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Preparation of polystyrene poly(β-hydroxy nonanoate) graft copolymers

Baki Hazer*

TUBITAK Marmara Research Center, Department of Chemistry, P.O. Box 21, Gebze 41470, Kocaeli, Turkey

Summary

Poly(β-hydroxy nonanoate)-polystyrene graft copolymers were prepared by the reaction of active polystyrene containing peroxide group with poly(β-hydroxy nonanoate) at 80°C. Graft copolymers with a wide graft composition range depending on the amount of active polystyrene in the original mixture were produced and separated from the grafting product by fractional precipitation.NMR and IR spectra of the graft copolymers were containing the characteristic bands of the corresponding blocks.DSC curves of the graft copolymers had a large endotherm between 50 and 110°C.

Introduction

Oligoperoxides are useful free radical initiators in a vinyl polymerization to obtaine active polymers having peroxide groups (1).These active polymers can be used as initiator in the polymerization of another vinyl monomer to obtaine block copolymers (2).

On the other hand,grafting is considered an important technique for modifying physical and chemical properties of polymers.It is well known that polyolefines can be modified with benzoyl peroxide ,thermally (3).Also the introduction of biodegradable segments into

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*Present address: Karadeniz Technical University, Department of Chemistry, Trabzon 61080, Turkey acrylate backbones directed toward biodisintegrable polymers possesing possible applications in medecine and environment protection.Biopolyesters,poly(β-hydroxy nonanoate) series including poly(β-hydroxy nonanoate),PHN, are biodegradable,biocompatible and of interest for biomedical applications (4,5). By using polymeric peroxides (6),the preparation of new graft polymers from polystyrene and PHN, is presented in this paper.Their composition was estimated.

Experimental

Materials

Oligo(adipoyl-5-peroxy-2,5-dimethyl hexyl peroxide),OAHP (1),was prepared from 2,5-dimethyl 2,5-dihydroperoxy hexane and adipoyl chloride.M_w=1120(cryoscopy) and peroxygen content was 22%.

Synthesis of oligo(dodecandioyl peroxide),ODDP (6): The solution of dodecandioyl chloride in 20 mL of diethyl ether was added into the mixture of 10 g of Na_2O_2 and 5 g of ice by stirring vigorously.The reaction temperature must stay under 5°C.The crude product was dissolved in 50 mL of H_2O and poured into the 20 mL of 50% of H_2SO_4 at room temperature.ODDP,was dried and crystallized in $CHCl_3$ as a white solid. M.p. 92-94°C (with decomposition) , M_w: 1270 (cryoscopy). Peroxygen analysis: 15.1 %; (calculated: 16.7%).

Poly(β-hydroxy nonanoate),PHN,was prepared by growing *Pseudomonas Oleovorans* with 20 mM nonanoic acid in 12 L of fermentation solution (5).The pure PHN yield was 5 g and M_w was 600 000 (by GPC according to polystyrene standards).

Synthesis of active polystyrene

In a pyrex tube,in which a given amount of styrene and the oligoperoxide were charged separately.Argon was introduced through a needle into the tube for about 3 min to expel the air.The tightly capped tube was then put in an oil bath at 70 or 80°C.After the required polymerization time,the content of the tube was coagulated into methanol.The active polystyrene sample was dried overnight under vacuum at 40°C.Table 1 shows the characteristic data of the resulting products.

Table 1.Synthesis of active polystyrene samples.

Run	Oligoperoxide		Styrene,	Polym.	Polym.	Yield,	-O-O-,	[η]*,
No.	OAHP,g	ODDP,g	g	temp.,°C	time,min	g	%	dL/g
a	3.8	-	15	70	70	2.01	0.6	0.31
b	-	0.82	18	70	70	3.03	0.2	0.43
c	-	0.42	15	80	40	2.56	0.1	0.32

*in benzene,at 30°C

Graft copolymerization

A given amount of this active polystyrene and PHN were dissolved in $CHCl_3$,and poured on a watch glass.After getting the mixture film,it was dried under vacuum and transferred into a pyrex tube.The tube was capped with a rubber septum and put into a thermostated oil bath at 80°C.After a given period of time,the polymer product was taken out by cracking the glass tube.The results of the grafting are shown in Table 2.

Analysis of the graft copolymers and measurements

The fractional precipitation method was carried out by measuring,γ, the volume ratio of nonsolvent to the solution of the polymers (2) to separate pure graft copolymer from the corresponding homopolymers.

IR spectra of the graft copolymers were taken by using a Perkin-Elmer 177 IR spectrometer.A typical IR spectrum of a graft copolymer is shown in Figure 1.

NMR spectra of the polymers were recorded by using a Bruker-AC 200 L,200 MHz NMR spectrometer.Figure 2 shows a typical NMR spectrum of a PHN -PSt graft copolymer.

Styrene content of the polymer fractions was determined by a Varian 635 D UV-VIS spectrometer.This method is based on measuring the absorbance of phenyl group of polystyrene at λ=269 nm (7).Figure 3 shows a typical UV spectrum of a graft copolymer.

