Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Mitomo, H. , Enjôji, T. , Watanabe, Y. , Yoshii, F. , Makuuchi, K. and Saito, T.(1995) 'Radiation-Induced Graft Polymerization of Poly(3-Hydroxybutyrate) and Its Copolymer', Journal of Macromolecular Science, Part A, 32: 3, 429 — 442
To link to this Article: DOI: 10.1080/10601329508013674
URL: http://dx.doi.org/10.1080/10601329508013674

J.M.S.—PURE APPL. CHEM., A32(3), pp. 429–442 (1995)

RADIATION-INDUCED GRAFT POLYMERIZATION OF POLY(3-HYDROXYBUTYRATE) AND ITS COPOLYMER

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Key Words: Methyl methacrylate; 2-Hydroxyethyl methacrylate; Radiation-induced graft polymerization; Poly(3-hydroxybutyrate); Poly(3-hydroxybutyrate-3-hydroxyvalerate); Biodegradability

ABSTRACT

Graft copolymerization of methyl methacrylate (MMA) or 2-hydroxyethyl methacrylate (HEMA) onto poly(3-hydroxybutyrate) (PHB) and its copolymer poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) {P(HB-HV)} was carried out by using simultaneous radiation and preirradiation techniques from a ^{60}Co γ-rays source. Degree of grafting (X_g) of

MMA onto both polymers increased as the irradiation dose increased. The X_g for PHB graft-polymerized by simultaneous radiation was lower than that for the copolymer of 24 mol% HV content (24 M sample). On the contrary, X_g of PHB graft-polymerized after preirradiation was higher than that of the 24 M sample. The X_g depended on differences in regularity in the crystalline regions or crystallinity and rate of radical decay. Crystalline regions of PHB remained almost unchanged after grafting, while crystalline regions of the 24 M sample were partially destroyed by the introduction of grafting. Glass transition temperatures of both grafted polymers increased up to 8°C. The number-average molecular weight ($\overline{M}_n$) of grafted PMMA was comparable to that of trunk polymers, while $\overline{M}_n$ of that graft-polymerized with simultaneous radiation was far larger, reflecting the introduction of crosslinking. Biodegradability steeply decreased by the introduction of MMA grafting, while that grafted with HEMA increased at first because of improvement of wettabiity between the polymer and an enzyme solution, then steeply decreased as X_g increased.

INTRODUCTION

Poly(3-hydroxybutyrate) (PHB) and its copolymer poly(3-hydroxybutyrate-3-hydroxyvalerate) {P(HB-HV)} are biodegradable polymers isolated from cells of many types of bacteria [1, 2]. Biodegradation by the enzyme [3], hydrolysis by amines [4], and thermal degradation [5] of these plastics have been investigated. Radiation-induced grafting onto popular polymers has been investigated by many authors. Radiation grafting of hydrophilic monomers onto polyethylene [6], polypropylene [7, 8], poly(4-methylpentene-1) [9], polyvinyl chloride [10], and silk [11] has been studied mainly for biomedical applications. P(3HB) per se is a thermoplastic, biodegradable, and biocompatible material [12–14]; however, improving its properties by radiation grafting would lead to wider usage.

In a previous paper, radiation-induced degradation of these polymers was examined, where the decrease in molecular weight of both polymers was only ca. 5% at a dose of 5 kGy in vacuum [15].

In the present study, methyl methacrylate (MMA), which is the most convenient monomer to examine for graft polymerization although it is a hydrophobic monomer, was graft polymerized onto PHB and P(HB-HV) by using simultaneous radiation and preirradiation techniques from a ^{60}Co γ-rays source. For comparison, 2-hydroxyethyl methacrylate (HEMA) monomer was used as a hydrophilic monomer for graft polymerization onto both trunk polymers. Degree of grafting, molecular weight, thermal properties, and biodegradability of grafted samples were studied. Based on these results the mechanism of radiation-induced graft polymerization is discussed.

EXPERIMENTAL

Materials

PHB and P(HB-HV) containing 24 mol% HV (hereinafter called the 24 M sample), which were of natural origin from *Alcaligenes eutrophus*, were purchased from Sigma and Aldrich Chemical Co., respectively. Both samples used for graft

polymerization were porous flake- or granule-like powders. The monomers used in this study were methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) obtained from Kanto Chemical Co. and Mitsubishi Rayon Co., respectively. They were passed through a neutral alumina column (Wölm Pharma GmbH & Co.) to remove any inhibitor before use.

