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New manufacturing processes for block and graft copolymers by radical reactions

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New radical processes to obtain block and graft copolymers were developed by using special organic peroxides. Polymeric peroxides excelling in safety and solubility were newly prepared. PM_1 having O–O bonds in its chain was prepared by polymerization of M_1 with polymeric peroxide, and M_2 was polymerized with PM_1 to provide PM_1-*b*-PM_2. A monomer having an O–O bond was copolymerized with M_1 at a temperature below the decomposition temperature of the O–O bond and PM_1 having pendant O–O bonds was obtained. M_2 was addition-polymerized to pendant O–O bonds to get PM_1-*g*-PM_2. Vinyl polymers having O–O bonds were thermally mixed in an extruder with polyolefins and polyolefin-*g*-vinyl polymer was obtained by the reactive processing.

(Keywords: block copolymer; graft copolymer; organic peroxide; polymeric peroxide; peroxide monomer; impregnation polymerization; reactive processing)

INTRODUCTION

Polymer alloys and blends are becoming more and more important for the forthcoming 21st century. RAPRA[1] in the UK predicted in February 1989 that polymer alloys and blends will occupy half of the high-performance polymers market in the 1990s.

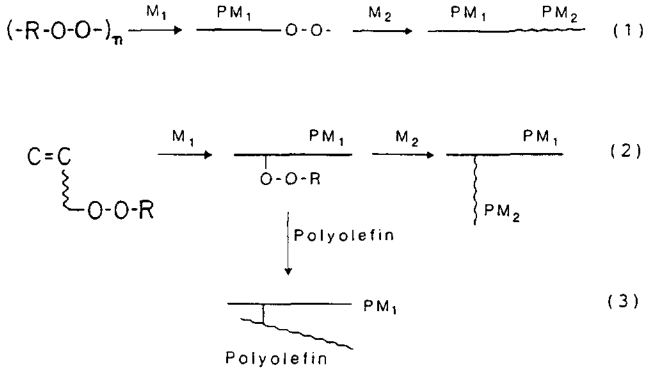
Recently, block and graft copolymers have been required in application fields of polymer alloys (blends), modifications, compatibility improvements, surface modifications and so on. There are no easy industrial manufacturing processes with cheap production costs to obtain block and graft copolymers from vinyl monomers. Only styrene–butadiene–styrene (SBS) and styrene–isoprene–styrene (SIS) (polystyrene-*b*-polyisoprene) have been manufactured by anionic living polymerizations[2].

Radical polymerization processes to obtain block copolymers with polymeric peroxides (PPO), which have several O–O bonds in a molecule, and to obtain graft copolymers with peroxide monomers, which have an O–O bond in a monomer, were studied.

Woodward and Smets[3] prepared polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) with poly(phthaloyl peroxide). Polystyrene-*b*-polyacrylonitrile (PS-*b*-PAN) was also synthesized[4] with PPO prepared with Na_2O_2 and azelaic acid dichloride or sebacic acid dichloride. However, these PPO were very dangerous and explosive chemicals, which are extremely sensitive to heat, shock and friction. Moreover, they have very poor solubility in solvents and monomers. Therefore, they have never been used in the manufacture of block copolymers.

In the preparation of graft copolymers, many processes[5] have been developed before, but they are not so good in grafting efficiency, production cost, plant cost and ease of processing.

We have developed new industrial processes to obtain block and graft copolymers, using special types of PPO and peroxide monomers. The synthetic schemes are shown in *Scheme 1*. In the preparation of block copolymers, first of all, polymers having O–O bonds in their polymer chains are synthesized as shown in step (1). The first monomer, M_1, is polymerized with PPO to provide polymers having O–O bonds. The second monomer, M_2, is polymerized with PM_1 having O–O bonds to get PM_1-*b*-PM_2 as shown in step (1). PM_1-*g*-PM_2 is obtained by polymerization of M_2 with PM_1 having pendant O–O bonds as shown in step (2). Moreover, we have developed new processes to get polyolefin-*g*-vinyl polymers. Vinyl polymers having pendant O–O bonds and polyolefins are thermally mixed in



Scheme 1 Synthetic scheme of block and graft copolymers with polymeric peroxides and peroxide monomers

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an extruder in which reactive processing takes place to provide polyolefin-*g*-vinyl polymer as shown in step (3).

Via our new processes, block and graft copolymers of many kinds of polymers are now available at reasonable prices and on an industrial scale. We expect that their use will expand in areas of polymer modification, compatibilization, low profile additives, surface modification, non-aqueous dispersions, adhesives and so on.

EXPERIMENTAL: SYNTHESIS OF BLOCK COPOLYMERS

Preparation of polymeric peroxide

$-[-C(O)C_4H_8C(O)-(OC_2H_4)_3-OC(O)C_4H_8C(O)-O-O-]_n-$

First, 29.7 g (0.198 mol) of triethylene glycol (TEG) was dropped into 72.3 g (0.396 mol) of adipic acid dichloride at 50°C, and hydrogen chloride was removed under light vacuum for 3 h at 50°C. The terminal groups of the oligoesters obtained are acid chlorides. A mixture of 22.5 g (0.05 mol) of the oligoester and 2.3 g of methyl ethyl ketone (MEK) was dropped into a solution of 5 g (0.125 mol) of sodium hydroxide, 4.3 g (0.06 mol) of 50% hydrogen peroxide, 100 g of water and 0.22 g of sodium dioctyl phosphate (surfactant) at 5°C for 20 min, and the reaction mixture was kept at 5°C for 20 min. After filtration and washing with water three times, 40 g of wet oligomer was obtained. The oligomer was purified as follows. The polymerization product was washed with methanol three times, then dissolved in benzene and the small amount that is insoluble was removed by filtration. Purified white powder was obtained by addition of methanol to the benzene solution and filtration.

Molecular weight was determined by g.p.c. based on standard polystyrene. The content of active oxygens was determined by iodometry. Polymeric peroxide (0.2 g) was dissolved in 10 ml of chloroform, and 30 ml of isopropyl alcohol, 2 ml of saturated KI aqueous solution and 2 ml of acetic acid were added. After boiling for 3 min, the solution was titrated with 0.1 N sodium thiosulphate. The name of this PPO was abbreviated to ATPPO.

