

γ -Ray induced graft copolymerization of methyl methacrylate onto poly(β -hydroxynonanoate)

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Received: 18 March 1998/Revised version: 7 May 1998/Accepted: 8 May 1998

Summary

Copolymers of poly(3-hydroxy-nonanoate), PHN, with methyl methacrylate, MMA, were prepared using ⁶⁰Co-gamma irradiator. The bulk solutions of PHN in MMA were prepared at different PHN feed concentration and they were irradiated to 8.5 kGy at room temperature. Polymer fractions obtained by solvent-nonsolvent fractional precipitation were carefully characterized using gel permeation chromatography (GPC), nuclear magnetic resonance spectroscopy (NMR), and thermal gravimetric analysis (TGA) techniques. High copolymerization yield was observed and the copolymer compositions obtained from the TGA measurements were consistent with the NMR results. PHN contents of the copolymer samples changed from 5 to 35 wt.-%. The strain at break and tensile strength values of copolymers were between the values of their respective homopolymers. It was observed that pure copolymer samples showed up to 13 % strain at break.

Introduction

Poly(β -hydroxynonanoate), PHN, is a biodegradable, biocompatible, and natural aliphatic polyester which was synthesized recently by growing *Pseudomonas Oleovorans* in the presence of nonanoic acid and then this polyester was accumulated inside the microorganism cell as a reserve of organic carbon and chemical energy(1,2). Due to the biodegradable, biocompatible, and natural properties, this polymer has been driving a considerable interests of biomedical and environmental applications. Despite these favorable properties PHN has low mechanical resistivity to be used directly as a polymer in the medical and industrial application. A common way to insert a broad applicability properties into the PHN and to minimize the undesirable properties is to prepare its block and graft copolymers, and blends with suitable well defined polymers. For this purpose, the graft copolymers of PHN with styrene and methyl methacrylate were synthesized by Hazer using active polystyrene (PS) and poly(methyl methacrylate) (PMMA) containing oligoperoxide end groups and their microstructure characteristics, thermal and mechanical behavior were investigated (3-5). The surface free energy properties of the graft copolymers and blends of PHN with PS was also reported (5).

The graft copolymerization of another microbial aliphatic polyester, poly(β -hydroxybutyrate), PHB, by means of free radical(6) and anionic (7) polymerization technique were previously reported. Here, benzoyl peroxide or dicumyl peroxide were used as radical generators in grafting polymerization (6,8).

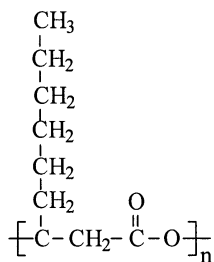
Despite the copolymerization by gamma-rays is non specific and the formation of radicalic sites on the polymer chains is a random process, this method is easier and much practical than the other polymerization techniques. The spotlighted advantageous of this technique is to be quite generally applicable to modify the great variety of natural and synthetic linear polymers. Therefore, for the synthesis of block and graft copolymers, the copolymerization with gamma-rays has been attracting the attention of many investigators (9-13). Misra et al. previously realized the graft copolymerization of acrylonitrile onto polypropylene fibers using preirradiation technique (14). The acceleration effect of the solvent on the rate of gamma-rays initiated graft copolymerization of MMA onto polypropylene was also investigated (15).

In the present study, the copolymerization of PHN with MMA was carried out using the ^{60}Co gamma-rays. Effect of the PHN feed content on the mechanical and thermal properties of the copolymers were observed.

Experimental

Materials

Poly(β -hydroxynonanoate), PHN, was prepared by growing *Pseudomonas Oleovorans* with 20 mM nonanoic acid in 12 L of fermentation solution (1) and the yield was 5.0 g. PHN has the weight average molecular weight (\overline{M}_w) and the polydispersity ($\overline{M}_w/\overline{M}_n$) of 138000 g/mole, and 1.9, respectively, as determined by gel permeation chromatography (GPC) using polystyrene as calibration standards. The chemical formula of PHN is as follows,



PHN

Methyl methacrylate, MMA, was supplied from Merck (Germany) and freed from inhibitor by passing through an alumina (Al_2O_3) filled absorption column. Chloroform and methanol were used as solvent and non-solvent, respectively. They were purchased from Merck(Germany) and used without further purification.

