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GRAFT COPOLYMERS BY FREE RADICAL COUPLING REACTIONS.

I. POLYSTYRENE-POLYBUTADIENE GRAFT COPOLYMERS

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ABSTRACT

Polybutadiene-polystyrene graft copolymers were prepared by free radical coupling method at 80^{o}C.Oligo(adipoyl-5-peroxy-2,5-dimethyl n-hexyl peroxide) or oligo dodecandioyl peroxide were used in the polymerization of styrene at 60 or 80^{o}C to prepare active polystyrene samples having undecomposed peroxy groups in the main chain.Homogeneous mixtures of active polystyrene and polybutadiene gave graft copolymers at 80^{o}C under vacuum.Polystyrene-g-polybutadiene copolymers were separated from corresponding homopolymers by fractional precipitation.UV,IR,NMR and GPC techniques were used for analysis of pure graft copolymers formed in the yield range between 12% and 92%. DSC curves of graft copolymers exhibited a wide endotherm transition between 40 and 80^{o}C while the corresponding homopolymers showed only glass transitions.

INTRODUCTION

Oligoperoxides are well known to yield block copolymers by free radical mechanism[1,2].Some oligoperoxides prepared by the reaction of sodium peroxide and aliphatic diacid chlorides were found to be slightly soluble in vinyl monomers,but those

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dangerous and explosive chemicals are extremely sensitive to heat,shock and friction[3].Oligophthaloyl peroxide[4] is not soluble in common organic solvents nor in vinyl monomers.So it can not be used as an initiator in block copolymerizations by free radical mechanism.Several oligoperoxides[1,5-7] were successfully used in block copolymerizations by free radical mechanism.For this purpose,a vinyl monomer can be polymerized with an oligoperoxide to yield a polymer with yet undecomposed peroxy groups[8,9]. These "active" polymers were used subsequently as initiators in the polymerization of another vinyl monomer to obtain block copolymer.Grafting is also considered an important technique for modifying the physical and chemical properties of polymers[10].Some studies have aimed at crosslinking polymers with benzoyl peroxide to improve their mechanical properties[11].In a very recent work,a polystyrene-polyolefin graft copolymer was prepared upon attaching polystyrene fitted with benzocyclobutene end groups to a polyolefin carrying double bonds through thermally induced Diels-Alder reactions[12].

In a recent work[13],synthesis of a new oligoperoxide, oligododecandioylperoxide,ODDP and polymerization kinetics of styrene with ODDP were studied.Some grafting reactions of polybutadiene with active polymers obtained by ODDP were also given.In the present work,more details on grafting reactions by using ODDP and oligo(adipoyl-5-peroxy-2,5-dimethyl hexyl peroxide)[1],OAHP, will be discussed. First,active polystyrenes were obtained by polymerization of styrene with OAHP, or ODDP.In the second step,a homogeneous mixture of polybutadiene and active polystyrene was reacted under vacuum in solid state or in a solution at 80°C(Scheme 1).

EXPERIMENTAL

Materials

A Nicolet 510 P FT-IR, a 200 MHz Bruker-AC 200L NMR and a Varian 635D UV-VIS spectrometers were used for recording the spectra of the polymer samples.

DSC thermograms of the polymers were taken on a Du Pont 910 Differential Scanning Colorimeter at a heating rate 10°C/min.

