a 2:1 mixture of isobutene and water was obtained quantitatively. This indicates that the decomposition occurred through the formation of poly(methacrylic acid) followed by dehydration of the polymer (Type I, Eq. 5). The other two possible mechanisms, Types II (Eq. 6) and III (Eq. 7), could be ruled out since *t*-BuOH and (*t*-Bu)₂O were not detected in the volatile products of the decomposition. The remaining polymer

was almost completely poly(methacrylic anhydride) after the first decomposition, evidenced by IR spectroscopy. This means that dehydration of the poly(methacrylic acid) occurred not at random but in a sequential way.

The weight loss at the second step should be due to the decomposition of the resulting poly(methacrylic anhydride). T_{d1} and T_{d2} for the syndiotactic poly(*t*-butyl methacrylate) are higher than those for the isotactic one, again indicating higher thermal stability of the syndiotactic polymer (Fig. 10). Matsuzaki *et al.* reported that the rate of weight loss of isotactic poly(*t*-butyl methacrylate) prepared with *s*-butylmagnesium bromide was larger than that of the syndiotactic one prepared by γ -ray irradiation, although the tacticity numerical values were not reported [44].

As proposed by Grant and Grassie [42], the decomposition at the first step may occur through the migration of β -hydrogen atoms in the ester group to the carboxylic acid group:



Then the decomposition is expected to be more favorable because the number of β -hydrogen atoms is larger. The T_d value for poly(*t*-butyl methacrylate) is surely lower than that for poly(isopropyl methacrylate) (Table 2). Poly(α,α -dimethylbenzyl methacrylate) decomposes at a lower temperature than does poly(α -methylbenzyl methacrylate). However, poly(α,α -dimethylbenzyl methacrylate) decomposes at a lower temperature than does poly(*t*-butyl methacrylate) which contains

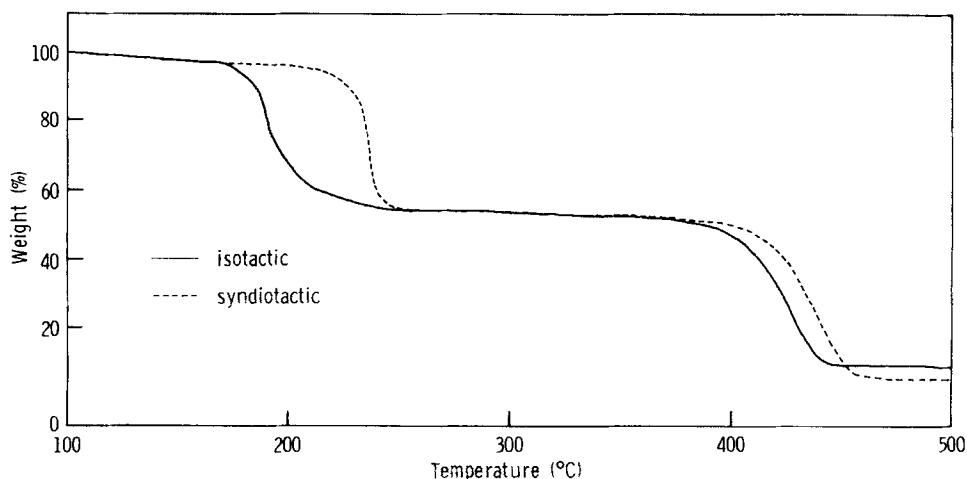


FIG. 10. TG curves measured in nitrogen of isotactic and syndiotactic poly(*t*-butyl methacrylate)s. (Heating rate, 10°C/min; nitrogen flow rate, 100 mL/min.)

1.5 times as many β -hydrogen atoms as does the former polymer. This indicates that the bulkiness of the ester group as well as the number of β -hydrogen atoms is an important factor for the formation of acid groups.