Graft Polymerization

The graft copolymerization was carried out by directly irradiating both polymers immersed in MMA (bulk and 20 vol% MMA in CH_3OH) or HEMA (10 vol% in CH_3OH) monomer in vacuum glass ampules at room temperature after being sealed under reduced pressure (10^{-3} torr). The samples were irradiated with ^{60}Co γ-rays at a dose rate of 1 kGy/h at 25°C for various periods of time (hereafter this is called in-source polymerization). For comparison, preirradiation grafting was carried out by a method described previously [8], i.e., both samples were preirradiated to 5 kGy (dose rate of 10 kGy/h) in vacuum at −78°C. Bulk MMA monomer was deaerated by bubbling nitrogen before it was introduced to the irradiated polymers. The reaction was carried out under nitrogen in a temperature-controlled bath for various periods of time (hereafter called postpolymerization). Grafted PHB was washed with ethanol, then extracted in a Soxhlet apparatus with acetone for 3 days to remove any MMA monomer and adhering homopolymer. Grafted 24 M sample was soaked with fresh acetone at room temperature (so as to prevent 24 M sample from dissolving) for 1 or 2 weeks. Both samples grafted with HEMA were Soxhlet extracted with methanol for 3 days and dried under vacuum at 35°C to constant weight.

The degree of grafting was determined by the percent increase of weight based on the original sample weight, using Eq. (1):

$$X_g = [(W_g - W_i)/W_i] \times 100 \quad (1)$$

where X_g is the degree of grafting (%), W_i is the weight of the original sample (g), and W_g is the weight of the sample after grafting (g).

Analytical Procedures

The melting point T_m and glass transition temperature T_g of the grafted samples (3 mg) were studied in a Perkin-Elmer Model DSC-7 differential scanning calorimeter (DSC) at a heating rate of 10°C/min under nitrogen atmosphere. The melting peak temperature, after being corrected for the thermal lag and calibrated with high-purity standards, was defined as the melting point T_m with an accuracy within ±0.1°C. Thermogravimetry (TG) and DTA of the samples (5 mg) were carried out in a Shimadzu DTG-30 at a heating rate of 5°C/min under nitrogen atmosphere.

Gel permeation chromatography (GPC) was carried out with an HLC-802A high performance liquid chromatograph (Tosoh Co., Ltd.) equipped with a series of four columns of TSK gel and an RI-8 differential refractometer at 38°C. The eluent was chloroform with a flow rate of 1 mL/min and a polymer concentration was 2–3 mg/mL. The number-average molecular weight $\overline{M}_n$ was calibrated using polystyrene standards, and typically degraded PHB samples having six different $\overline{M}_n$

values (from 4.29×10^3 to 5.64×10^5) were evaluated by GPC and a small-angle laser light-scattering system.

Electron spin resonance (ESR) measurements were done using a JEOL LES-FE3X X-band spectrometer with 100 kHz modulation. The samples were irradiated with 5 kGy in vacuum at −78°C, and immediately measured in an ESR spectrometer at 25, 50, and 70°C (and 0°C for the 24 M sample).

Enzymatic Degradation

Biodegradability of the grafted polymers was studied at 37°C in a 0.1 M phosphate buffer (pH 7.4) of extracellular PHB depolymerase purified from *Alcaligenes faecalis* T1 as already described [16]. A solvent-cast film (initial weights, 11–13 mg; initial dimensions, 10 × 10 mm in size and 0.1 mm thick) from chloroform solution was used. The reaction was started by adding 1 mL of an aqueous solution of PHB depolymerase (net weight: 8 μg), which was incubated at 37°C with shaking. Samples were removed after an incubation time of 24 hours, washed with ethanol, and dried to constant weight in vacuo. The weight loss of the film is calculated from the following equation:

$$\text{Weight loss (\%)} = [(W_g - W_d)/W_g] \times 100 \quad (2)$$

where W_g and W_d are the weights of films before and after the enzymatic degradation test, respectively.