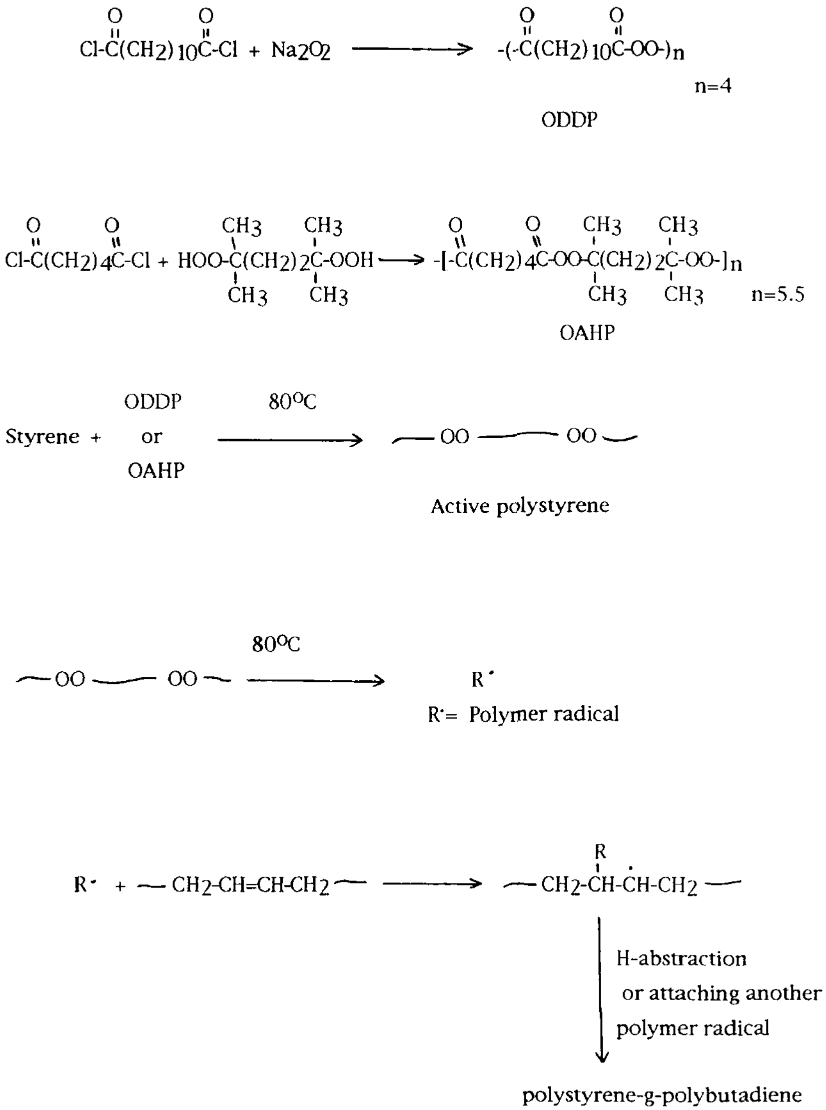
GPC chromatograms were taken on a Knauer GPC instrument.

Polybutadiene prepared anionically was a gift from DuPont and $[\eta]_{int}$ was 0.87 dL/g.

OAHP was prepared from 2,5-dimethyl 2,5-dihydroperoxy hexane and adipoyl chloride according to the literature cited[1].M_w=1120 g/mol(cryoscopy) and the peroxygen content of OAHP was 22%(n=4).

Synthesis of ODDP

A solution of 10 mL of dodecandioyl chloride in 20 mL of diethyl ether was added to the mixture of 10 g of Na_2O_2 and 5 g of ice under vigorous stirring.The crude product was



Scheme 1.The preparation of polystyrene-g-polybutadiene copolymers .

dissolved in 50 mL of H_2O and poured into the 20 mL of 50 % 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) ,molecular weight of the oligoperoxide:1270 g/mol(cryoscopy). Peroxygen analysis[6] : 15.6 %,(calculated: 16.7 %).

Synthesis of the "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 expell the air . The tightly capped tube was then put in an oil bath at 60 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.

Graft copolymerization

A given amount of this active polystyrene and polybutadiene were dissolved in $CHCl_3$,and poured on a watch glass.After getting the film,the polymer mixture was dried and transferred into a pyrex tube.The tube was sealed under vacuum 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.

Analysis of the graft copolymers

Analysis of graft copolymers was carried by fractional precipitation upon measuring γ,the volume ratio of non solvent to the solution of the polymer[2].IR and NMR spectra of pure graft copolymer were taken(Figure 1 and 2).Styrene content of the polymer fractions was determined by UV spectroscopy at 269 nm.This method is based upon measuring the absorbance of the phenyl groups of polystyrene at 269 nm(ref.14).Figure 3 shows a typical UV spectrum of a graft copolymer.Grafting and analysis data are listed in Table 2. DSC curves of polymers were obtained by using a Du Pont instrument and a typical one is given in Figure 4.