Among the polymers examined, poly(*t*-butyl methacrylate) and poly(α,α -dimethylbenzyl methacrylate) exhibited weight losses in the first step of degradation which agreed well with those expected for the complete elimination of the ester groups *via* Type I degradation (Eq. 5). On the other hand, in the cases of poly(isopropyl methacrylate) and poly(α -methylbenzyl methacrylate), the weight losses in the first step of degradation exceeded the expected values. T_{d1} for syndiotactic poly(isopropyl methacrylate) was larger than that for the isotactic-rich one, as in the case of poly(*t*-butyl methacrylate). The volatile products from isothermal degradation under vacuum for 30 minutes of isotactic-rich and syndiotactic poly(isopropyl methacrylate)s at 300 and 330°C, respectively, were found to contain propylene, isopropyl alcohol, the monomer, methacrylic acid, and water. The formation of propylene and water indicates the occurrence of the Type I, degradation process, while the formation of the alcohol should be the result of the Type II process. Furthermore, unzipping also took place to some extent as evidenced by the formation of the monomer. The residue of the degradation products was found by IR spectroscopy to contain methacrylic anhydride units and isopropyl methacrylate units. Therefore, the first step of degradation of poly(isopropyl methacrylate) does not consist of a single type of degradation but is a concurrent degradation of at least three types of reaction processes (Types I and II and unzipping). The frequencies of these three degradation steps seem to be different for isotactic-rich and syndiotactic polymers as seen from the product distribution. A detailed study is now under way.

A similar phenomenon was also observed for the degradation of poly(α -methylbenzyl methacrylate) in which the volatile products were styrene, α -methylbenzyl alcohol, the monomer, and water. The styrene content in the products exceeded 80%, indicating that degradation of the ester group was the predominant process. The T_{d1} values for these two polymers were higher than those of poly(*t*-butyl methacrylate) and poly(α,α -dimethylbenzyl methacrylate) and close to the T_{d2} s. This may be the reason for the concurrent occurrence of different types of degradation.

The TG curve of syndiotactic poly(allyl methacrylate) showed a two-step degradation profile ($T_{d1} = 287^\circ\text{C}$, $T_{d2} = 417^\circ\text{C}$). Isothermal degradation at 290°C under vacuum gave the monomer almost exclusively as a volatile product. This means that unzipping degradation is the main process for poly(allyl methacrylate), even in the first step of degradation, although the exact mechanism for the two-step degradation of this polymer is not clear at present.

The thermal degradation of poly(methacrylic acid) was examined using isotactic ($\overline{DP} = 250$, *mm:mr:rr* = 93:5:2) and syndiotactic ($\overline{DP} = 124$, *mm:mr:rr* = 3:24:73) polymers which were derived from poly(trimethylsilyl methacrylate)s prepared by anionic polymerization with 1,1-diphenylhexyllithium and *t*-C₄H₉Li-(*n*-C₄H₉)₃Al (Al/Li = 3), respectively, in toluene at -78°C [45]. The TG curves of isotactic and syndiotactic poly(methacrylic acid)s showed weight losses due to dehydration at 195 and 243°C and main-chain scission degradation at 433 and 402°C, respectively. The weight losses due to dehydration, 11.4% for the isotactic polymer and 9.6% for the syndiotactic polymer, are close to the theoretical maximum of 10.4% based on the assumption that dehydration proceeds completely. The temper-

ature for dehydration of the syndiotactic polymer is higher than that of the isotactic one as in the case of the polymethacrylates in the second group. Contrary to the case of poly(*t*-butyl methacrylate), the temperature for the second decomposition step is higher than for the case of isotactic poly(methacrylic acid). The reason for this is not clear at present, but one of the possibilities is the difference in tacticities of the poly(methacrylic anhydride)s.