RESULTS AND DISCUSSION

Grafting with MMA and HEMA by In-Source Polymerization

Typical DSC thermograms of PHB and 24 M samples grafted with MMA are shown in Fig. 1. Melting points of both samples decreased with the introduction of MMA grafting, and the melting peaks significantly decreased in area. DSC curves of the second run are shown as broken lines, which display that the introduction of MMA grafting hardly prevented recrystallization of PHB but prevented that of the 24 M sample. This implies that MMA grafting onto the 24 M sample was introduced not only into amorphous regions but also into crystalline regions because crystal lattices of the HB component were distorted by occlusion of the HV units [17].

Figure 2 shows plots of the degree of grafting (X_g) with the MMA (bulk and 20 vol% MMA in CH_3OH) onto PHB and 24 M samples against the irradiation dose. The X_g of the 24 M sample increased far faster than that of PHB. A few reports state that the crystallinity of P(HB-HV) is hardly decreased irrespective of the amount of HV component [18, 19], and some reports state that the crystallinity is considerably decreased by introduction of the HV component [20, 21]. In either case, the reason why X_g of the 24 M sample becomes larger than that of PHB is explained by the looser packing of crystal lattice of the HB component by occlusion of the HV units [20]. Both samples showed a slight increase in X_g when used with 20 vol% MMA in CH_3OH. This is explained by the MMA solution becoming less viscous by dilution and the diffusion of monomer improving during polymerization. However, the effect of monomer concentration in CH_3OH on X_g was not very significant as long as the concentration was higher than 10%.

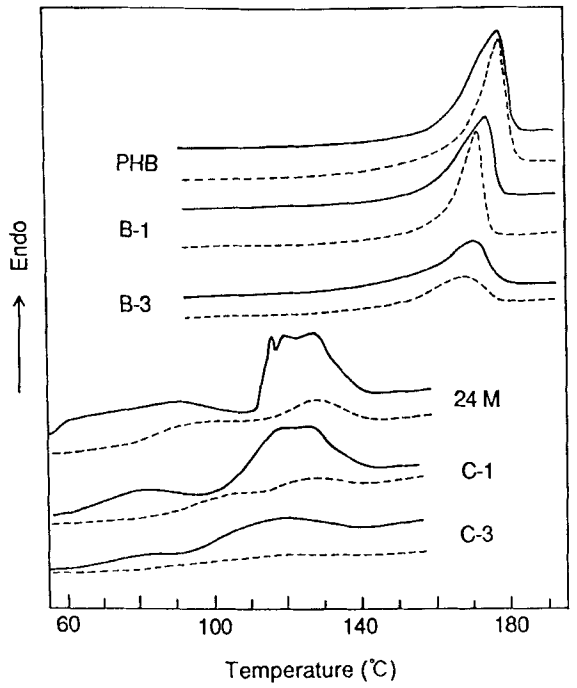

FIG. 1. DSC heating curves of PHB and 24 M samples grafted with MMA by in-source polymerization. B-1 and B-3 are PHB samples grafted with irradiation doses of 1 and 3 kGy, and C-1 and C-3 are 24 M samples grafted with doses of 1 and 3 kGy, respectively.

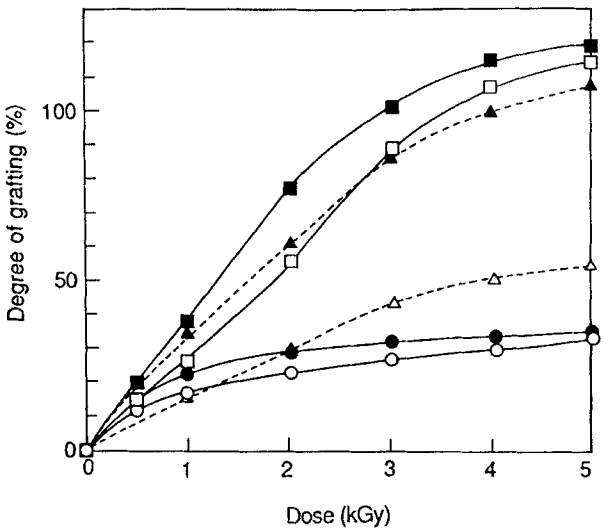

FIG. 2. Plots of degree of grafting (X_g) with MMA (bulk) onto PHB (○) and 24 M (□) samples and X_g with 20% MMA in CH_3OH onto PHB (●) and 24 M (■) against the irradiation dose. Broken lines show plots of X_g with 10% HEMA in CH_3OH onto PHB (△) and 24 M (▲) samples.