Safety test of polymeric peroxides

Shock sensitivity was tested by hammering 100 mg PPO on a concrete plate. For heat sensitivity, 1 g of PPO in a test-tube of 15 mm diameter and 150 mm length was heated at a rate of 3°C min^{-1}, and the exothermic temperature at which the exotherm begins, the decomposition temperature at which rapid decomposition takes place and the decomposition condition (sound, smoke) were observed.

Polymerization of styrene with polymeric peroxide

Styrene was purified by washing with 2% sodium hydroxide, followed by washing with water and vacuum distillation at 40°C. Styrene was polymerized with ATPPO (concentration 0.01 M based on O–O bond) at 70°C in a sealed ampoule. After polymerization, benzene was added to the ampoule in order to get a solution of below 10 centipoise, and polystyrene was precipitated with methanol.

Preparation of polymers having O–O bonds in their chains

By suspension polymerization. A solution of 5.2 g of ATPPO in 100 g of methyl methacrylate (MMA) was added to 200 g of water containing 1 g of partially saponified poly(vinyl alcohol) (PVA) ($\bar{P} = 1500$, saponification degree = 80 mg g^{-1}). After polymerization at 60°C for 2 h, the polymers were filtered, washed and dried. 98 g of PMMA having O–O bonds in the chains was obtained: $M_v = 59\,000$; active oxygen content = 0.16%.

By bulk polymerization. 9.5 g of MMA was polymerized with 0.5 g of ATPPO at 65°C for 2 h in an ampoule.

Thermal decomposition of polymers having O–O bonds

In order to find the location of O–O bonds in the polymers polymerized with PPO, the polymers were thermally decomposed and the molecular weights of the decomposed polymer segments were measured. 50 g of isopropylbenzene solution of 1 g of PMMA having O–O bonds ($M_v = 581\,000$, active oxygen content = 0.16%) and 0.1 g of *p*-t-butylcatechol were heated at 135°C for 7.5 h in an ampoule. The polymer solution was added to 1 litre of methanol and the precipitated polymers were separated. The molecular weights of the polymers before and after thermal decomposition were compared.

Preparation of block copolymers

Preparation of PMMA-b-*PS.* 50 g of PMMA having O–O bonds ($M_v = 581\,000$, active oxygen content = 0.16%) and 50 g of styrene (St) were added to 300 g of water containing 1 g of PVA mentioned above, and kept at room temperature for 1 h under stirring to impregnate St into PMMA. The temperature of the suspension was raised to 75°C and kept there for 4 h. 99 g of PMMA-*b*-PS was obtained after filtration. Suspension and bulk polymerizations are also possible.

Purification of PMMA-b-*PS.* Homopolymers of MMA and St made as by-products in the preparation of PMMA-*b*-PS were separated by solvent extractions. 2 g of polymer product was extracted with cyclohexane for 100 h by Soxhlet extractor to extract polystyrene, using cylindrical filter paper (Toyo Roshi 80R). The dried residue was extracted with acetonitrile for 100 h to extract PMMA. The remaining polymer was extracted with benzene for 100 h to extract PMMA-*b*-PS. Each extract solution was concentrated and they were added to 400 ml of methanol to precipitate each polymer.

The composition of block copolymers was determined by ^{1}H n.m.r. and block efficiency was calculated as follows:

$$\begin{array}{c}\text{block efficiency}\\ \text{of styrene}\end{array} = \frac{\text{PS in PMMA-}b\text{-PS}}{\text{polymerized styrene}} \times 100(\%)$$

Molecular weight was determined by g.p.c. calibrated with PS at 40°C, using tetrahydrofuran (THF).

Preparation of PVAc-b-*PS.* 100 g of vinyl acetate (VAc) was polymerized with 5 g of ATPPO to provide poly(vinyl acetate) (PVAc) having O–O bonds at 60°C for 2 h. 100 g of styrene was polymerized with PVAc obtained above at 80°C for 4 h to get PVAc-*b*-PS.

EXPERIMENTAL: PREPARATION OF GRAFT COPOLYMERS

Synthesis of peroxide monomers

$CH_2{=}CHCH_2OC(O){-}O{-}O{-}tBu$ (ALPO). A peroxide monomer, t-butylperoxyallylcarbonate (ALPO),

was prepared according to (4) and (5):

$$\mathrm{CH_2{=}CHCH_2OH + COCl_2 \longrightarrow CH_2{=}CHCH_2OC(O)Cl} \quad (4)$$

$$\xrightarrow[\text{NaOH}]{\text{tBuOOH}} \mathrm{CH_2{=}CHCH_2OC(O){-}O{-}O{-}tBu} \quad (5)$$

Phosgene (51.3 g) was introduced to 43.4 g of allyl alcohol at 5°C for 60 min. The temperature of the reaction mixture was raised to 20°C and nitrogen was introduced to remove unreacted phosgene. The product was washed three times with water and dehydrated with magnesium sulphate. Allyl chloroformate was obtained by distillation: b.p. 53–54°C/81 mmHg (lit. 56°C/97 mmHg); Cl = 29.2%.

Then 26.4 g of 80% t-butylhydroperoxide was added to an aqueous solution of 10.6 g of sodium hydroxide in 95.8 g of water at 5°C. 29.2 g of allyl chloroformate was dropped into the solution at 5°C for 20 min. The temperature was raised to 20°C and kept there for 1 h. The upper organic layer was separated and washed three times with water. After dehydration with magnesium sulphate, 33.9 g of ALPO was obtained. The temperature giving a 10 h half-life is 97°C.

$\mathrm{CH_2{=}C(CH_3)COOC_2H_4OC(O){-}O{-}O{-}tBu}$ (HEPO). 134.4 g (0.24 mol) of 10% potassium hydroxide aqueous solution was added dropwise to a solution of 49.4 g (0.24 mol) of 2-methacryloyloxyethyl chloroformate (purity 93.6%) and 31.3 g (0.24 mol) of t-butylhydroperoxide (conc. 60%), which was kept at 0°C. The reaction mixture was kept at 0°C for 1 h and the oil layer was separated and washed twice with water. After dehydration with magnesium sulphate, 51.9 g of HEPO (purity 90%) was obtained. Yield 95%. The temperature giving a 10 h half-life is 104.3°C.