RESULTS AND DISCUSSION

Synthesis of oligoperoxides for "active" polystyrene

Two oligoperoxides were used as initiators for the polymerization of styrene to synthesize active polystyrenes still containing undecomposed peroxy groups in their main

TABLE 1

Polymerization of styrene by oligoperoxides to obtain active polymers.

						Active polystyrene:		
Run No.	Oligoperoxides:		Styrene, g	Polym. time, min	Polym. temp., °C	Yield, %	Peroxygene content, wt-%	$[\eta]^*$, dL/g
	ODDP,g	OAHP,g						
1	0.61	-	14	110	60	1.06	0.3	0.70
2	-	4.38	18	200	60	1,78	0.2	0.45
3	0.42	-	15	40	80	2.56	0.1	0.32

* 30°C,in benzene

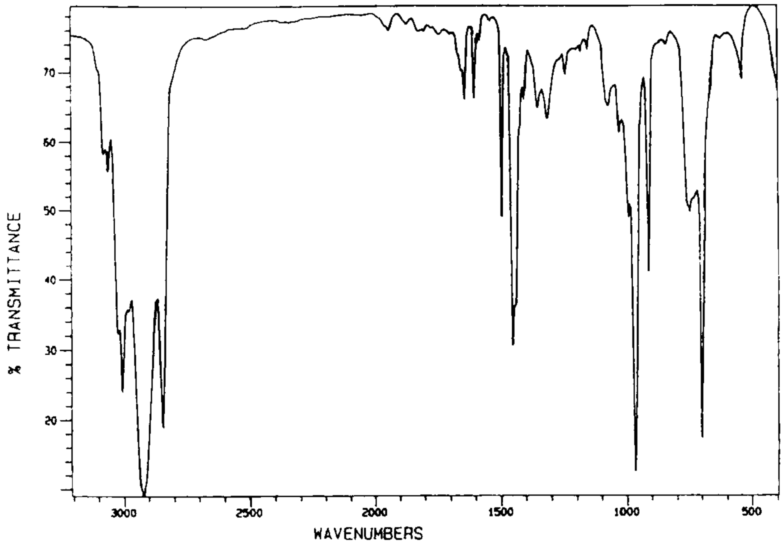


Figure 1. IR spectrum of poly(styrene-g-butadiene) (run no. 4 in Table 2).

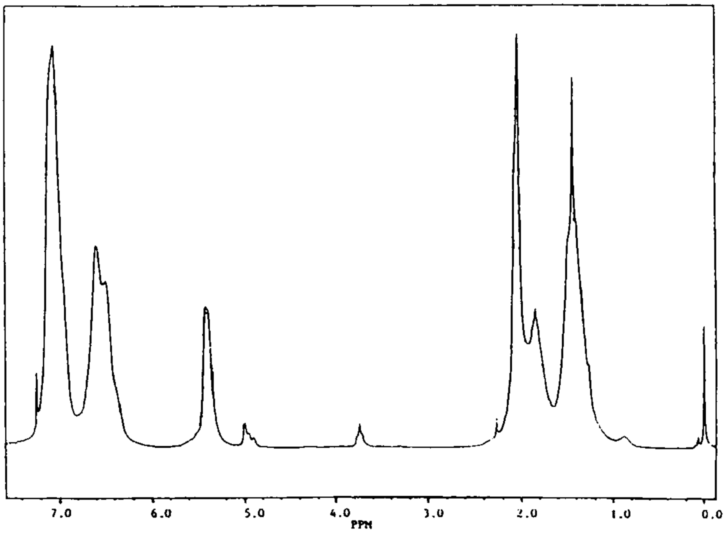


Figure 2. NMR spectrum of poly(styrene-g-butadiene) (run no. 4 in Table 2).