Figure 2 also shows plots of X_g of HEMA onto both samples against the irradiation dose as broken lines. The monomer solution used was 10 vol% HEMA in CH_3OH. Very similar to the case of MMA grafting, X_g of the 24 M sample increased faster than that of PHB. The X_g of the 24 M leveled off to a value of 110%, while X_g of PHB leveled off at 55% at a dose of 5 kGy. This is similar to the result of polypropylene grafted with HEMA [8], where X_g increased sharply as the dose increased and leveled off at ca. 75% at 3 kGy without showing any induction period [22].

There are a few reports where X_g decreased as the dose rate increased [7, 11], and similar results were obtained in this study at a lower dose rate. However, X_g increased at dose rates higher than 2 kGy/h, suggesting that crosslinking is concurrently occurring between graft PMMA, homopolymer of MMA, and trunk polymer chains. Moreover, X_g was compared with various 20% MMA solutions in such diluents as methanol, carbon tetrachloride, acetone, and chloroform. The highest X_g was obtained by using MMA solution in methanol, the second was in carbon tetrachloride (X_g was about half of the former), and the lowest was in acetone or chloroform (X_g was less than one-fifth). This order coincides with the increment of solubility of both polymers and PMMA. Further experimental results are needed to explain this mechanism, because the X_g value obtained by in-source polymerization in a diluent solution is influenced by such factors as radical concentration, radical lifetime, and solubility or molecular mobility at each stage of initiation, propagation, and termination.

Melting points (T_m), enthalpies of melting (ΔH_m), and glass transition temperatures (T_g) for PHB and 24 M samples grafted with MMA are listed in Table 1. The decrease in T_m of 24 M was larger than that of PHB, reflecting the introduction of MMA grafting into crystalline regions in addition to amorphous regions. The ΔH_m of PHB decreased from 86.1 to 62.8 J/g; however, this decrease is due to the relative decrease in PHB content in the grafted sample. The ΔH_m may be corrected by the

TABLE 1. Melting Points (T_m) and Enthalpies of Fusion (ΔH_m) of PHB and 24 M Samples Grafted with MMA

Sample	Dose, kGy	T_m, °C	ΔH_m, J/g	$(\Delta H_m)_{corr.}$, J/g	T_g, °C	X_g, %
PHB	0	176.8	86.1	86.1	2.5	0
B-0.5	0.5	174.3	78.0	87.4	3.5	12
B-1	1	173.3	73.7	86.2	5.5	17
B-2	2	172.5	66.9	82.3	6.5	23
B-3	3	171.8	62.8	79.8	—	27
24 M	0	123.5	64.2	64.2	−5.5	0
C-0.5	0.5	122.5	52.4	59.2	−1	13
C-1	1	120	46.6	57.8	2.5	24
C-2	2	116	33.4	51.4	—	54
C-3	3	111.5	21.3	39.8	—	87

weight fraction of both polymers in the grafted samples according to the following equation:

$$\text{Corrected enthalpy of melting } (\Delta H_m)_{corr.} = \Delta H_m(1 + X_g) \quad (3)$$

where X_g is the degree of grafting. The $(\Delta H_m)_{corr.}$ of PHB remains almost unchanged irrespective of an increase in irradiation dose, implying that MMA grafting was hardly introduced into crystalline regions, whereas $(\Delta H_m)_{corr.}$ of the 24 M sample decreased significantly, implying that MMA grafting considerably destroyed crystalline regions. The T_g values of PHB and 24 M were 2.5 and -5.5°C, which increased up to 4 and 8°C with increasing X_g value, respectively. The increase in T_g of the 24 M sample was almost twice that of PHB, probably implying the superior miscibility of the former polymer with grafted PMMA. Since T_g of PMMA appeared in a broad temperature range of ca. 80°C, it is natural that T_g of the grafted polymers increased with increasing X_g. However, any additive relation of T_g values, such as the Fox equation [23], was not observed in this study. It became difficult to detect T_g for samples whose X_g values were larger than 27% (e.g., Samples B-3 and C-2).