DSC thermograms were taken on a Du Pont 910 Differential Scanning Colorimeter at a heating rate 10°C/min.Figure 4 shows a typical DSC thermograms of a graft copolymer.

Table 2. Grafting of PHN with active polystyrene (active-PSt) at 80°C .

Run	Active-PSt		PHN,	Grafting	Analysis of graft copolymers			
no.	type	amount,g	g	time,min	γ	amount,%	PSt %	[η]*,dL/g
23	c	0.1	0.4	240	1.3	68	27	
					2.4	32	12	
24	c	0.25	0.4		1.1	33	homo-PSt	0.50
					1.3	66	12	0.67
25	c	0.4	0.4		1.0	38	homo-PSt	0.48
					1.3	60	28	
26	c	0.4	0.2		0.7	48	44	0.60
					1.3	50	26	
41	a	0.25	0.4	190	1.2	19	homo-PSt	0.33
					1.9	51	27	0.70
					2.4	29	8	
42	a	0.4	0.3		1.0	36	homo-PSt	
					1.8	41	34	0.76
					2.4	22	10	
43	b	0.25	0.4		1.0	21	homo-PSt	0.45
					1.6	30	61	0.65
					2.3	49	12	
44	b	0.4	0.3		1.2	47	homo-PSt	
					2.2	50	11	
45 1)	b	0.25	0.3	163	1.0	26	homo-PSt	0.45
					1.9	16	64	0.66
					2.4	58	11	
46	ODDP	0.1	0.4	240				0.45
PHN					2.5			0.77

*in benzene, 30°C.

1) grafting reaction was carried at 92°C.

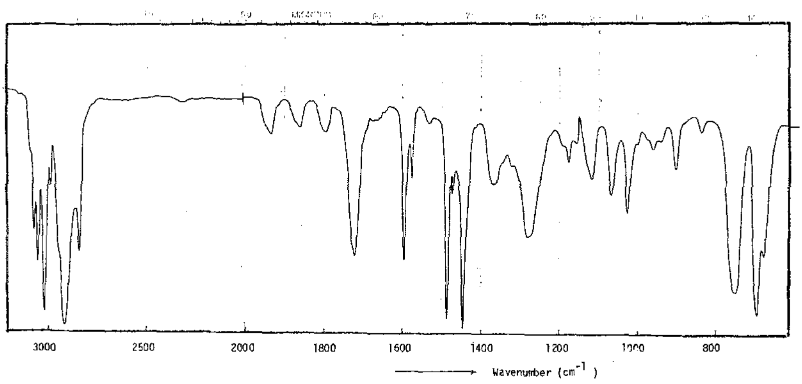


Fig.1. IR spectrum of poly(styrene-g-β-hydroxynonanoate),sample 24 (12% PSt) in Table 2.

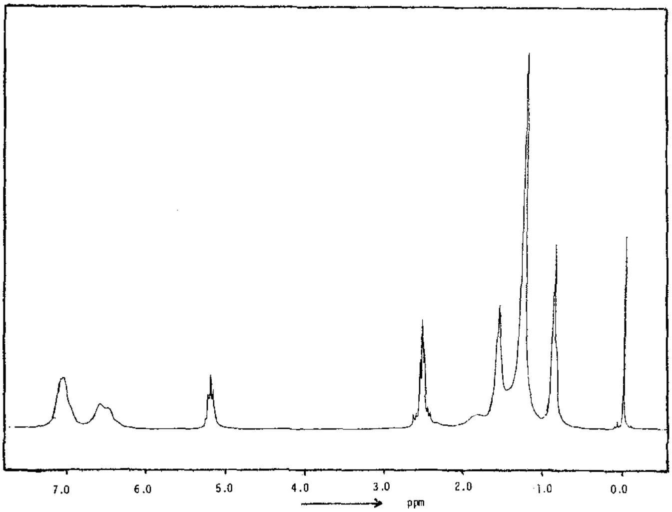


Fig.2. NMR spectrum of poly(styrene-g-β-hydroxy nonanoate),sample 42 (34% PSt) in Table 2.

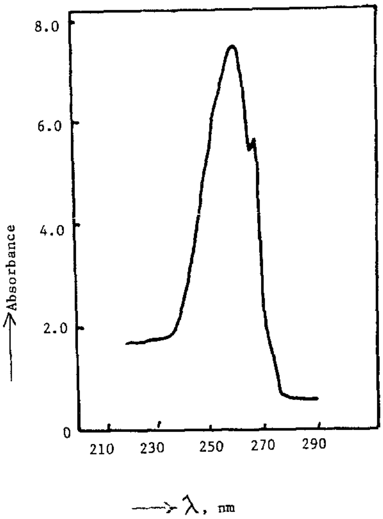


Fig.3. UV spectrum of poly(styrene-g-β-hydroxynonanoate),sample 42 (34% PSt) in Table 2.