$\mathrm{iPrOOCCH{=}CHC(O){-}O{-}O{-}tBu}$ (PFPO). 40 g (0.2 mol) of fumaroyl chloride monoisopropyl ester (purity 88%) was added dropwise to a mixture of 31.3 g (0.24 mol) of t-butylhydroperoxide (conc. 70%) and 96 g (0.24 mol) of 10% sodium hydroxide aqueous solution at 0°C, and the reaction mixture was kept at 0°C for 1 h. 48 g (purity 92%) of PFPO was obtained after the same treatment mentioned above for the separated oil layer. Yield 96%. The temperature giving a 10 h half-life is 106.7°C.

Synthesis of graft copolymers

*PVAc-*g*-PS with ALPO.* Styrene was copolymerized with PVAc having pendant O–O bonds to provide PVAc-*g*-PS. 100 g of vinyl acetate and 3 g of ALPO were copolymerized with 0.8 g of lauroyl peroxide at 63°C for 2 h, 70°C for 3 h and 80°C for 0.5 h in 400 g of water containing 3 g of PVA and 10 g of Aerosil (fine silica, Japan Aerosil). 20 g of styrene was polymerized in an autoclave at 100°C for 6 h with 5–20 g of obtained PVAc having O–O bonds in 200 g of water containing 1.5 g of PVA and 5 g of Aerosil.

*PMMA-*g*-PS with HEPO.* 100 g of MMA and 5 g of HEPO were copolymerized with 0.5 g of t-butylperoxypivalate at 65°C for 10 h and 80°C for 0.5 h. 96.7 g of polymer products (crude PMMA having pendant O–O bonds) was obtained after filtration, washing and drying. 90 g of styrene was grafted to 10 g of PMMA at 115–120°C for 5 h and 130°C for 2 h in 600 g of water containing 6 g of PVA in an autoclave. After the same treatment, 88.1 g of crude PMMA-*g*-PS was obtained.

*PVAc-*g*-PS with PFPO.* 100 g of vinyl acetate and 5 g of PFPO were copolymerized with 0.3 g of di-2-ethylhexyl peroxydicarbonate at 60°C for 2 h and 65°C for 0.5 h in 500 g of water containing 1 g of PVA, using a 1 litre four-necked flask. 90.5 g of crude polymer was obtained after filtration, water washing and drying. 70 g of styrene was grafted to 30 g of obtained PVAc at 90°C for 5 h and 95°C for 0.5 h in 300 g of water containing 1 g of PVA, and 96.5 g of graft copolymer was obtained after filtration.

Determination of active oxygen of pendant O–O bonds by iodometry

About 1 g of polymers having pendant O–O bonds obtained as above was dissolved in a solution of 40 ml of chloroform, 70 ml of acetic acid and 3 g of potassium iodide, and the solution was kept at room temperature in the dark. 80 g of pure water and 2 ml of 1% starch aqueous solution were added to the solution and it was titrated with 0.1 N sodium thiosulphate.

Determination of molecular weight

Molecular weight was determined at 38°C by g.p.c. with calibrated PS by *RI*, using THF as solvent.

Solvent separation of graft copolymers

By-product homopolymers and gel were separated by solvent extraction. For the polymer products of PMMA-*g*-PS with ALPO, PS was extracted with cyclohexane and PVAc with ethanol/water (90/10 wt). For the polymer products of PMMA-*g*-PS, PS was separated with cyclohexane, and PMMA with acetonitrile. Remaining polymer was refluxed with benzene to extract PMMA-*g*-PS. PMMA-*g*-PS was precipitated by adding methanol to the benzene solution. The insoluble material in benzene was a gel.

EXPERIMENTAL: PREPARATION OF POLYOLEFIN-*g*-VINYL POLYMER

As shown in *Scheme 1*, step (3), vinyl polymers having pendant O–O bonds and polyolefins are thermally mixed in an extruder in which grafting reactions take place to give polyolefin-*g*-vinyl polymer. However, it is very hard to obtain graft copolymers by straight mixing in extruders. We have reported that, in this grafting reaction, pendant O–O bonds dangling on soft polymers such as PVAc, and poly(butyl acetate) (PBAc) work well to give polyolefin-*g*-vinyl polymers, but it is very hard to obtain them by pendant O–O bonds dangling on hard polymers such as PS. We considered that the key point of the grafting reaction is to increase the contact of O–O bonds with polyolefins.

In order to increase the contact, vinyl monomers, peroxide monomers and organic initiators were impregnated into polyolefin pellets and polymerized at elevated temperature in polyolefin pellets (we call this 'impregnation polymerization'). The obtained polyolefins including vinyl polymers that have pendant O–O bonds were thermally mixed in extruders to give polyolefin-*g*-vinyl polymer.

Preparation of PE-g-PS

700 g of low-density polyethylene (LDPE) pellet and 270 g of styrene were added to 300 g of water containing 2 g of PVA ($\bar{P} = 1500$, saponification degree = 80 mg g^{-1}) in a 5 l stainless-steel reactor equipped with a thermometer and a reflux condenser. The temperature was raised to 90°C and styrene was impregnated in the polyethylene (PE) pellet for 2 h. The temperature was dropped to 80°C and 30 g of styrene, 9 g of HEPO and 3 g of benzoyl peroxide (BPO) were impregnated into the PE pellet and polymerized for 3 h. 994 g of LDPE including PS that has pendant O–O bonds was obtained after filtration and washing. The LDPE was thermally mixed at 200°C in an extruder of 100 rpm and LDPE-*g*-PS was obtained.

Determination of grafting efficiency of PS onto LDPE

1 g of the extruded polymer was dissolved at 120–130°C in 50 g of xylene and the solution was added to 1 litre of equivolume ethyl acetate and acetone and settled for 24 h. The precipitate was removed by filtration and the filtrate was concentrated to get LDPE-*g*-PS as residue. Grafting efficiency was calculated as follows:

$$\text{grafting efficiency} = \frac{\text{grafted vinyl polymer onto PE}}{\text{polymerized vinyl monomer in PE pellet}}$$

Determination of gel

0.5 g of polymer product obtained as above was extracted for 24 h with xylene by Soxhlet extractor, using a No. 86R filter of Toyo Roshi. What remains in the filter is a gel.

