Acetals as Nucleating Agents for Polypropylene

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SYNOPSIS

Nucleating agents increase the impact strength, tensile strength, and tensile elasticity modulus of semicrystalline polymers. Nucleating agents also decrease product cycle times, resulting in a cost savings per product unit. We have synthesized and tested 15 compounds as nucleators for polypropylene. Of these, trinaphthylidene sorbitol, tri(4-methyl-1-naphthylidene)sorbitol, tri-(4-methoxy-1-naphthylidene)sorbitol, and dibenzylidene xylitol are efficient nucleators of polypropylene. Trinaphthylidene sorbitol (tns) has two major diastereomers: The "S" diastereomer yields a faster crystallization rate for polypropylene than does the commercial nucleator dibenzylidene sorbitol (Millad 3905). Crystallization rates are 208 and 88, respectively ($t_{.05}^{-1}$ min^{-1} × 1000). The "R" diastereomer, however, is a poor nucleator and interferes with the nucleating activity of the "S" diastereomer. A 52/48 mixture of diastereomers does not nucleate polypropylene, even at twice the concentration. This is the first time that the importance of stereochemistry has been demonstrated in the nucleating action. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polypropylene is a semicrystalline polymer with a typical molecular weight in the 200,000–600,000 range.[1] Whereas the amorphous portions of polypropylene are in a random coil conformation, the crystalline portions are in a helical conformation.

Polypropylene crystallization begins at crystallization sites. Nucleators increase the number of crystallization sites in a polymer, resulting in an increase in the overall crystallization rate and a decrease in the spherulite size.[2] The enhanced crystallization rate also results in crystallization errors such as intercrystalline links. Intercrystalline links are bridges between and within spherulites generated by one polypropylene chain that has one segment crystallized in one spherulite and another segment crystallized in another spherulite or another part of the same spherulite. Thus, one polypropylene chain can "link" two spherulites together. Nucleators, through intercrystalline links and smaller spherulites, improve the impact strength, tensile elasticity modulus, tensile strength, and clarity of polypropylene. Nucleators also increase crystallization rates that decrease product cycle times because the product requires shorter cooling times.[3]

EXPERIMENTAL

Synthesis of Trinaphthylidene Sorbitol

1-Naphthaldehyde (85.00 g) and D-sorbitol (33.05 g) were combined with water (14.5 mL), dimethylsulfoxide (23 mL), cyclohexane (700 mL), and methane sulfonic acid (2.2 mL) and heated under nitrogen to reflux. Water was removed by distillation. Heating was stopped after water distillation was complete. The product was filtered from the reaction mixture, washed with aqueous sodium carbonate, and purified by a solid/liquid extraction with a tetrahydofuran/aqueous sodium bicarbonate (1.25 : 1) solution to yield 1,3;2,4;5,6-trinaphthylidene sorbitol (tns) (58.4 g). Short reaction times (several hours) yield almost pure "S" tns (Fig. 1). Long reaction times (12 h) yield a mixture of "R" and "S" diastereomers. The assignment of "R" and

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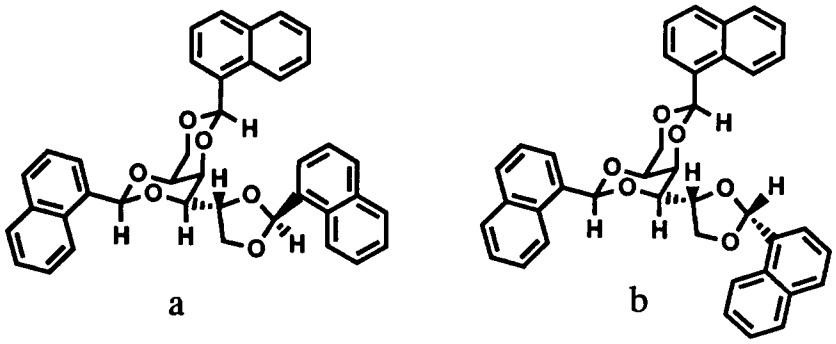

Figure 1 Trinaphthylidene sorbitol (tns): a) "*S*"; (b) "*R*."