Figure 3 shows typical TG thermograms of the 24 M samples. The 24 M sample decomposed in the 230 to 260°C range while PHB decomposed in a temperature range ca. 10°C higher. PMMA decomposed in the 280 to 420°C range, which is close to the reported values (e.g., 330°C [24]). Therefore, 24 M samples grafted with MMA shows two steps in their weight loss curve. The X_g of grafted PMMA is estimated by dividing the entire weight loss at the intersection of the steepest tangent line of the first drop to the tangent line of the plateau prior to the second drop as

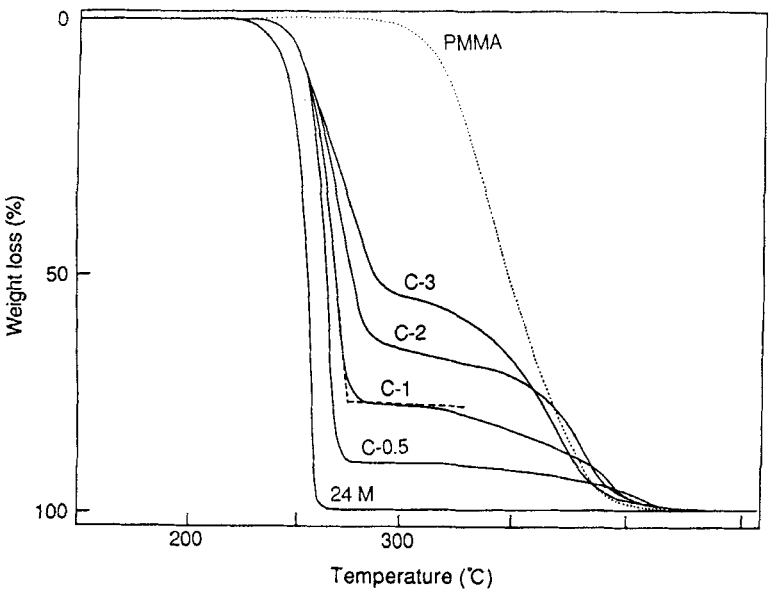

FIG. 3. Typical TG thermograms of 24 M samples grafted with MMA. A dotted line shows the TG curve of PMMA. The intersection of the steepest tangent line of the first drop to the tangent line of the plateau as shown with broken lines divides the whole weight loss into those of trunk polymer and grafted PMMA.

exemplified with dotted lines for Sample C-1 in the figure. The X_g value estimated from TG curves is very close to that estimated from weight increase (add-on) after grafting. Decomposition temperatures of both polymers shifted to higher temperatures as the X_g increased, e.g., that for Sample C-3 shifted to ca. 20°C higher and that for Sample B-3 shifted to 10°C higher temperature because the X_g of Sample B-3 was smaller than that of Sample C-3.

Grafting with MMA by Postpolymerization

Figure 4 shows plots of X_g of MMA onto PHB and 24 M samples against polymerization time at temperatures of 25, 50, and 70°C (and 0°C for 24 M). The X_g onto PHB at 50°C is largest, whereas X_g onto 24 M samples at 25°C is largest among these reaction temperatures.

Figure 5 shows plots of radical concentration (C) in the irradiated samples at different temperatures against various periods of time (t) measured by an electron spin resonance (ESR) spectrometer. The relation of the logarithmic scale of C (%) of both samples and time seems to be almost linear, obeying the following equation of a first-order reaction:

$$\log C = -kt + c \tag{4}$$

where k and c are constants. All decay lines are composed of two lines with a steeper and a gentler gradient, showing the breaking points at a time range of 30–60 minutes. It is considered that these initial and second decreasing lines correspond to the decay lines of radicals occurring in amorphous and crystalline regions, respec-

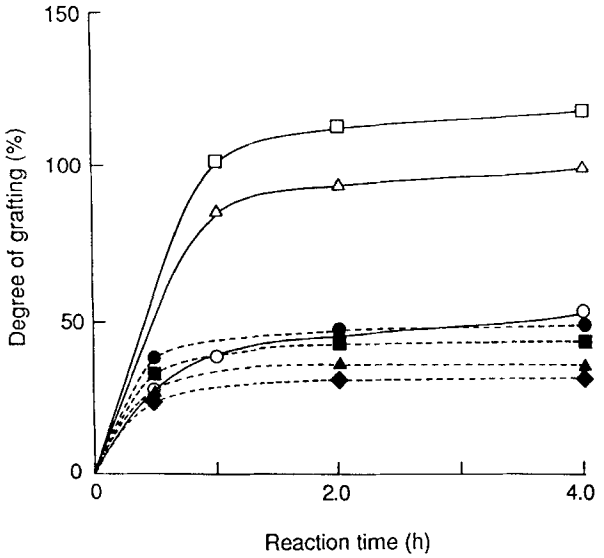

FIG. 4. Plots of X_g of MMA onto PHB and 24 M samples against reaction time at postpolymerization temperatures of 25°C (○, ●), 50°C (□, ■), and 70°C (△, ▲), respectively, and 0°C (◆) for the 24 M sample.