Instrumentation

The irradiation of reaction mixture was performed in a Gammacell 220 type ^{60}Co -gamma irradiator at room temperature. ^1H -NMR spectra of copolymers were recorded by a Bruker-AC 200L, 200 MHz NMR spectrometer. Weight-loss and derivative weight-loss curves of the copolymers were recorded by using Du Pont TGA-951 module, with TA-9900 data processing system under nitrogen atmosphere at $10\text{ }^\circ\text{C}/\text{min}$ heating rate. TGA was calibrated with calcium oxalate. GPC chromatograms were taken by using Waters-510 HPLC Pump with Waters-410 differential refractometer and Waters Styragel HR1+HR2 column system, THF being elution solvent at $40\text{ }^\circ\text{C}$. The mechanical properties of the copolymers were measured on a Tensilon (UTM II) tester at room temperature with a crosshead speed of $10\text{ mm}/\text{min}$.

Synthesis of the copolymers

The copolymers were synthesized in bulk solution of PHN in MMA monomer. For this purpose, various amount of PHN samples were dissolved in 1 ml (0.94 g) of MMA monomer to get reaction mixtures having 5,10,15,20 and 25 wt.-% PHN feed contents. After the freezing and thawing cycles were applied until all dissolved air present in the reaction mixture was removed, reaction tubes were evacuated to 10^7 mmHg and flame sealed. The reaction mixtures were irradiated to 8.5 kGy with ^{60}Co -gamma irradiator at room temperature. The dose rate was measured as 0.6 kGyh^{-1} using standard Fricke dosimeter. After the irradiation was completed, each reaction product was dissolved in 5 ml chloroform and precipitated with 100 ml methanol. The precipitated samples were filtered and dried under 650 mmHg vacuum at $35\text{ }^\circ\text{C}$ until the constant weight was attained. The graft copolymers were isolated from the related homopolymers by using the fractional precipitation(16) and characterized by using spectroscopic (NMR), mechanical, thermal (TGA) and chromatographic (GPC) techniques. Homo-PMMA sample was also prepared by the same procedure. After 8.5 kGy irradiation the conversion of homo-PMMA was 95%. Table 1 and 2 offer the isolation and characterization results of the graft copolymers and homopolymers.

Preparation of tensile stress-strain test samples

The mechanical test specimens of homo-PHN, homo-PMMA and their copolymers were prepared by solution casting from chloroform. To obtain the copolymer and homopolymer films having the uniform thickness, about 0.5 g sample was dissolved in 25 ml chloroform. The clear solution was poured into the aluminum dish. After chloroform was allowed to slowly evaporate at room temperature for 24 hours, copolymer samples were kept in a vacuum oven at $35\text{ }^\circ\text{C}$ until their constant weight was attained. The mechanical test specimens were punched from the well dried film using a die prepared in accordance with ASTM D 412-68. These measurements were made for four samples of each copolymer composition and the results are averaged. The tensile stress-strain test results are collected in Table 2.

Table 1. Characterization results of the copolymers synthesized from the solution of PHN in MMA.

Run no	PHN in MMA*, g	Yield of crude polymer, g	Sample no	γ^{**}	Amount of fractionated polymer, g	Copolymer fractions			
						$M_n \times 10^{-3}$	M_w/M_n	PHN% From TGA NMR	
1	0.046	0.962	11	1.5-2.0	0.009	225	5.5		
			12	2.0-3.8	0.060				
			13	>3.8	0.902	370	4.5	5	
2	0.104	1.036	21	1.6-2.4	0.022	112	2.5		
			22	2.4-3.0	0.798	473	3.9	15	14
			23	>3.0	0.238	95	5.0		
3	0.166	0.958	31	1.6-2.4	0.071	92	3.4	85	
			32	2.4-3.0	0.865	433	3.6	10	6
			33	>3.0	0.093	63	3.1	12	12
4	0.235	0.904	41	1.6-1.7	0.112	116	3.7		
			42	1.7-2.5	0.057	58	5.8	12	
			43	>2.5	0.848	330	4.0	20	
5	0.313	0.979	51	1.5-2.3	0.179	73	2.5	95	92
			52	2.3-3.1	0.908	417	3.5	15	7
			53	>3.1	0.070	55	3.6	35	25

* The amount of MMA was kept constant as 0.94 g in each run.

