

# I. ADDITIVES

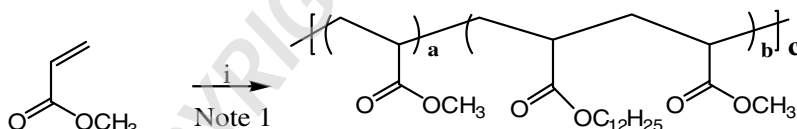
## Title: Controlled Radical Acrylic Copolymer Thickeners

**Author:** S. C. Schmidt et al., US Patent Application 2007-0082827 (April 12, 2007)  
**Assignee:** Arkema, Inc. (Philadelphia, PA)

### SIGNIFICANCE

Di- and triblock polymers have been prepared by nitric oxide mediated polymerization using t-butyl 1-diethylphosphono-2,2-dimethylpropyl nitroxide. Materials prepared from this process are useful as paint thickeners and viscosity index improvers in paint.

### REACTION



### EXPERIMENTAL

#### Preparation of Poly(Methacrylate-*b*-(Dodecyl Methacrylate-*co*-Methacrylate))

A steel resin kettle was charged with t-butyl 1-diethylphosphono-2,2-dimethylpropyl nitroxide (30.0 mmol) and methyl acrylate (6.97 mol) and then heated to 110°C for 3 hours, at which point the reaction had reached 50% conversion. The reaction mixture was cooled to ambient temperature and the  $M_w$  determined to be 12,600 daltons. In a

glass reactor dodecyl methacrylate (159.4 mmol) was heated to 100°C and treated with the previously prepared polymer mixture (25.3 g) and methyl acrylate (25.3 mmol). This mixture was then treated with polymethacrylate (12.65 g) and methyl acrylate (4.83 g) and heated to 100°C to 105°C for several hours. The resultant viscous liquid was diluted with an equal volume of THF and precipitated into cold stirring methanol; the product was isolated having a  $M_w$  of 56,500 daltons and  $M_n$  of 39,600 daltons.

## DERIVATIVES

**TABLE 1. Selected di- and triblock polymers prepared by controlled free radical polymerization using t-butyl 1-diethylphosphono-2,2-dimethylpropyl nitroxide.**

Entry	Polymer* <sup>1</sup>	$M_n$	PDI	Notes
1C	PDDMA-b-PS	28,000	1.6	PS = 16%
1D	PDDMA-b-PS-b-PDDMA	31,600	1.7	PS = 35%
1E	(PDDMA- <i>co</i> -PS)-b-PS-b-(PS- <i>co</i> -PDDMA)	31,600	1.7	PS = 48%
1F	PDDMA-b-PMA-b-PDDMA	23,000	1.5	PMA = 48%
1I	PDDMA-b-PMA-b-PDDMA	76,000	2.0	PMA = 60%

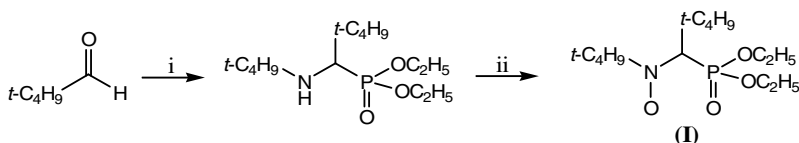
Note: All materials were used as viscosity index improvers in paint.

\*<sup>1</sup>PDDMA = Polydodecyl methacrylate

PMA = Polymethacrylate

## NOTES

1. The nitric oxide mediated polymerization agent t-butyl 1-diethylphosphono-2,2-dimethylpropyl nitroxide, (I), was prepared according to the method of Gillet [1] as illustrated below:



i: t-Butylamine, diethyl phosphate

ii: 3-Chloroperbenzoic acid

2. Random copolymers effective as paint viscosity index improvers were prepared by Shoaf as provided in Table 2.

**TABLE 2. Random copolymers used as viscosity index improvers and thickeners in paints.**

Entry	Polymer <sup>*1</sup>	Monomer Ratio <sup>*2</sup> (wt%)
1	PS- <i>co</i> -PEHA- <i>co</i> -PAAEM- <i>co</i> -PMAA	51.8/22.7/8.0/2.5
5	PS- <i>co</i> -PEHA- <i>co</i> -PAAEM- <i>co</i> -PMAA- <i>co</i> -PAA	45.9/21.1/8.0/1.25/3.75
7	PS- <i>co</i> -PEHA- <i>co</i> -PMAA	63.7/18.9/2.5