Analysis of polymer compositions

0.1 g of polymer product obtained as above was analysed at 550°C by pyrolysis gas chromatography: column, PEG-20M; carrier gas, N_2; 50 ml min^{-1}; column temp., 80°C.

Tensile test and impact test

The tensile test was done at 50 mm min^{-1} for JIS No. 2 dumbbell of polymer obtained as above. The Izod impact value was determined according to JIS-k-7110.

RESULTS AND DISCUSSION

Block copolymers

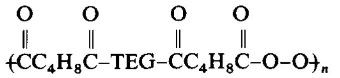
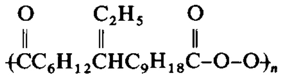
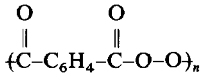
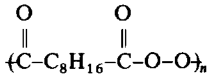
Polymeric peroxide (PPO). The former PPOs were very dangerous and explosive chemicals, being extremely sensitive to heat, shock and friction. Moreover, they were very poorly soluble in solvents and monomers. Therefore, they have never been used in the production of block copolymers.

In order to resolve these defects, we made the molecular weight of the PPO larger than that of the former ones to decrease the active oxygen content, and also introduced ester and ether bonds into the structure of the PPO.

The chemical structures of our PPO and former ones and their active oxygen contents are shown in *Table 1*. Safety data and solubility of PPOs are shown in *Tables 2*, *3* and *4*. Our PPOs are much superior to the former ones in terms of safety and solubility.

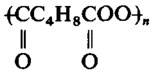
Polymerization with PPO. Polymerization of styrene with ATPPO in bulk is shown in *Figure 1*. The polymerization rate was the same as with lauroyl

Table 1 Active oxygen content of polymeric peroxides

Derivative	PPO	Active oxygen (%)	Prepared by
Adipic acid and TEG[a]	 $\left(\overset{O}{\overset{\Vert}{C}}C_4H_8\overset{O}{\overset{\Vert}{C}}\text{-TEG-}\overset{O}{\overset{\Vert}{C}}C_4H_8\overset{O}{\overset{\Vert}{C}}\text{-O-O}\right)_n$	4.0	Us
C_{19} acid	 $\left(\overset{O}{\overset{\Vert}{C}}C_6H_{12}\overset{C_2H_5}{\overset{\Vert}{C}}HC_9H_{18}\overset{O}{\overset{\Vert}{C}}\text{-O-O}\right)_n$	4.7	Us
Phthalic anhydride	 $\left(\overset{O}{\overset{\Vert}{C}}\text{-}C_6H_4\text{-}\overset{O}{\overset{\Vert}{C}}\text{-O-O}\right)_n$	9.8	Tobolsky
Sebacic acid	 $\left(\overset{O}{\overset{\Vert}{C}}\text{-}C_8H_{16}\text{-}\overset{O}{\overset{\Vert}{C}}\text{-O-O}\right)_n$	8.0	Tsvetkov

[a] TEG, triethylene glycol

Table 2 Safety of polymeric peroxides

PPO	Hammering test: explosion	Exothermic[a] temp. (°C)	Decomposition		
			Temp.[b] (°C)	White smoke	Sound
ATPPO	no	not detectable	not detectable	no	no
 $\left(\underset{\underset{O}{\Vert}}{C}C_4H_8\underset{\underset{O}{\Vert}}{C}OO\right)_n$	yes	74	78	yes	yes

[a] Temperature at which exothermic reaction begins

[b] Temperature at which rapid decomposition takes place

Table 3 Solubility of polymeric peroxides[a]

	Benzene	Toluene	Styrene	Vinyl acetate
ATPPO	14.8	5.4	5.7	5.3
$\{COC_4H_8COOO\}_n$	1.9	1.0	0.5	0.5

[a] At 25°C in 100 g of solvent

Table 4 Solubility of polymeric peroxides[a]

	ATPPO		$\{COC_4H_8COOO\}_n$	
Solvent[b]	25°C	60°C	25°C	60°C
MMA	s.sol	sol	insol	s.sol
2HEMA	s.sol	sol	insol	s.sol
DMF	sol	sol	s.sol	s.sol
Chloroform	sol	sol	insol	s.sol
MEK	s.sol	sol	insol	insol
Methanol	insol	s.sol	insol	insol
Ethanol	insol	s.sol	insol	insol

[a] sol, soluble; s.sol, slightly soluble; insol, insoluble

[b] MMA, methyl methacrylate; 2HEMA, 2-hydroxyethyl methacrylate; DMF, dimethylformamide; MEK, methyl ethyl ketone

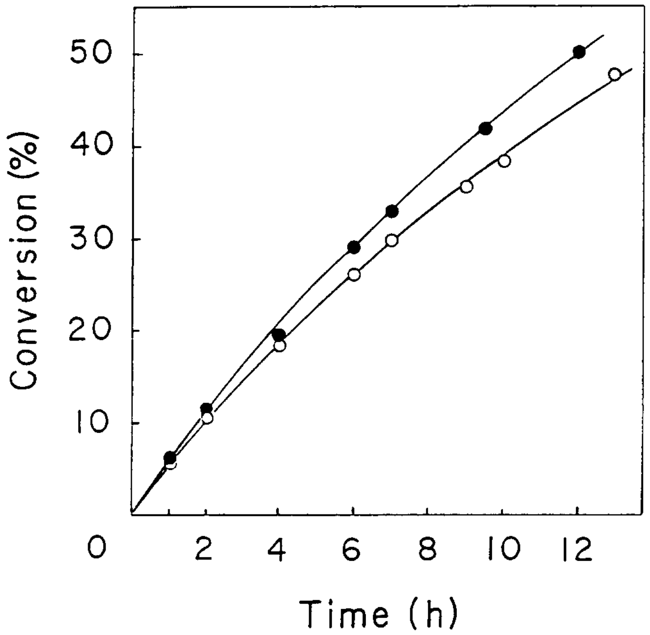


Figure 1 Polymerization of styrene: initiator concentration, 0.01 M; temperature, 70°C; (○) ATPPO, (●) lauroyl peroxide

peroxide but the molecular weight of polystyrene polymerized with ATPPO was much larger than that with lauroyl peroxide, as shown in *Figure 2*. This is due to the formation of PS having O–O bonds in its polymer chain during polymerization (this was assured as mentioned later) and further addition of monomers to the O–O sites. These extra-high-molecular-weight polymers are very useful as polymer modifiers.