2.3. Thermal Degradation of Copolymer of Methacrylates

The thermal stability of copolymer depends on its molecular weight, tacticity, and copolymer composition. Thus, the composition dependencies of the thermal properties of methacrylate copolymers were studied by using highly syndiotactic copolymers of MMA and butyl or benzyl methacrylate with similar molecular weights and narrow MWDs. Figure 11 shows the copolymer composition dependencies of T_d and T_g of syndiotactic poly(MMA-*co*-butyl methacrylate) with a \overline{DP} of 103–169. T_g of the copolymer increased almost linearly as the MMA content increased, while T_d increased only slightly with an increase of MMA content up to 80% and then rapidly increased, reaching the T_d of the PMMA homopolymer. Even a copolymer with an MMA content of 74% ($\overline{DP} = 169$) showed the T_d only 6°C higher than poly(butyl methacrylate), although the T_d of PMMA was 26°C higher

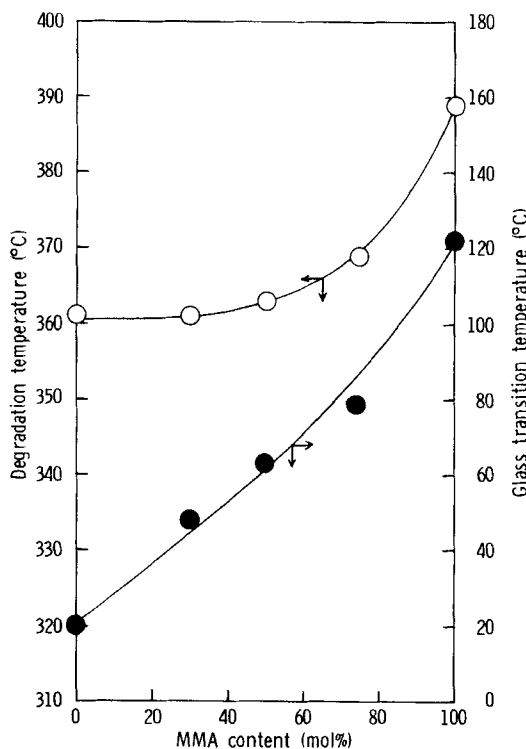


FIG. 11. Degradation temperature of poly(MMA-*co*-butyl methacrylate) with various compositions ($\overline{DP} = 103.0$ – 168.9) measured in nitrogen.

than that of poly(butyl methacrylate). By assuming a random distribution of the monomer sequence, the average number of the butyl methacrylate dyad (B-B) is calculated to be 7.5 per chain. The lower T_d for poly(butyl methacrylate) than for PMMA indicates the lower thermal stability of the B-B linkage. Therefore, the amount of B-B linkage, which is most labile in the above copolymer, is enough to govern the thermal stability of the whole copolymer.

Poly(MMA-*co*-benzyl methacrylate) showed similar composition dependencies of T_d and T_g as did poly(MMA-*co*-butyl methacrylate) (Fig. 12). A poly(MMA-*co*-benzyl methacrylate) with a benzyl methacrylate content of 20% ($\overline{DP} = 109$) showed an 8°C higher T_d than did poly(benzyl methacrylate). The expected amount of benzyl methacrylate dyad (Bz-Bz) is 4.4 per chain, which seems to be enough to govern the stability of the whole chain as in the case of poly(MMA-*co*-butyl methacrylate). The T_d of the copolymer containing only 0.7% of the benzyl methacrylate unit ($\overline{DP} = 103$), which may contain a negligible amount of Bz-Bz linkage, was found to be 19°C higher than that of the homopolymer. The T_d value of 379°C is, however, still 9°C lower than that of PMMA. The result suggests that the MMA-benzyl methacrylate linkage existing in the copolymer in a small amount