\*1 AA = Acrylic acid

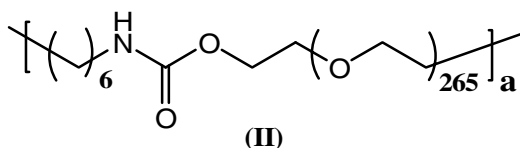
AAEM = Acetoacetoxy ethyl methacrylate

EHA = 2-Hydroxyethyl acrylate

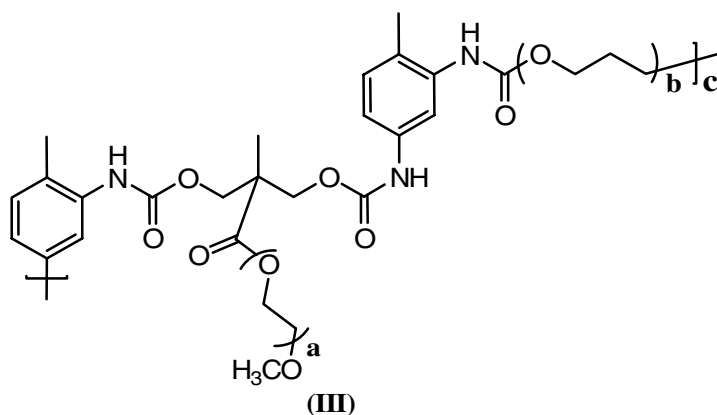
MMA = Methylmethacrylate

\*2 The remainder of the composition consisted of alkyd.

3. Blankenship [3] prepared polyethylene glycol carbamate, (II), as paint thickeners containing poly(ethylene oxide-*b*-propylene oxide-*b*-ethylene oxide) and either 1,6-hexamethylene diisocyanate or 4,4'-methylene bis-(isocyanatocyclohexane). Polycarbamates were also prepared by Bauer [4] using a block polymer initiated by stearyl alcohol and consisting of poly(ethylene oxide-*b*-propylene oxide-*b*-butylene oxide-*b*-dodecene oxide-*b*-tetradecene oxide) coupled with the diisocyanate, Desmodur N<sup>®</sup>.



4. Polycarbamates, (III), prepared by Martin [5] consisting of toluene diisocyanate, methoxypolyethylene glycol, polypropylene glycol, and dihydroxymethyl propanoic acid were also effective as paint thickeners and viscosity index modifiers.



*References*

1. J.-P. Gillet et al., US Patent 6,624,322 (September 23, 2003)
2. G.L. Shoaf et al., US Patent Application 2006-0270769 (November 30, 2006)
3. R.M. Blankenship et al., US Patent Application 2006-0106153 (May 18, 2006)
4. S. Bauer et al., US Patent 7,189,772 (March 13, 2007)
5. E. Martin et al., US Patent 7,144,945 (December 5, 2006)

# Title: Polymer-Filler Coupling Additives

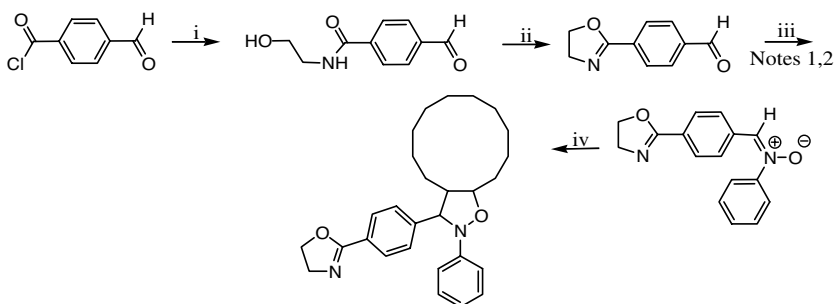
Author: A. Fukushima et al., US Patent 7,186,845 (March 6, 2007)

Assignee: Bridgestone Corporation (Tokyo, JP)

## SIGNIFICANCE

A method for preparing and covalently bonding either 4-(2-oxazoly)-phenyl- or methyl-*N*-phenylnitron to natural rubber in automotive tires is described. The effect has been a 40% overall reduction in tire hysteresis and superior performance over existing polyamine formulations.

## REACTION



Model reaction product

- i: 2-Aminoethanol,  $\text{CCl}_3\text{H}$
- ii: Sulfuric acid, sodium hydroxide,  $\text{CCl}_3\text{H}$
- iii: *N*-Phenyl-hydroxyamine, ethanol
- iv: Cyclododecene

## EXPERIMENTAL

### 1. Preparation of 4-Formyl-*N*-(2-Hydroxyethyl)-Benzamide

A solution of 4-formyl-benzoylchloride (1 eq) in 300 ml of  $\text{CCl}_3\text{H}$  was added dropwise at  $-10^\circ\text{C}$  to a solution of 2-aminoethanol (2 eq), dissolved in 200 ml of  $\text{CCl}_3\text{H}$ , and then stirred at  $25^\circ\text{C}$  for 2 hours. The mixture was filtered, dried, and concentrated, and 17.4 g of product were isolated as a yellow liquid.

### 2. Preparation of 4-(2-Oxazolyl)-Benzaldehyde

The Step 1 product (17.4 g) was treated dropwise with 50 ml of 18 M  $\text{H}_2\text{SO}_4$  and then heated to  $100^\circ\text{C}$  for 60 minutes. The mixture was added dropwise with stirring to 500 ml 20% sodium hydroxide and 500 ml of  $\text{CCl}_3\text{H}$  while the solution temperature was kept below  $15^\circ\text{C}$ . The organic phase was separated and dried, and 6.3 g of product were isolated.