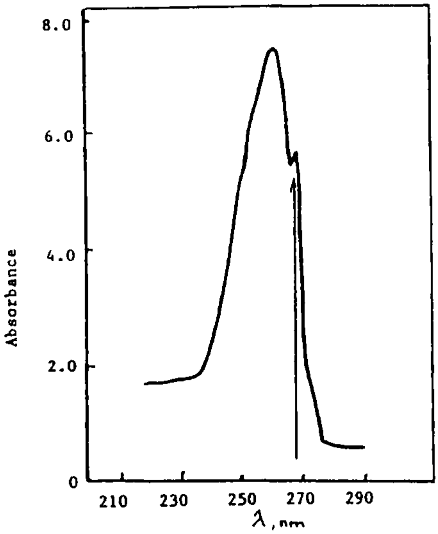


Figure 3. UV spectrum of poly(styrene-g-butadiene) (run no. 4 in Table 2).

TABLE 2

Grafting process of active polystyrene with polybutadiene at 80°C for 250 min.

Run No.	Polymeric per-oxide(in Table 1)		PBtd, g	The ratio of PSt to PBtd	γ	Analysis of the product : amount in the mixture,%	PSt con-tent,%	[η],* dL/g
4	2	0.1 g	0.5	0.2	0.3	79	homo-PBtd	
					0.6	16	38	
					0.8	5	homo-PSt	
5	2	0.3 g	0.5	0.6	0.3	78	homo-PBtd	
					0.6	12	66	
					0.8	10	homo-PSt	
6-a	2	0.5 g	0.5	1	0.3	44	homo-PBtd	
					0.5	44	65	0.66
					0.8	12	homo-PSt	
6-b[1]	2	0.35	0.35	1	0.3	42	homo-PBtd	
					0.6	50	58	
					1.0	8	homo-PSt	
7	2	0.5 g	0.25	2	0.3	10	homo-PBtd	
					0.4	22	56	0.60
					0.7	68	homo-PSt	0.50
8	3	1.3 g	0.65	2	0.3	35	homo-PBtd	
					0.7	56	78	
					1.0	9	homo-PSt	
9[2]	3	0.5 g	0.1	5	1.0	92	81	
10	ODDP	0.1 g	0.5		Crosslinked polybutadiene (swelling degree in $CHCl_3$ = 2200 %-wt)			

* 30°C,in benzene

[1] homo-PSt could not separate from the product.[2] in 5 mL of tluene solution.

chain.OAHP[1] was recently synthesized in our laboratories and successfully used in the preparation of active polystyrene.Another polymeric initiator,ODDP, also soluble in organic solvents,can be easily handled without explosion as an initiator, unlike oligosebacoyl,adipoyl and azelaoyl peroxides[3]. The active polystyrene samples obtained in high yields with either ODDP or OAHP, contained enough undecomposed peroxy groups in their main chain(Table 1).It is possible to obtain active polystyrene with different peroxygen content by changing the polymerization conditions as shown in Table 1. The peroxygen contents of the active polystyrene depends on oligoperoxide concentration,polymerization temperature and polymerization time.

Graft copolymerization

After the grafting reaction involving the active polystyrene and polybutadiene,1-5 % gel was found in the row polymer occured depending on the ratio of the two polymers.Higher

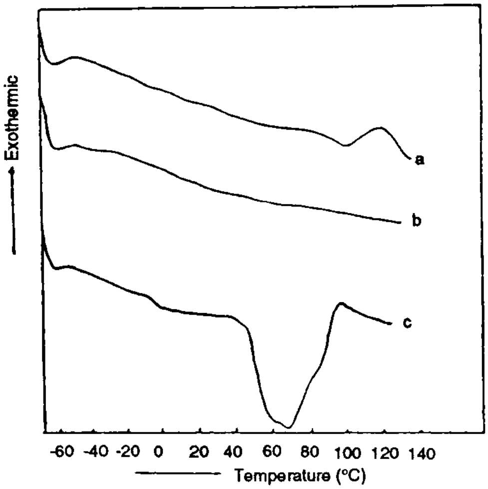


Figure 4. DSC curves of (a) active polystyrene-2 in Table 1,
(b) homopolybutadiene in Table 2,
and (c) poly(styrene-gbutadiene)(run no. 6-b in Table 2).

