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GRAFT COPOLYMERS BY FREE RADICAL COUPLING REACTIONS. II. POLY(METHYL METHACRYLATE)-POLYBUTADIENE GRAFT COPOLYMERS

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Summary

"Active" poly(methyl methacrylate) having peroxygen groups of 1.6 wt-% and with M_n=15000 g/mol, were prepared and used in the free radical coupling reactions of polybutadiene. Poly(methyl methacrylate)-polybutadiene cross-linked and soluble graft copolymers were obtained in moderate yields. Swelling degrees of the cross-linked block copolymers in $CHCl_3$ were between 319-759. NMR and FTIR spectra were containing the characteristic bands of the graft copolymers. Broad melting peaks on DSC curves of the graft copolymers appear from about 40-85°C. From the GPC measurements, the number average molecular weights of the soluble graft copolymers produced were in range between 22000-26000 with polydispersity indices(M_W/M_n) in the range of 2.0-2.3.

Introduction

Grafting is considered an important technique for modifying the physical and chemical properties of polymers. It was very recently reported the new grafting technique to obtaine polystyrene-polybutadiene graft copolymers[1]. In the first step, polymerization of styrene initiated with oligoperoxides, oligododecandioyl peroxide[2], ODDP, or oligo(adipoyl-5-peroxy-2,5- dimethyl hexyl peroxide)[3], OAHP, yields active polymer having undecomposed peroxygen groups in the main chain.

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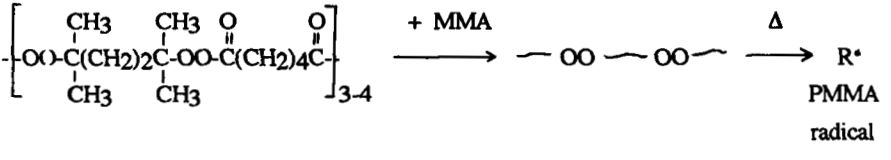
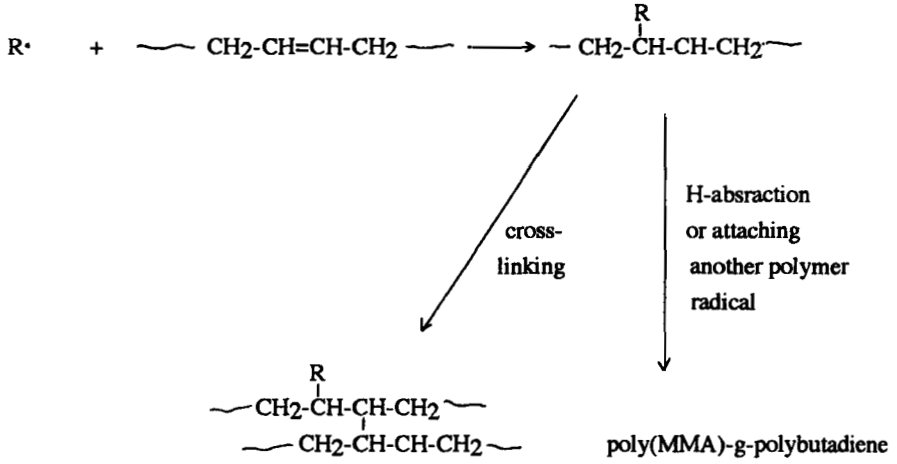
The present work refers to the grafting reactions of polybutadiene with "active" poly(methyl methacrylate), PMMA, having higher peroxygen content obtained by the polymerizaion of MMA with OAHP. The reaction schemes can be designed as follows:



OAHP



Experimental

Materials

A 200 MHz Bruker-AC 200L NMR and a Nicolet 510 P FT-IR 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 Shimadzu GPC instrument including C-R4A Chromatopac computer and printer, CTO-6A colon furnace, RID-6A detector and, LC-9A liquid pump.THF was used as the eluent at a flow rate of 0.75 mL/min. A calibration curve

was generated with three polystyrene standards 250 000, 90 000 and, 50 000 g/mol of low dispersity which were purchased from Polyscience.

Cis-polybutadiene(1,4: 75 wt-%; 1,2: 25 wt%) was kindly supplied from Du Pont.Its [η] was 0.87 dL/g. OAHP was prepared from 2,5-dimethyl 2,5-dihydroperoxy hexane and adipoyl chloride according to the literature cited[3].

Synthesis of the "active" PMMA

In a pyrex tube, in which a given amount of MMA and the OAHP 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 70°C for 70 min. Then the content of the tube was coagulated into methanol. The active PMMA sample was dried overnight under vacuum at 40°C. Table 1 shows the characteristic data of the resulting products.