** By fractional precipitation. Solvent:CHCl₃, nonsolvent:Methanol. γ : volume ratio of non-solvent to solvent, 1.5-2.0 for homo-PHN, > 3 for homo-PMMA

copolymer mixture, the fractional precipitation method was used (16). Volume ratio of non-solvent (MeOH) to solvent (CHCl_3), γ , was observed as 1.5-2.0 for homo-PHN, 2.4-3.1 for graft copolymers. As can be seen from Table 1, three fractions of polymers were mostly obtained which the first one was homo-PHN (at $\gamma = 1.5$ -2.0), and the second one was copolymers in yield of 80-90 wt.-% (at $\gamma = 2.4$ - 3.1) and the last one which was the fraction precipitated (at $\gamma > 3$) is homo PMMA. GPC was used to determine the molecular weight of each polymer fractions. In Figure 1, the GPC chromatograms of each three fractions of the sample (run No.5 in Table 1) are shown. The first and the third fractions have nearly the same molecular weight but their γ values were different as $\gamma_{s1} = 1.5$ -2.3, $\gamma_{s3} = 3.0$ -4.0 which means that they have different chemical structure (run no 5 in Table 1). Sample 51 is unreacted PHN, and sample 53 contains mostly PMMA.

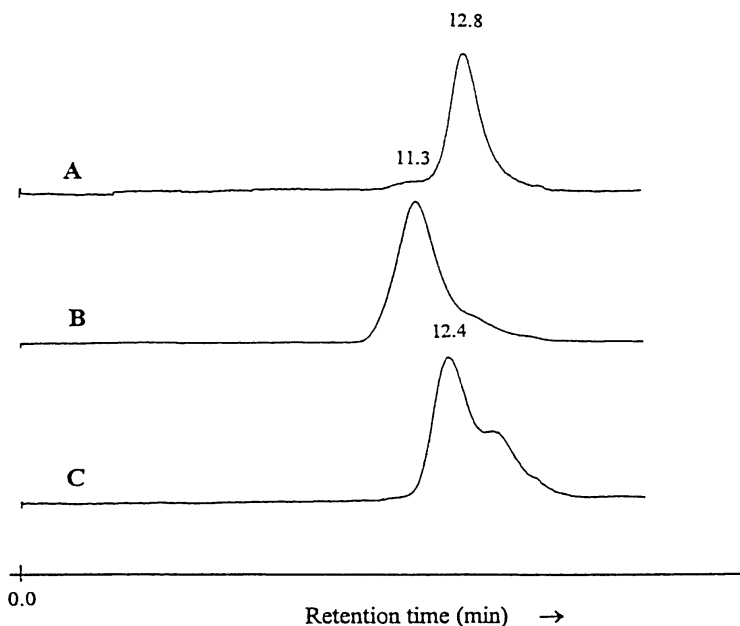


Fig.1. GPC chromatograms of (A) sample 51, (B) sample 52, (C) sample 53 in Table 1

For the spectroscopic characterization of copolymers, their $^1\text{H-NMR}$ spectra were taken. Figure 2 exhibits a typical $^1\text{H-NMR}$ spectrum of a copolymer sample carrying PHN and PMMA units (sample no 52 in Table 1). The characteristic peaks of the copolymer units were clearly observed (δ , ppm) at $\delta=3.6$ (due to $-\text{OCH}_3$ protons of MMA), $\delta=1.8$ (due to $-\text{CH}_2$ protons of PMMA and aliphatic pendant chains of PHN), $\delta=2.5$ (due to $-\text{CH}_2$ groups of PHN next to the carbonyl), $\delta=5.2$ (due to $-\text{CH}$ groups of PHN next to the oxygen in ester group). The composition of copolymers calculated from the NMR spectra were listed in Table 1.