amount of active polystyrene in the original mixture gave higher gel content(5%) in the grafting product.After separation of the crosslinked gel,a fractionation was carried out. 12-58 % of the mixture was pure graft copolymer,depending on the peroxygen content and on the amount of the "active" polymer in the initial reaction mixture(Table 2). γ for poly (styrene-g-butadien) was 0.4-0.5 while γ the values for homopolybutadiene is 0.27 and for homopolystyrene 0.8-1.0 .(γ is the volumetric ratio of the precipitant to solution volume).The graft copolymer structure is thus confirmed since the γ value of graft copolymer is located between the γ values of the corresponding homopolymers.IR spectroscopy is also in favor of the graft copolymer structure.The IR spectra of the graft copolymer samples fractionated (γ = 0.4-0.7) were also recorded.Figure 1 shows the phenyl peak of polystyrene at 1600 cm^{-1} and the characteristic double bonds of polybutadiene at 1620 cm^{-1}.Increasing the amount of active polystyrene in the original reaction mixture causes higher graft copolymer yield but less homopolybutadiene in the grafting reaction product (compare run nos 4 and 7 in Table 2).Grafting reaction in toluene solution gave also the same graft copolymer yield(compare runs 6-a and 6-b in Table 2).

The reaction of polybutadiene with ODDP gave a highly elastomeric crosslinked material(run no 10).Because of the clevage ofperoxygen bonds,intrinsic viscosities of active polymers come down to nearly half of their initial value by heating at 80°C for 3 hours[5].It

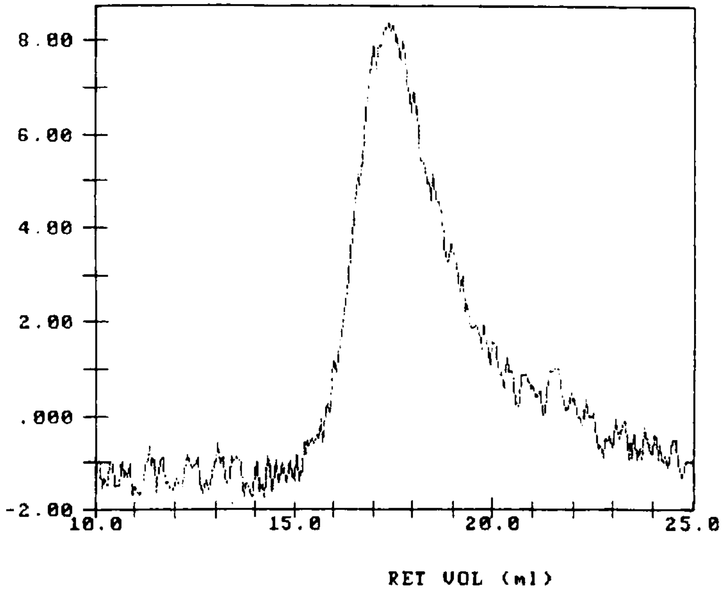


Figure 5. GPC chromatogram of poly(styrene-g-butadiene) (run no.5 in Table 2).

has found that intrinsic viscosities of graft copolymer fractions can be higher than that of corresponding active polystyrene but they are lower than that of polybutadiene,0.87 dL/g(run nos : 6 and 7).One can conclude that grafting reaction also causes cleavage of polybutadiene[15] together with the addition to double bonds of polybutadiene and hydrogene abstraction by polystyrene radicals.

NMR spectra of graft copolymers fractionated exhibited characteristic peaks of double bonds of PBd at δ=5.4 ppm and of phenyl groups of polystyrene at 6.4-7.2 ppm.Graft copolymers with a wide range of polystyrene contents were also analysed by UV at λ=269 nm characteristic absorbtion of phenyl groups of polystyrene(Figure 3).DSC thermograms of graft copolymers observed wide endotherm transitions between 40 and 80°C which is characteristic of grafting formation since polybutadiene and active polystyrene did not contain any endotherm transition, but only exothermic transition arising from the decomposition of its peroxide groups.In Figure 5,GPC chromatogram of a typical graft copolymer has only one peak which is attributable the sample is a graft copolymer,not a blend of polymers.

As a conclusion,active polystyrene samples prepared two different oligoperoxide,OAHP and ODDP were used the grafting reactions of polybutadiene in solid state or in solution to obtain graft copolymer.Fractionated pure graft copolymer samples were characterized by ir,uv,nmr spectroscopy ; dsc and gpc technique.

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