Grafting reactions and analysis of the graft copolymers

A given amount of the active PMMA and polybutadiene were dissolved in $CHCl_3$ and poured on a glass plate.After getting the film of the polymers mixture, it was dried under vacuum at room temperature and transferred into a pyrex tube. The tube was stoppered under N_2 and kept at 95°C for 1 h. The gel fraction was separated by leaching the polymer product in $CHCl_3$. The soluble part was fractionated by precipitating methanol as non-solvent. γ was calculated as volume ratio of the non-solvent to solvent[4]. Number average of molecular weight (M_n) of the soluble graft copolymers were determined by GPC. The data of the results of the grafting reactions were collected in Table 2.

Swelling properties of the cross-linked polymers were also studied and the results were collected in Table 3. PMMA content of the cross-linked block copolymers was determined by comparing the length of carbonyl band at 1750 cm-1.Figure 1 shows a typical FT-IR spectrum of PMMA-PBd cross-linked block copolymer. PMMA contents of the soluble graft copolymers were calculated by comparing vinyl peak of butadiene at 5.4 ppm with methyl peak of esther group of PMMA at 3.6 ppm in their NMR spectra (Figure 2).

DSC curves of polymers were obtained by using a Du Pont instrument and a typical one is given in Figure 3.

Results and Discussion

Active PMMA's having high peroxygen content were obtained by the polymerization of MMA with OAHP. High concentration of oligoperoxide in the polymerization mixture and

Table 1. Polymerization of MMA by OAHP to obtain active polymers.

Run No:	OAHP, g	MMA, g	Polym. time, min	Polym. temp, °C	Active PMMA: Yield, wt-%	Active PMMA: Peroxygen content, wt-%	Active PMMA: $M_n.10^{-4}$
4	5.4	23	70	70	1.8	1.6	1.5
6	7.8	26	70	70	1.7	1.6	1.5

Table 2. Grafting reactions of the "active" PMMA with polybutadiene at 95°C for 1 h.

Run No:	active PMMA, g	polybutadiene, g	Analysis of the polymer product[b]: X'linked polymer, wt-%.	γ = 0.3 (homo-PBd) wt-%.	γ = 3-4 (block cop.) wt-%	γ = 3-4 (block cop.) $M_n.10^{-4}$	γ = 5-6 (homo-PMMA) wt-%	γ = 5-6 (homo-PMMA) $M_n.10^{-4}$
200	**6** 0.5	0.5	32	-	-		32	
201	**4** 0.5	0.5	43	-	16	2.2	14	
203	**4** 0.33	0.5	44	-	25		8	
210	**6** 0.36	0.26	45	-	13		16	
209[a]	**6** 0.5	0.5	-	40	25	2.6	23	1.4

a) in 5 mL of toluene, under N_2. b) The rest of the polymer fractions was oily residue.

Table 3. Swelling properties of PMMA-PBd cross-linked graft copolymers.

Polymer no:	PMMA,wt-%	Degree of swelling
200	30	573
201	70	757
203	30	612
210	50	319

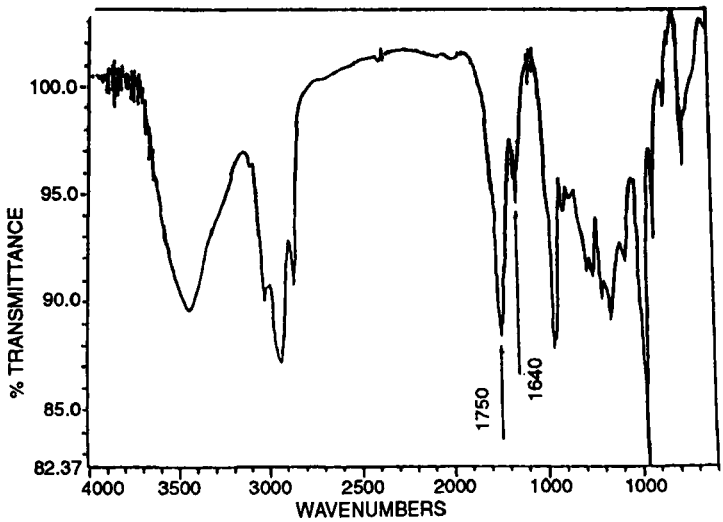


Figure 1. FT-IR spectrum of PMMA-g-PBtd X'linked polymer (Run no:210 in Table 2).

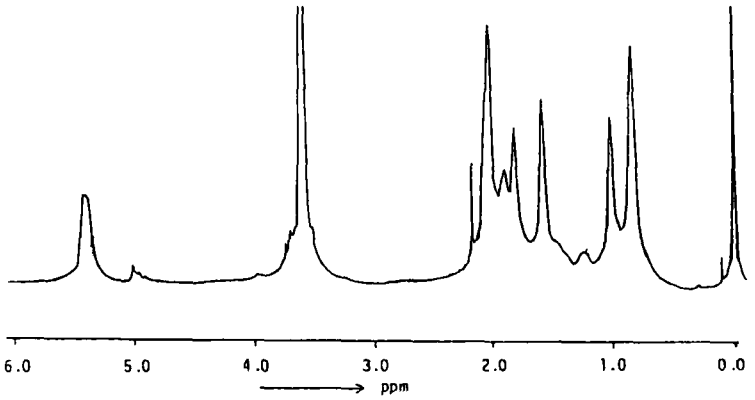


Figure 2. NMR spectrum of PMMA-g-PBtd (Run no: 209, γ=4, in Table 2).