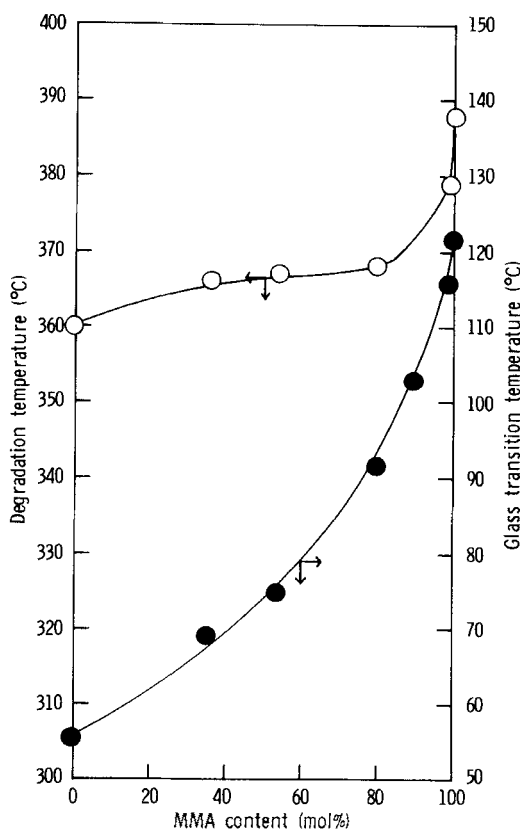


FIG. 12. Degradation temperature of poly(MMA-*co*-benzyl methacrylate) with various compositions ($\overline{DP} = 97.3$ –114) measured in nitrogen.

(1.44 per chain) is less stable than MMA-MMA linkage in the chain, and the degradation begins from this point, followed by unzipping.

Syndiotactic PMMA-*block*-syndiotactic poly(methacrylic acid) ($\overline{DP} = 55$ (PMMA) and 56(poly(methacrylic acid))) and isotactic PMMA-*block*-syndiotactic poly(methacrylic acid) ($\overline{DP} = 82$ (PMMA) and 90(poly(methacrylic acid))) showed a two-step degradation behavior [45]. Although the T_{d1} s due to dehydration of poly(methacrylic acid) blocks were almost the same (248–249°C), the T_{d2} s due to main-chain scission were different. The T_d for isotactic PMMA-*block*-syndiotactic poly(methacrylic acid) (391°C) was lower than that for syndiotactic PMMA-*block*-syndiotactic poly(methacrylic acid) (405°C). The \overline{DP} s of the PMMA block of the copolymers were less than 100, and thus the syndiotactic PMMA block is expected to have a higher T_d than the isotactic PMMA block (see Fig. 7). Therefore, the higher T_{d2} of syndiotactic PMMA-*block*-syndiotactic poly(methacrylic acid) suggests that the difference in thermal stability in PMMA block governs the stability of the whole block copolymers.

3. Glass Transition Temperature of Polymethacrylates

As described in the previous sections, there is a significant correlation between the T_d and the T_g of polymethacrylates. Therefore, knowledge of the structural dependence of T_g is very important for understanding in the thermal stability of the polymers. T_g itself can also be regarded as one of the important thermal properties.

The T_g s of polymethacrylates depend on the structure of their ester group, molecular weight, stereoregularity, and copolymer composition. The molecular weight dependence of T_g can be expressed by Eq. (9) with infinite molecular weight ($T_g(\text{inf.})$) and a constant K [46]. The constant K is on the order of 10^5 , and thus the T_g of PMMA with an \overline{M}_n over 10^5 may change little with an increase of \overline{M}_n .

$$T_g = T_g(\text{inf.}) - K/\overline{M}_n \quad (9)$$

It is well known that syndiotactic PMMA has a much higher T_g than does isotactic PMMA, and several equations describing the tacticity dependence of T_g have been proposed:

$$T_g = 41(mm) + 92(mr) + 124(rr) \quad (10) \quad [47]$$

$$= 41(m) + 126(r) \quad (11) \quad [47]$$

$$= 133.4 - 76.6(m) \quad (12) \quad [48]$$

All these equations assume a linear correlation between T_g and tacticity.