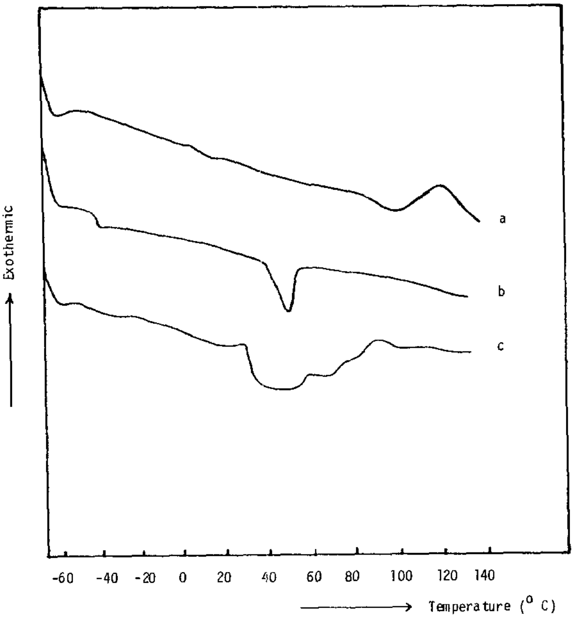


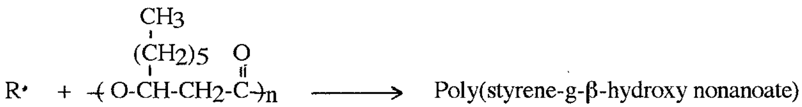
Fig.4. DSC curves of (a) active polystyrene b in Table 1, (b) PHN in Table 2 and (c) poly(styrene-g-β-hydroxynonanoate),sample 42 (34% PSt) in Table 2.

Results and Discussion

Active polystyrenes containing peroxide groups were synthesized by the polymerization of styrene with oligoperoxide initiators.Active polymers with a wide range peroxide content and molecular weight can be obtained by this way (Table 1).Active polymers thermally produce polymer radicals (1,2,7).These polymer radicals can lead to grafting reaction with biodegradable polyester,PHN.Grafting reactions can be designed as follows.

$$\begin{matrix}\text{ODDP}\\ \text{or}\\ \text{OAHP}\end{matrix} + \text{Styrene} \xrightarrow{\Delta} \underset{\text{active polystyrene}}{\text{—OO——OO—}}$$

$$\text{—OO——OO—} \xrightarrow{\Delta} R^{\cdot}\ \text{(polystyrene radical)}$$



$$R^{\bullet} + \left(O-\overset{\overset{CH_3}{|}}{\overset{(CH_2)_5}{\overset{|}{CH}}}-CH_2-\overset{O}{\overset{\|}{C}} \right)_n \longrightarrow \text{Poly(styrene-g-}\beta\text{-hydroxy nonanoate)}$$

The results from grafting reaction of PHN and active PSt are listed in Table 2.Grafting reaction product was analysed by fractional precipitation method (2).Volume ratio of nonsolvent to the solution of the polymer, γ , for pure graft polymers was 1.3-1.9 while 0.7-1.0 for homopolystyrene and 2.3-2.5 for homo-PHN.As expected,γ values of pure graft copolymers were between those of corresponding homopolymers.IR,NMR and UV spectra of purified graft copolymers were containing characteristic bands of each polymer block.In Figure 1 , IR spectrum of sample 24 (12% PSt) in Table 2 has phenyl band of polystyrene at 1600 cm^{-1} and carbonyl band of PHN at 1720 cm^{-1}.In Figure 2,NMR spectrum of sample 42 (34% PSt) in Table 2 has also characteristic phenyl peaks of polystyrene segments at δ = 6.5-7.2 ppm and characteristic PHN segment peaks at δ=0.9 ppm,2.5 ppm(CH_2 next to the carbonyl,5.2 ppm(CH group next to oxygen in ester group) (5).

Characteristic band of phenyl group of polystyrene at 269 nm,in UV spectrum of a graft copolymer in Figure 3,was used to determine polystyrene content of block copolymer and also homopolymers (Table 2).We also checked the polystyrene content of graft copolymer from NMR spectrum.Polystyrene content of the samples (in Table 2) calculated from their

NMR spectra were also in a very good agreement with the result obtained from UV analysis.

The grafting reaction of PHN with ODDP at 80^{o}C gave the sample 46 in Table 2,its molecular weight is less than original PHN(compare the viscosities of PHN and PHN grafted with ODDP,0.77 and 0.45 dL/g,respectively).In fact,after grafting reaction ,there is an increase in the viscosity values of graft copolymers according to that of active polystyrene used(its molecular weight comes down during the grafting reaction by the time (7).We might say the active polystyrene radicals,during the grafting reaction , cut some ester bonds of PHN and bound the PHN segments.NMR spectrum of the graft copolymer in Figure 2 also confirms this idea because the integral ratio of the characteristic groups of PHN was the same as those of virgine PHN.

DSC curves of the graft copolymer sample 42 (34% PSt) in Table 2,had a large endotherm between 50 and 110^{o}C while homo-PHN had sharp melting endotherm at 55^{o}C (5) and only exotherm transition for active polystyrene at 120^{o}C coming from the decomposition of its peroxide groups.Apart from this,when comparing runs 45 and 43 in Table 2,one can conclude higher grafting temperature leads to lower yield of graft polymer.

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