Synthesis of block copolymers with PPO. How block copolymers are synthesized with PPO is shown in *Scheme 2* with PPO having three O–O bonds as a model. The first monomer, M_1, is polymerized with PPO, and PM_1 having O–O bonds in its chain is formed. The second monomer, M_2, is polymerized with PM_1 having O–O bonds to give PM_1-*b*-PM_2. PM_1 and PM_2 are by-products.

The polymerization process to get PMMA-*b*-PFA8 (poly(perfluorooctyl acrylate)) with ATPPO is shown in *Figure 3*. The first-step polymerization was almost complete after 6 h, still leaving O–O bonds in the polymerization mixture, and the second monomer was almost 100% polymerized after 7 h.

Formation of polymers having O–O bonds in the first-step polymerization was assured by differential thermal analysis, as shown in *Figure 4*. PMMA having O–O bonds showed an exothermic peak at about 110°C and no such peak was shown in PMMA polymerized with a conventional organic peroxide. This means that PMMA polymerized with PPO has some O–O bonds in its chain.

Tables 5 and *6* show the location and number of O–O bonds in the polymer polymerized with PPO. In order to obtain this information, polymers formed during the first-step polymerization with PPO were thermally destroyed in the presence of hydroquinone, and the molecular weight of polymer was compared before and after destruction. The molecular weights of polymers were almost the same before and after thermal destruction, as shown in *Table 5*. This means that O–O bonds

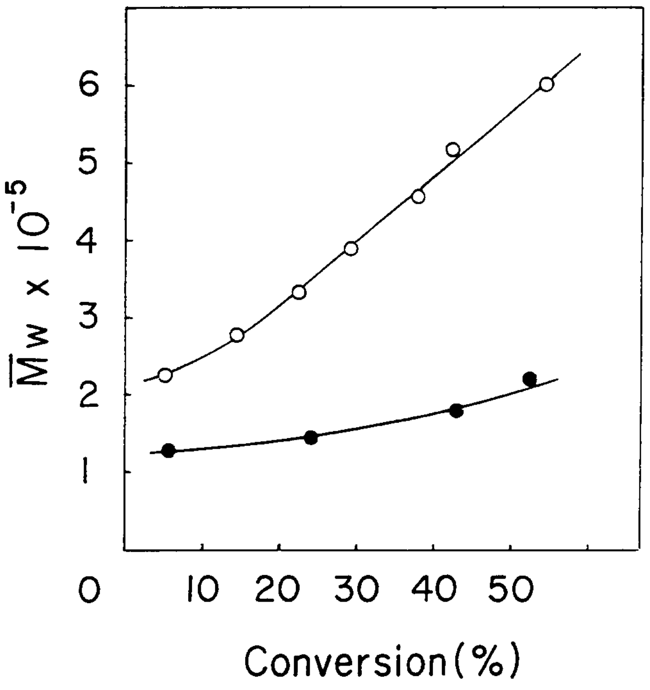
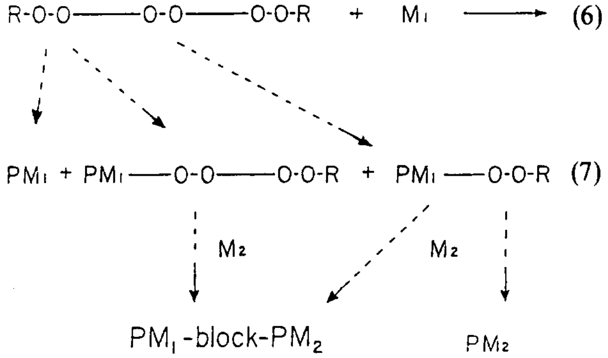


Figure 2 Molecular weight of polystyrene: initiator concentration, 0.01 M; temperature, 70°C; (○) ATPPO, (●) lauroyl peroxide



Scheme 2 Synthetic scheme of block copolymers with polymeric peroxide

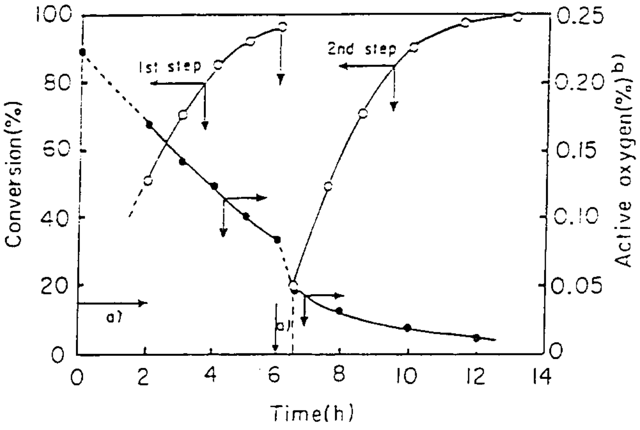


Figure 3 Block copolymerization of MMA and FA8 ($CH_2{=}CHCOOC_8F_{17}$) with ATPPO. First-step polymerization: MMA/ATPPO, 47/6 wt, 70°C. Second-step polymerization: FA8, 47 wt, 70°C. (a) Dropping time. (b) In the polymer solution