### 3. Preparation of 4-(2-Oxazolyl)-Phenyl-*N*-Phenylnitron

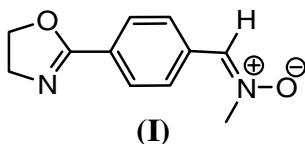
A mixture of the Step 2 product (1 eq) and *N*-phenyl-hydroxyamine (1 eq) was refluxed in 100 ml of ethanol for 30 minutes and then concentrated to 50 ml. The concentrate was treated with 50 ml of water and cooled in a refrigerator to  $5^\circ\text{C}$  overnight. White crystals were obtained; these were isolated by filtration, dried, and 6.7 g of product were isolated.

### 4. Model Reaction: Reactivity of 4-(2-Oxazolyl)-Phenyl-*N*-Phenylnitron with Cyclododecene

In selected amounts the Step 3 product was mixed with 1 ml cyclododecene and then heated to  $171^\circ\text{C}$ . The amount of recoverable Step 3 compound at various time periods during the reaction with cyclododecene was an indication of the reactivity of this product with unsaturated carbon-carbon bonds. Scoping results are provided in Table 1.

## DERIVATIVES

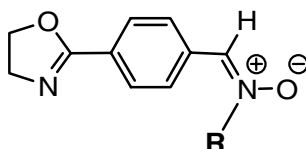
4-(2-Oxazolyl)-phenyl-*N*-methylnitron, (I), was also prepared:



## TESTING

### 1. Reactivities

Reactivities of the Step 3 product and 4-(2-oxazolyl)-phenyl-*N*-methylnitronne, (I), with cyclododecene at 170°C are provided in Table 1.



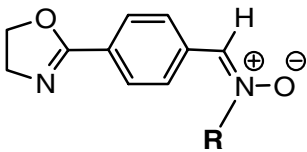
**TABLE 1. Percent incorporation of the Step 3 product and derivative into cyclododecene at 170°C.**

Entry	R	Heating Time @ 170°C (min)	Nitronne Amount (mg)	Amount of Incorporated Experimental Nitronne (%)
2	Phenyl	5	5.52	97
4	Phenyl	15	5.65	100
5	Phenyl	30	5.60	100
7	Methyl	5	4.09	39
9	Methyl	15	3.83	78
10	Methyl	30	4.05	98

Note: No characterization data for either experimental agents or cyclododecene addition products were provided by author.

### 2. Tan $\delta$

The effect of the experimental agents on natural rubber hysteresis was determined by measuring tan  $\delta$  at 5% strain using an ARES-A Rheometer at 50°C and 15 Hz. Testing results are provided in Table 2.

**TABLE 2. Effect of experimental additives on  $\tan \delta$  of natural rubber at various treatment levels.**


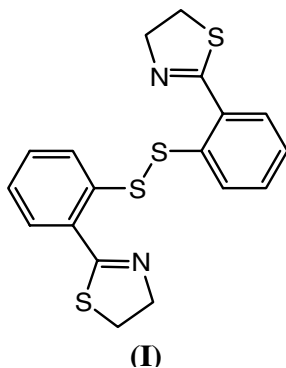
R	Nitronium Dosage (mmol)	Tan $\delta$
Unadditized	—	0.21
Reference <sup>*1</sup>	0.16	0.20
Phenyl	0.2	0.18
Phenyl	0.4	0.16
Phenyl	0.8	0.14
Phenyl	1.6	0.13
Methyl	0.2	0.2
Methyl	0.4	0.19
Methyl	0.8	0.16
Methyl	1.6	0.20

Note: Lower tan  $\delta$  values are preferred.

<sup>\*1</sup>Sumifine<sup>®</sup> 1162 = (*N,N'*-di(2-nitro-2-methyl-propyl)-hexamethylenediamine

## NOTES

1. In a subsequent investigation by the author [1] styrene butadiene rubber functionalized with the Step 3 product was prepared and was effective in lowering tire hysteresis.
2. Bis-[2-2-thiazolyl-phenyl]disulfide, (I), derivatives were also prepared by the author [2] in a subsequent investigation and were effective in reducing tire hysteresis.



3. Polymer nanostrings consisting of block terpolymers of butadiene, styrene, and divinyl-benzene having a  $M_n$  of 46,744 daltons were prepared Wang [3] and used as additives in natural and synthetic automotive tires. The nano strings were then postmodified to enhance tire surface and bulk performance.
4. Parker [4] end-group functionalized poly(1,3-butadiene) polymers with isopropyl hydroxyl-amines to improve the affinity and interaction with carbon black and silica fillers to extend tire lifetime.

### *References*

1. A. Fukushima et al., US Patent Application 2006-0084730 (August 20, 2006)
2. S. C. Schmidt et al., US Patent Application (2007-0161756 (July 12, 2007)
3. X. Wang et al., US Patent 7,179,864 (February 20, 2007)
4. D.K. Parker, US Patent Application 2007-0004869 (January 4, 2007)