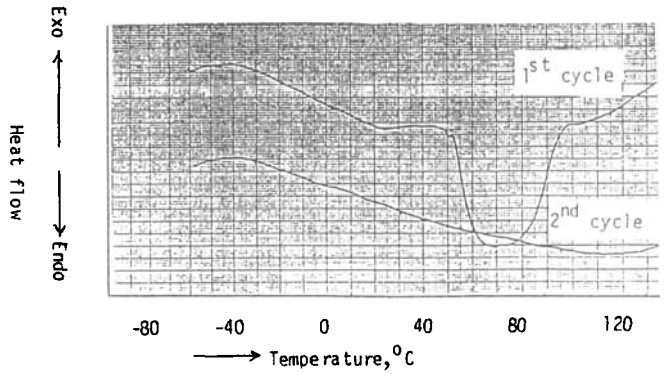


Figure 3. DSC thermograms of PMMA-g-PBtd X'linked polymer (Run no: 210 in Table 2).

short polymerization time cause low polymer yield but also having high undecomposed peroxygen groups in the main chain(Table 1). In fact the grafting reactions of polybutadiene with active PMMA having higher peroxide groups lead to cross-linked block copolymers with the yield 32-35 wt-% (Table 2). Fractional precipitation method was used to isolate soluble graft copolymers having PMMA segment less than 15 wt-% , from the polymer product.. γ for PMMA-g-PBd was 3-4 while γ values were 0.3 for homo-PBd and 5-6 for homo PMMA.Swelling properties of cross-linked PMMA-g-PBd samples were also

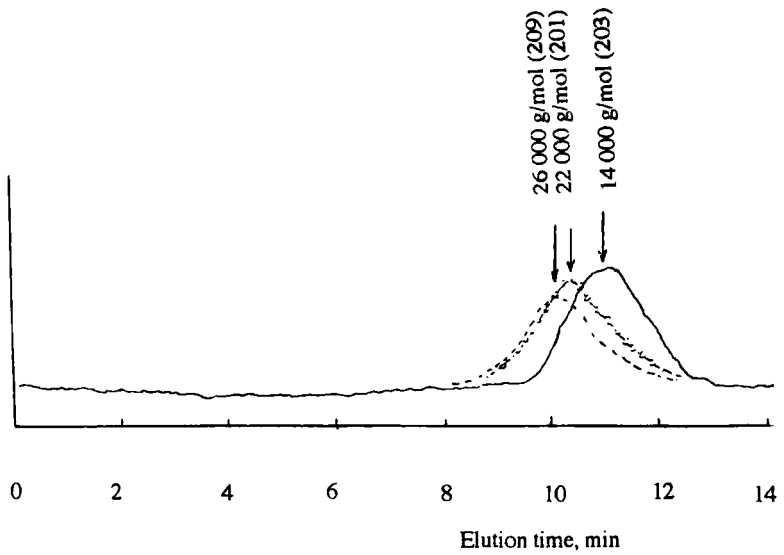


Figure 4. Some typical GPC chromatograms of the soluble graft copolymers(run nos: 209, 22000 g/mol, γ=3-4 ; 201, 26000 g/mol, γ=3-4) and inactive homo-PMMA(run no:203, 22000 g/mol, γ=5-6).

determined in $CHCl_3$, at room temperature. M_n values of these graft copolymers(γ=3-4) were two times greater than inactive homo-PMMA. As expected, the graft copolymers with the same γ values(γ=3-4) had near molecular weights, 22 000 and 26 000 g/mol. Figure 4 shows some typical GPC chromatograms of the polymers. Swelling degrees ,[(swollen gel,g/dry polymer,g)x100] of the polymers were lying between 319 and 759. IR and NMR spectra of the cross-linked blockcopolymers were containing the characteristic bands at 1640 cm^{-1} (double bonds of PBd) and 1750 cm^{-1} (carbonyl groups of PMMA) (Figure 1); δ (ppm) = 5.4 (double bonds of PBd) and 3.6 (-$COOCH_3$ of PMMA) (Figure 2). Inactive homo-PMMA samples produced were characterized by FT-IR. Any characteristic bands of PBd were not observed in their FT-IR spectra.

In Figure 3. wide endotherm transitions which are characteristic grafting formation[1] between 40 and 80°C were observed in DSC thermograms of graft copolymers. Interestingly, grafting reactions in solution ,run no: 209 in Table 2, gave soluble graft copolymer without cross-linking.

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