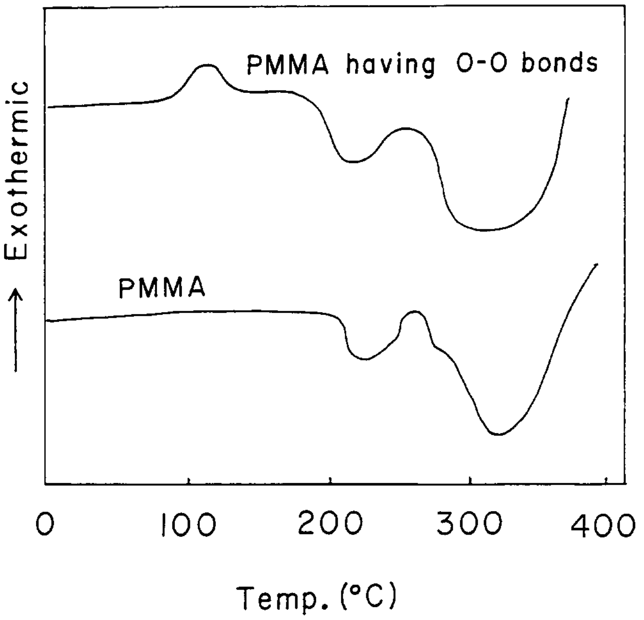


Figure 4 Differential thermal analysis of PMMA having O–O bonds

in the polymers polymerized with PPO are located near the terminals of the polymer chains. The molecular weight after decomposition is a little bit higher than before, and this is due to the fact that some ATPPO remaining in the polymerization system was decomposed to low-molecular-weight chemicals, which are not detectable by g.p.c. *Table 6* shows that the polymer after 4 h polymerization has about two O–O bonds each, and about 1.3 O–O bonds are in the final polymer chains. It was also shown that about 40% of the O–O bonds of the initial ATPPO are included in PMMA and 60% remain in the solution. *Tables 7*, *8* and *9* show the composition and molecular weights of block copolymerization products of MMA/St and VAc/St.

Graft copolymers

The prepared peroxide monomers and their temperatures giving a 10 h half-life are shown in *Table 10*. Copolymers with the peroxide monomers and their temperatures giving a 10 h half-life are shown in *Table 11*. The temperatures giving a 10 h half-life are near 100°C. Therefore, we can keep these O–O bonds without decomposition during polymerization with vinyl monomers, which is run at 60–70°C.

The temperature giving a 10 h half-life of pendant O–O bonds of copolymers with PFPO is about 20°C lower than that of PFPO alone. This is due to the change of type of peroxy bond from secondary to tertiary.

Synthesis results of graft copolymers with three peroxide monomers are shown in *Tables 12*, *13* and *14*. Homopolymers are by-products in the process. Grafting

Table 5 Change in molecular weight by thermal destruction of polymers obtained in the polymerization of MMA with ATPPO

Polymerization time (h)	Conversion of MMA (%)	$\bar{M}_n$	
		Initial	Destroyed
3	70	11 100	12 300
4	85	11 700	12 000
5	96	11 500	12 800

Table 6 Characterization of polymerization products in the first-step polymerization

			Purified PMMA	
Polymerization time (h)	O–O bond[a] remaining (%)	Active oxygen (%)	$\bar{M}_n$	Number of O–O bonds[b]
4	53	0.186	18 100	2.0
5	44	0.136	18 600	1.6
6	37	0.110	18 800	1.3

[a] Undecomposed O–O bond/initial O–O bond (mol/mol)
[b] O–O bond in PMMA/O–O bond in polymer solution (mol/mol)

Table 7 Block polymerization products of MMA and St with ATPPO

	Composition of polymers (%)			
Monomer MMA/St (wt)	PMMA-*b*-PS	PMMA	PS	Block efficiency of St (%)
1/9	34	6	60	33
3/7	48	16	36	49
5/5	68	24	8	83
7/3	72	27	1	99

efficiencies of styrene to PVAc were 42, 64 and 50% respectively, in the ratio of PVAc/St = 1/4, 1/2 and 1/5 (wt) from the calculation with each yield, as shown in *Table 12*. About 50% of styrene reacted with pendant O–O bonds of PVAc to give PVAc-*g*-PS, and 74, 65 and 71% of PVAc converted to PVAc-*g*-PS respectively.

Causes of formation of PVAc homopolymer were considered as follows: some vinyl acetate did not copolymerize with peroxide monomers, or pendant O–O bonds of PVAc decomposed without formation of grafting.

The optimum amount of peroxide monomers was about 5% to monomers to prepare polymers having pendant O–O bonds, as shown in *Table 14*.

*Synthesis of polyolefin-*g*-vinyl polymer*

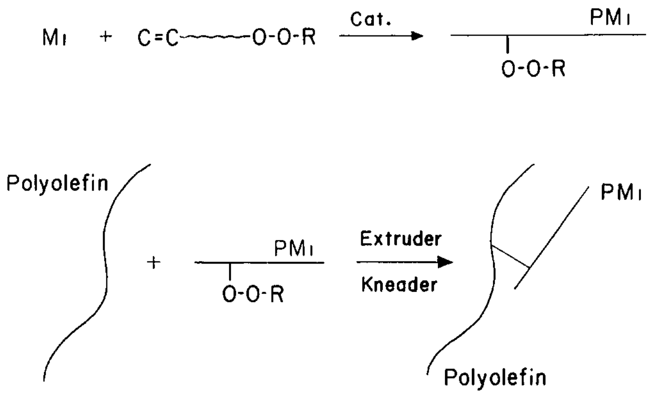
Grafting processes via thermal mixing of polyolefins with vinyl polymers having O–O bonds in extruders were studied (*Scheme 3*). As we have reported before[6], soft polymers (such as PVAc and PBAc) having pendant O–O bonds were grafted onto polyolefins, but hard polymers (such as PS and PMMA) were not grafted onto polyolefins, as shown in *Tables 15* and *16*. These grafting reactions were affected by the probability of O–O bonds meeting polyolefins. Pendant O–O bonds on soft polymers have a high probability of meeting polyolefins during thermal mixing. However, pendant O–O bonds connected to hard polymers have little or zero probability of meeting polyolefins during thermal mixing.