For thermal characterization of copolymers first TGA thermograms of homo-PHN and homo-PMMA, which was synthesized under the same condition with copolymers, were recorded separately at heating rate of 10 °C/min. The maximum weight loss rate of the PHN and the PMMA were observed at $T_{d,PHN} = 285$ °C and $T_{d,PMMA} = 376$ °C, respectively (see Table 1). These characteristic peak temperatures were further used for determination the composition of copolymers from their weight-loss curves. The composition of the copolymers obtained from TGA studies were listed in Table 2. The PHN contents of the samples calculated from weight loss curves were agreed with the data obtained by NMR spectra (see Table 1). In Table 2, the maximum weight loss temperatures, T_{d2} and T_{d3} , were belong to PHN and PMMA units of copolymers, respectively. Some samples showed three decomposition temperature (sample no 22,32,52, in Table 2). For these samples, the first decomposition temperature obtained at around 230 °C which is probably due to the lower molecular weight fraction of copolymer mixture. Figure 3 shows TGA traces of the copolymer sample (no 43 in Table 1) together with the derivative thermogram as a clear evidence of the weight loss characteristic of copolymers. It was observed from this figure that the derivative thermogram of this sample has two characteristic peak corresponding to its respective homopolymers. From the weight loss curve, the PHN content of this copolymer is determined nearly as 20 wt.-%.

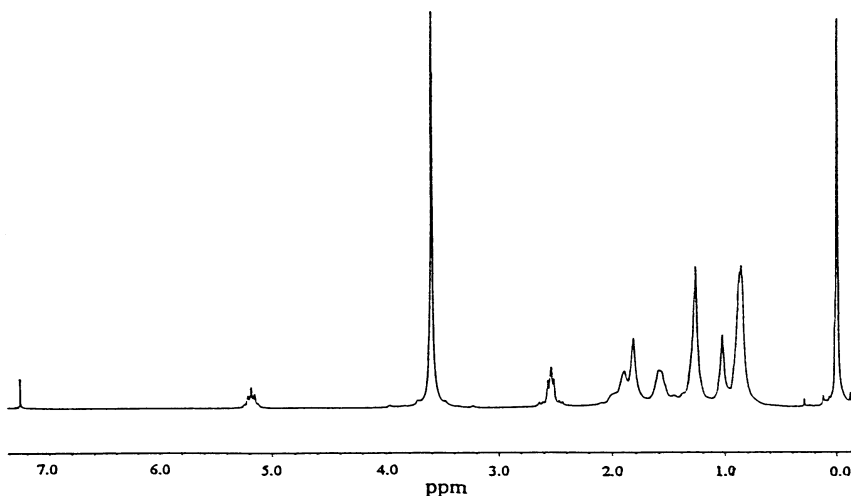


Fig.2. $^1\text{H-NMR}$ spectrum of the sample 52 in Table 1.

As can be seen from Table 2, a trend is apparent when the strain at break values of fractionated copolymer samples are compared to the PHN feed content. The strain at break values of graft copolymers increase with increasing the PHN in feed. The strain at break and tensile strength values of PHN-PMMA copolymers are between the values of their respective homopolymers. This results are another proof of the copolymer formation.

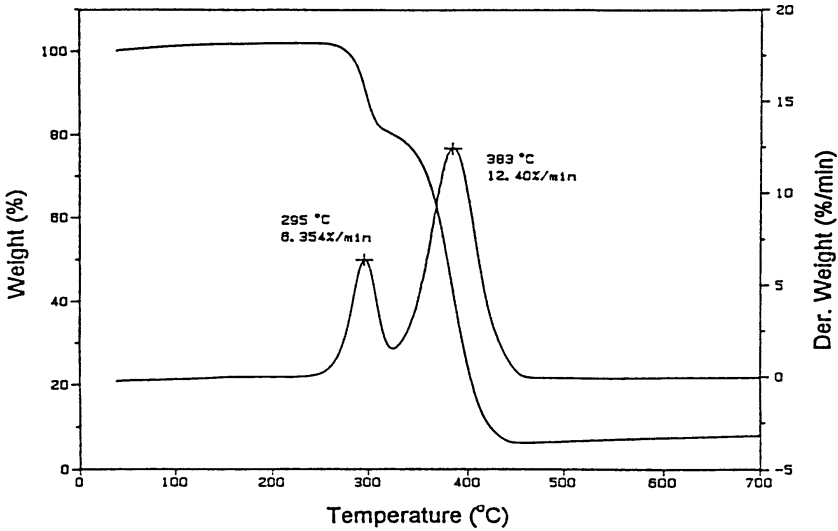


Fig.3. Weight-loss and derivative weight-loss curves of the sample 43 in Table 1.

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