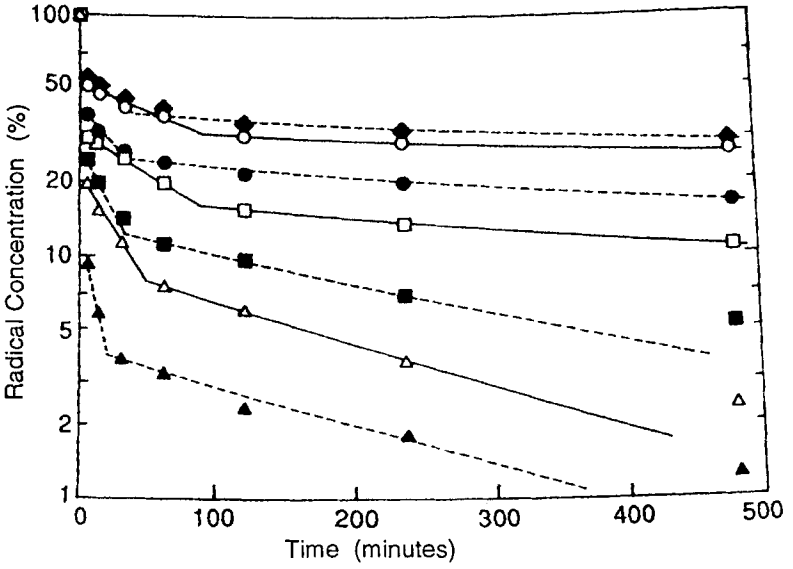

FIG. 5. Radical concentration in the irradiated polymers at different temperatures against various periods of time obtained by ESR measurement. The temperatures are 25°C (○, ●), 50°C (□, ■), and 70°C (△, ▲) for PHB and 24 M samples, respectively, and 0°C (♦) for the 24 M sample.

tively. The radical concentration of 24 M decreased more steeply than that of PHB at the same temperature. The reason why the largest X_g is obtained at 50°C for PHB and at 25°C for 24 M is explained as the most optimum temperature balance between two factors, i.e., the higher temperature is advantageous for promoting the polymerization reaction and the lower temperature for preventing decay of the radical. In general, the radicals generated in crystalline regions are more stable than those in amorphous regions and migrate to the crystallite surfaces in time and then work efficiently for grafting. Therefore, X_g onto PHB became larger than that of the 24 M sample because of the more ordered crystalline structure or the higher crystallinity. In Fig. 4 the highest X_g of the 24 M sample is obtained at 25°C, where the two factors are suitably balanced. The final percent of grafting can be observed at around 30 minutes for the 24 M sample, and in less than 2 hours for PHB at these tempertures. A similar behavior was observed in a study of acrylic acid onto poly(4-methylpentene-1) (TPX) with a different crystallinity [9]. In the previous paper [9], the initial rate of grafting of low crystalline TPX was faster than that of high crystalline TPX; however, it was difficult to find such a difference in the present study.

Figure 6 shows GPC chromatograms of PHB and 24 M samples grafted with MMA by in-source polymerization. The molecular weight $\overline{M}_n$ values of PHB and 24 M samples were 2.84×10^5 and 2.09×10^5, respectively. The grafted PHB irradiated with 3 kGy (B-3) showed a broad peak, and its $\overline{M}_n$ value was extraordinarily large, i.e., 13.3×10^5. The grafted 24 M irradiated with 1 kGy (C-1) showed a double peak corresponding to 21.9×10^5 and 1.49×10^5. The larger M_n compo-