In order to graft hard polymers onto polyolefins, block copolymers of hard polymer segments and soft polymer segments to which pendant O–O groups are connected

Table 8 Characteristics of PMMA-*b*-PS

Monomer MMA/St (wt)	Component[a] of polymer MMA/St (wt)	$\bar{M}_w \times 10^{-4b}$	$[\eta]$ (dl g^{-1})[c]
1/9	7/93	19	1.092
3/7	17/83	50	2.254
5/5	29/71	48	1.915
7/3	55/45	18	1.608

[a] By n.m.r.
[b] Calculated with a universal calibration curve method by g.p.c.
[c] At 30°C in benzene



Scheme 3 Grafting of polymers having pendant O–O bonds onto polyolefins

Table 9 Block polymerization products of vinyl acetate and St with ATPPO

Monomer VAc/St (%)	Composition (%) PVAc-*b*-PS	PVAc	PS	Block efficiency (%)	$\bar{M}_w \times 10^{-4a}$	M_w/M_n[b]
1/9	79.7	3.8	16.5	81.7	14	2.4
5/5	83.8	6.3	9.9	82.0	42	3.7

[a] Calculated with a universal calibration curve
[b] G.p.c.

Table 10 Peroxide monomers prepared

Code	Name and structure	$_{1/2}T_{10h}$[a] (°C)
ALPO	t-Butylperoxyallyl carbonate $CH_2{=}CHCH_2{-}OC(O)OOt{-}Bu$	97
HEPO	t-Butylperoxy-2-methacryloyloxyethyl carbonate $CH_2{=}C(CH_3)COOC_2H_4OC(O)OOt{-}Bu$	104.3
PFPO	t-Butylperoxyisopropyl fumarate $i{-}PrOOCCH{=}CHC(O)OOt{-}Bu$	106.7

[a] Temperature giving a 10 h half-life

Table 11 Copolymers with peroxide monomers

Monomer/peroxide monomer (wt)		Active oxygen (%)	$\bar{M}_w$ ($\times 10^{-3}$)	$_{1/2}T_{10h}$ of pendant O–O bond (°C)
VAc/ALPO	100/3	0.17	400	105
MMA/HEPO	100/5	–	898	104.3
VAc/PFPO	100/1	–	29	79.7
VAc/PFPO	100/3	–	19	79.7
VAc/PFPO	100/5	0.28	20	79.7

Table 12 Preparation of PVAC-*g*-PS with ALPO

PVAc having pendant O–O bonds[a]/St (wt)	Yield (%)	Polymer composition (%)		
		PVAc-*g*-PS	PVAc	PS
1/4	86	50	5	45
1/2	90	64	13	23
1/1	91	59	17	24

[a] Active oxygen = 0.17%

were useful to prepare polyolefin-*g*-hard vinyl polymer (*Scheme 4*), as we reported before[6].

Another important fact is that if pendant O–O bonds are connected to random copolymers of both monomers, grafting reactions do not take place and a lot of gel forms, as shown in *Table 17*. The gel formed was analysed by pyrolysis gas chromatography, and it became clear that the gel did not contain LDPE and was crosslinked vinyl polymers. Pendant O–O bonds on random copolymers could not have sufficient probability of meeting polyolefins and crosslinked by themselves.

Table 13 Preparation of PMMA-*g*-PS with HEPO

PMMA[a] having pendant O–O bonds/St (wt)	Composition (%)				$\bar{M}_w \times 10^{-3}$		
	PMMA-*g*-PS	PMMA	PS	Gel	PMMA-*g*-PS	PMMA	PS
1/9	19	4	61	16	97	160	128
1/1	43	33	23	1	541	137	96

[a] $\bar{M}_w$ by g.p.c. = 9×10^5

Table 14 Preparation[a] of PVAc-*g*-PS with PFPO

PFPO[b] (wt% to VAc)	Composition (%)				$\bar{M}_w \times 10^{-4}$		
	PVAc-*g*-PS	PVAc	PS	Gel	PVAc-*g*-PS	PVAc	PS
1	23	26.9	50	0.1	30	112	200
3	24	22.6	53	0.4	20	67	107
5	52	7.8	39	1.2	20	49	70

[a] VAc/St = 3/7 wt
[b] For the preparation of PVAc having pendant O–O bonds

Table 15 Grafting of vinyl copolymers having pendant O–O bonds onto LDPE

Copolymers (wt%)	Grafting efficiency (%)
VAc/ALPO[a] (97/3)	11
MMA/HEPO (97/3)	0
St/HEPO (97/3)	0

[a] Shown in *Table 10*

Table 16 Grafting of PS-*b*-vinyl copolymers[a] having pendant O–O bonds onto LDPE[b]

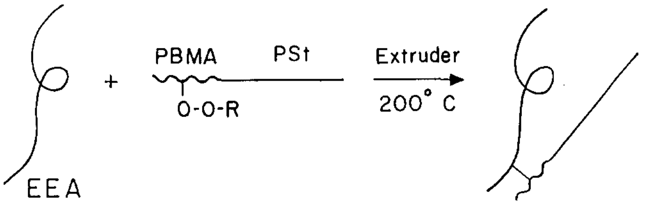
Vinyl polymers having pendant O–O bonds	T_g (°C)	Grafting efficiency (%)
PVAc	32	15
PBMA[c]	20	13
PBAc	−54	12
PMMA	105	0
PS	100	0

[a] PS/vinyl monomer/peroxide monomer = 90/10/0.3 wt
[b] LDPE/block copolymer = 50/50
[c] PBMA, poly(butyl methacrylate)

Table 17 Effect of polymer structures having pendant O–O bonds on grafting[a] onto LDPE

Polymers having pendant O–O bonds (wt)		Grafting efficiency (%)	Gel fraction (%)
P(St-*stat*-HEPO)	97/3	0	61
P(BMA-*stat*-HEPO)	97/3	0	75
PS-*b*-P(BAc-*stat*-HEPO)	90/10/0.3	13	11

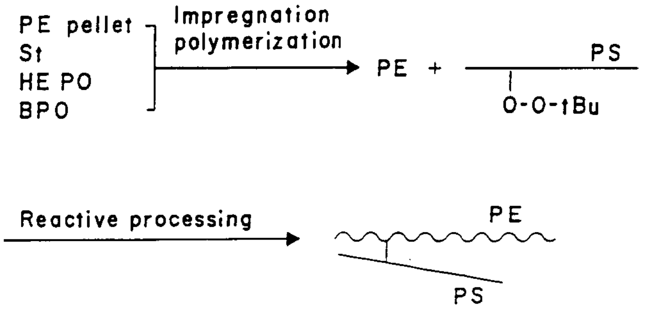
[a] LDPE/polymer (1/1 wt) at 180°C for 10 min in a kneader



Scheme 4 Grafting of block copolymers of soft polymer segments having pendant O–O bonds and hard polymer segments onto polyolefins

Furthermore, we sought good grafting processes with vinyl polymers having pendant O–O bonds onto polyolefins, and found a new grafting process, which is called 'impregnation polymerization'.