We recently determined $T_g(\text{inf.})$ and K values for three series of PMMA with different syndiotacticities (Table 3) [49]. Plots of $T_g(\text{inf.})$ against the racemo dyad (r) fraction showed a positive deviation from a linear relationship when the r content is close to 100%. Extrapolation of the plots of $T_g(\text{inf.})$ vs r fraction to 100% showed $T_g(\text{inf.})$ for 100% syndiotactic PMMA to be 141°C, which is higher than those expected from Eqs. (10)–(12). A much higher $T_g(\text{inf.})$ (160°C) for 100% syndiotacticity was reported by Thompson, who used a series of PMMA samples of varying molecular weight prepared by electron irradiation of PMMAs of different tacticities [50]. However, the problem is that the change of tacticity during electron irradiation might be underestimated, although the same author reported the change of tacticity by electron irradiation [51].

TABLE 3. $T_g(\text{inf.})$ and K Values for Syndiotactic PMMAs^{a,b}

Initiator	Solvent	Temperature, °C	Racemo dyad, %	Range of \overline{M}_n	$T_g(\text{inf.}), K \times 10^{-5},$ °C	$K \times 10^{-5},$ °C
$m\text{-VBzMgCl}^c$	THF	-98	95.8-98.2	4,300-44,900	135	1.32
$\text{Ph}_3\text{P-Et}_3\text{Al}$	Toluene	-93				
DPhMPLi^d	THF	-78	89.8-91.6	5,600-599,000	128	0.99
AIBN	Bulk	60	78	8,700-87,200	123	0.76

$$^a T_g = T_g(\text{inf.}) - K/\overline{M}_n$$

^bPMMA_s of different \overline{M}_n s were prepared by varying the ratio of monomer to initiator.

^c m -Vinylbenzylmagnesium chloride.

^d1,1-Diphenyl-3-methylpentyllithium.

The effect of the structure of the ester group on the T_g s of polymethacrylates was studied by using several syndiotactic polymethacrylates with a \overline{DP} of about 100. The T_g s of a series of poly(butyl methacrylate)s increased in the order poly(n -butyl methacrylate) (22°C) < poly(i -butyl methacrylate) (55°C) < poly(t -butyl methacrylate) (123°C). The results indicate that T_g increases with increasing bulkiness of the ester group. The T_g s of a series of poly(n -alkyl methacrylate)s decreased with an

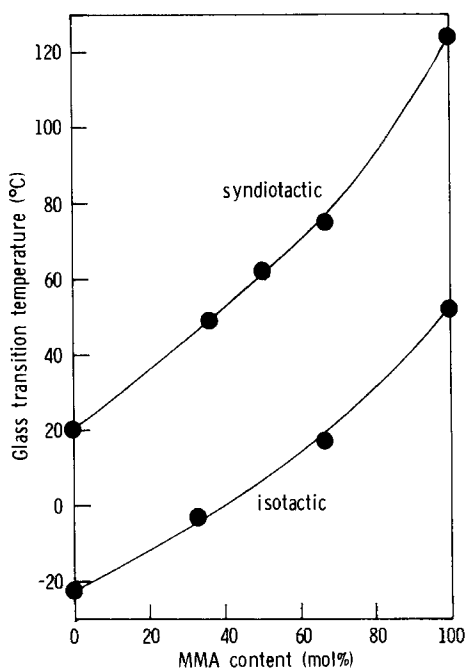


FIG. 13. Glass transition temperature of stereoregular copolymers of MMA and butyl methacrylate with various compositions.

increasing number of carbons in the ester group: PMMA > poly(ethyl methacrylate) > poly(butyl methacrylate) > poly(octyl methacrylate) (Table 1). Thus, the side-chain flexibility affects the T_g of the poly(*n*-alkyl methacrylate). Segmental mobility of polymethacrylates as depicted by their T_g values was well related to their thermal stability, as described in Section 2.2.

The T_g s of copolymers generally depend on composition, as mentioned previously. Figure 13 shows the T_g s of isotactic and syndiotactic random copolymers of MMA and butyl methacrylate of various compositions [52]. The T_g s of the syndiotactic copolymers lay between 120 and 22°C, and those of the isotactic copolymers lay between 50 and -22°C, both of which increased as the MMA content increased. Thus, the T_g s of the copolymer can be adjusted to the -22 to 120°C range by changing the copolymer composition and tacticity.

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