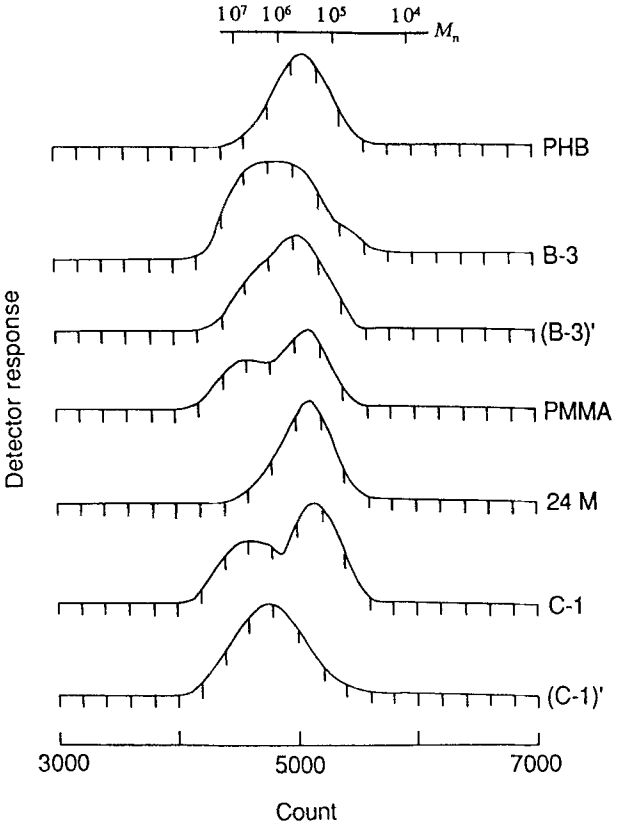

FIG. 6. GPC chromatograms of PHB and 24 M samples with MMA obtained by in-source polymerization. (B-3)′ and (C-1)′ are chars of Samples B-3 and C-1 obtained by heating up to 313 and 290°C, respectively.

nent is assigned to grafted 24 M, while the lower $\overline{M}_n$ is assigned to the original 24 M sample. The $\overline{M}_n$ of the char of grafted PHB obtained by heating up to 313°C, (B-3)′, was 6.51×10^5, and that of 24 M heated up to 290°C, (C-1)′, was 18.5×10^5, which are far larger than the $\overline{M}_n$ values of the trunk polymers, implying the introduction of crosslinking between grafted PMMA chains or trunk polymer chains. In fact, PMMA which was solely in-source polymerized from MMA monomer with 3 kGy showed two $\overline{M}_n$ values, an ordinary one (1.55×10^5) and an extraordinary large one (34.0×10^5), demonstrating the partial introduction of crosslinking.

Table 2 lists $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ values for both polymers grafted with MMA by using two grafting methods. The $\overline{M}_n$ values of PMMA grafted onto both polymers were estimated from the chars heated up to 313 or 290°C, i.e., $\overline{M}_n$ values for in-source polymerization were 2.2–8.1 times larger than those of trunk polymers, while $\overline{M}_n$ values for postpolymerization were 1.3–1.6 times larger. These values are comparable to other reported ones, e.g., around 10^6 for the $\overline{M}_n$ of polystyrene for nylon 6 fibers grafted with styrene [25].

TABLE 2. $\overline{M}_n$ of PHB and 24 M Samples and Those Grafted with MMA

In-source polymerization				Postpolymerization (at 25°C)			
Sample	Dose, kGy	$\overline{M}_n$ ($\times 10^{-4}$)	$\overline{M}_w/\overline{M}_n$	Sample	Time, h	$\overline{M}_n$ ($\times 10^{-4}$)	$\overline{M}_w/\overline{M}_n$
PHB	0	28.4	3.42				
PHB (B-3)	3	133.0	3.31	PHB	0.5	53.0	2.02
Char of B-3 at 313°C		65.1	2.96			7.4	2.35
				Char at 313°C		46.2	3.06
PHB (B-3) (20% MMA)	3	128.1	3.67	PHB	4	84.9	2.55
		11.6	1.90			11.1	1.95
Char of B-3 at 313°C		63.2	3.06	Char at 313°C		37.2	6.33
24 M	0	20.9	3.05				
24 M (C-1)	1	219.3	3.34	24 M	0.5	203.8	3.25
		14.9	2.0			7.1	2.97
Char of C-1 at 290°C		168.7	3.10	Char at 290°C		30.9	4.96
24 M (C-1) (20% MMA)	1	197.0	2.41	24 M	4	219.0	3.64
		14.5	1.95			7.7	2.15
Char of C-1 at 290°C		89.0	4.95	Char at 290°C		31.6	5.19
PMMA	3	340.0	3.93				
(homopolymer)		15.5	2.35				

The T_m and ΔH_m of the samples obtained by postpolymerization were very similar to those obtained by in-source polymerization, implying that grafting was introduced mainly into amorphous regions for PHB and 24 M samples.