Impregnation polymerization. The most important point in grafting of vinyl polymers having pendant O–O bonds onto polyolefins is that O–O bonds have as great a probability as possible of meeting polyolefins during thermal mixing. For this purpose, vinyl monomers, peroxide monomers and organic initiators were impregnated into polyolefin pellets and were polymerized in the pellets at elevated temperature. The polyolefins obtained containing vinyl polymers that have pendant O–O bonds were thermally mixed in extruders in which grafting reactions take place. The synthetic scheme is shown in *Scheme 5* with polyethylene and styrene. The polyolefins used were LDPE, EVA, EEA, EGMA and EPDM and monomers used were styrene, MMA and a mixture of styrene and acrylonitrile (*Table 18*).



Scheme 5 Preparation of PE-*g*-PS, using impregnation polymerization

Table 18 Impregnation polymerizations of vinyl monomers in polyolefins

Polyolefin[a]	Vinyl monomer[b]	Conversion of monomers in polyolefin (%)	Polyolefin/vinyl polymer (wt)
LDPE	St/HEPO[c]	98	70/30
PP	St/HEPO	95	71/29
EVA	St/HEPO	96	70/30
EEA	St/HEPO	97	70/30
EGMA	St/HEPO	96	70/30
EPDM	St/HEPO	83	73/27
EEA	MMA/HEPO	99	70/30
EGMA	St/AN/HEPO[d]	93	71/29

[a] LDPE, low-density polyethylene; PP, polypropylene; EVA, ethylene vinyl acetate; EEA, ethylene ethyl acetate; EGMA, ethylene glycidyl methacrylate; EPDM, ethylene propylene diene monomer
[b] Ratio of polyolefin/vinyl monomer is 7/3 wt
[c] Amount of HEPO is 3 wt% to vinyl monomers
[d] Ratio of St/AN is 7/3 wt

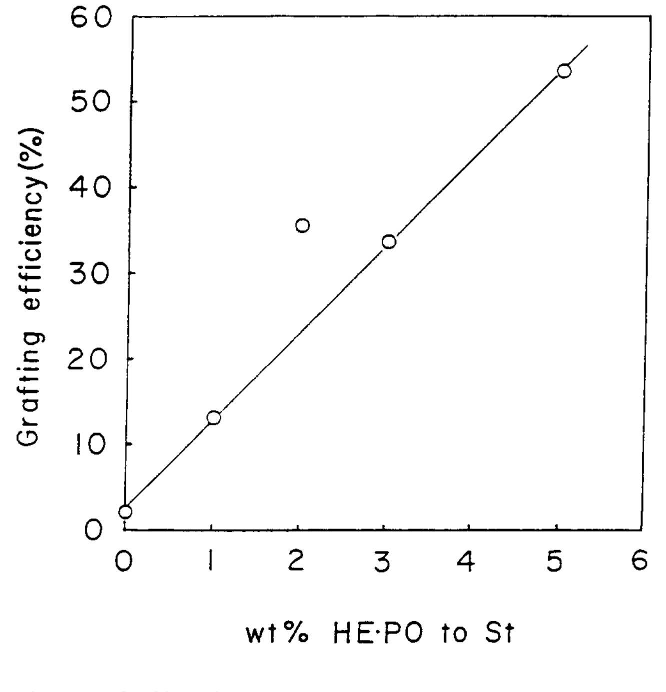


Figure 5 Grafting of poly(St-*stat*-HEPO) onto LDPE. LDPE/poly(St-*stat*-HEPO) = 7/3 wt

Table 19 Grafting efficiency of vinyl polymers onto polyolefins[a]

Polyolefin	Vinyl polymer (monomer ratio, wt)		Grafting efficiency (%)
PP	P(St-*stat*-HEPO)	(100/3)	59
EVA	P(St-*stat*-HEPO)	(100/3)	46
EEA	P(St-*stat*-HEPO)	(100/3)	50
EPDM	P(St-*stat*-HEPO)	(100/3)	56
EGMA	P(St-*stat*-AN-*stat*-HEPO)	(70/30/3)	49

[a] Polyolefin/vinyl polymer = 7/3 wt

Table 20 Grafting of PS onto LDPE[a]

	Grafting with	
Grafting reaction	PS having pendant O–O bonds	PS and DCP
Grafting efficiency (%)	41	5
Gel formation (%)	33	34
Composition of gel, LDPE/PS (wt)	50/50	93/7

[a] LDPE/PS = 7/3 wt

Impregnation polymerization rates were over 90%, except for EPDM, and compositions of obtained impregnation polymerizations were almost the same as the monomer ratio.

Reactive processing. In reactive processing in extruders, the relation between the amount of HEPO used and the grafting efficiency of poly(St-*stat*-HEPO) onto LDPE is shown in *Figure 5*; grafting efficiency increased with amount of HEPO used.

Grafting efficiencies of PS onto various polyolefins are shown in *Table 19*; grafting efficiency was about 50–60%. The composition of the gel formed was determined by pyrolysis gas chromatography, and it was very similar to the composition of the mixture before thermal mixing.

Our new grafting process was compared with the conventional grafting process. Styrene, dicumyl peroxide (DCP) and BPO were impregnated into LDPE and polymerized at elevated temperature, but below the decomposition temperature of dicumyl peroxide. The obtained LDPE containing PS and DCP was thermally mixed in an extruder. The grafting results are compared with those in our process in *Table 20*. The grafting efficiency of the conventional process was extremely low and the gel formed consisted almost entirely of LDPE. It is very clear that our new grafting process is much superior to the conventional process.

CONCLUSIONS

Various kinds of block and graft copolymers that until now have not been very easy to obtain became easily available on an industrial scale, using general polymerization equipment. It is possible by our process to get block and graft copolymers of many kinds of combinations of vinyl polymers. Block and graft copolymers will expand more and more in the application of polymer alloys and blends.

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