Enzymatic Degradation

The enzymatic degradation (erosion) profiles on these grafted samples are shown in Fig. 7. The weight loss of PHB (60%) was larger than that of the 24 M sample (46%), implying that introduction of the HV component causes a slight decrease in biodegradability [5]. The PHB and 24 M samples grafted with MMA steeply decreased to 13 and 16% at X_g of ca. 50%, respectively, and both leveled off at ca. 10% for a higher value of X_g, whereas the weight loss values of both samples grafted wtih HEMA increased clearly at X_g to ca. 10–20% and then decreased almost parallel to those of samples grafted with MMA and leveled off at ca. 20%. This is because the sample was modified and became hydrophilic. There was improvement of wettability with the enzyme solution by introduction of HEMA grafting; nevertheless, P(HEMA) per se showed poor biodegradability. A more predominant increase in biodegradability was observed when these polymers were grafted with a more hydrophilic monomer such as acrylic acid. The results will be reported in the subsequent paper [26].

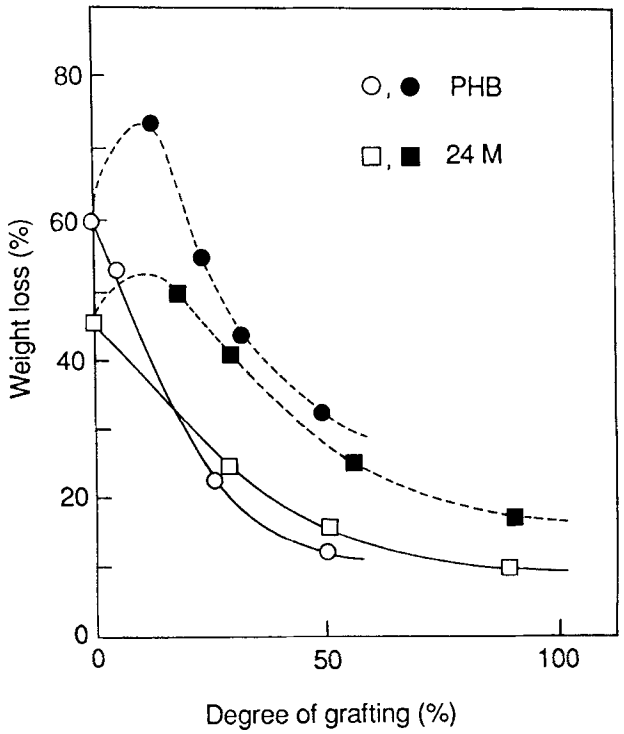

FIG. 7. Weight loss values of PHB (○) and 24 M (□) samples grafted with MMA (solid lines) and those of PHB (●) and 24 M (■) grafted with HEMA (broken lines) obtained by enzymatic degradation test.

CONCLUSIONS

The degree of grafting X_g onto PHB obtained by in-source polymerization was lower than that onto the 24 M sample. In contrast with this, X_g onto PHB obtained by postpolymerization was higher than that onto the 24 M sample. The X_g values were maximum at postpolymerization temperatures of 50°C for PHB and 25°C for 24 M.

Crystalline regions of PHB remained almost unchanged after grafting, while crystalline regions of the 24 M sample were partially destroyed. The glass transition temperatures of both polymers increased considerably with the introduction of grafting. TG curves of both grafted polymers show two weight loss steps, from which X_g was estimated. The $\overline{M}_n$ of PMMA grafts formed by postpolymerization was comparable to the $\overline{M}_n$ of trunk polymers, while that by in-source polymerization was far larger, reflecting the introduction of crosslinking.

Biodegradability was steeply decreased by the introduction of MMA grafting, while the introduction of hydrophilic HEMA grafting first led to an increase and then to a steep decrease of biodegradability because of improvement in the wettability of trunk polymers with the enzyme solution.

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Received April 8, 1994
Revision received June 27, 1994