"*S*" diastereomers was made by comparison of the NMR spectra with the NMR spectra of tribenzylidene sorbitol.[4] The two diastereomers differ only at the methine carbon attached to the oxygens on carbons 5 and 6 of the sorbitol moiety. This methine carbon can either be in the "*R*" or "*S*" conformation.

Melt-Mixing Procedure

The nucleators (25 mg) were added to powdered, isotactic polypropylene (5 g) and tumble-mixed on a roll mill. This mixture was fed into the reservoir of an Instron capillary rheometer, equilibrated at 180°C for 5 min, and extruded into strands of about 3 mm diameter. The strands were chopped and reextruded under the same conditions in order to provide a better dispersion of the additive in the polymer. Polypropylene alone was also treated similarly to obtain a control sample. The loading of the additives was 0.5% unless otherwise noted. Good mixing is critical in the above procedure.

Differential Scanning Calorimetry

The melt-mixed sample (10 mg) was crimped in an aluminum cup, heated from 0 to 200°C at a rate of 20°C/min, held at 200°C for 5 min, and cooled at a rate of 10°C/min. The crystallization temperature (T_{cc}, °C) was measured on an automated DuPont 9900 DSC operating in an argon atmosphere.

Selected samples were also analyzed by isothermal DSC. In these experiments, the samples were cooled to 135°C and isothermally crystallized at 135°C/4 h following the 200°C/5 min treatment.

Optical Microscopy

The samples crystallized isothermally in the DSC (see above section) were cross sectioned and the photomicrographs prepared in transmitted polarized light.

Dispersant Testing

An example of dispersant testing using 25% stearic acid is as follows: trinaphthylidene sorbitol (0.064 g), stearic acid (0.016%), and mineral oil (3.0 g) were stirred with a spatula in a small glass vial. The vials were sonicated for 10 min and the tns was allowed to settle. After several days, the height of the tns was measured. The settling is a function of time.

Dispersed tns in Polypropylene

An example of dispersed tns using 0.5% soybean oil is as follows: A flask containing tns (11.00 g), soybean oil (0.055 g), acetonitrile (1.9 L), and *n*-pentane (20 mL) was heated until tns dissolved. The flask was removed from heat and covered. At this point, tns recrystallized out of the solution. The solvent was rotary-evaporated to yield 11.06 g of material. The product was mixed with polypropylene and extruded into a plaque mold (see Tables I–IV).

RESULTS AND DISCUSSION

We began our search for a new nucleator for polypropylene by synthesizing and purifying 10 g of each prospective nucleator, blending it with polypropylene, and making polypropylene plaques. Although informative, this method was too labor-intensive. It required running preliminary reactions to obtain the desired product, a scale-up of the best reaction, followed by a purification of 10 g of pure nucleator.

We then developed a method to obtain a crystallization temperature of the various nucleator/polypropylene blends that required less than 100 mg of pure nucleator. This simplified the synthesis

Table I T_{cc} of Various Nucleated Polypropylenes

Compound	% Nucleator	T_{cc} (°C)
Dibenzylidene sorbitol—(Millad 3905)	0.50	123
Trinaphthylidene sorbitol—"*R*"	0.50	124
Tri(4-methyl-1-naphthylidene)-sorbitol	0.50	122
Dibenzylidene xylitol	0.50	120
Tri(4-methoxy-1-naphthylidene)-sorbitol[a]	0.50	119
Tri(4-isopropylbenzylidene)sorbitol	0.50	119
Tribenzylidene mannitol	0.50	117
Naphthylidene sorbitol	0.25	117
Tribenzylidene sorbitol	0.50	116
Benzylidene glycerol	0.50	114
Trinaphthylidene sorbitol—"*S*"	0.50	113
Dinaphthylidene sorbitol	0.50	112
Dibenzylidene ribitol	0.50	111
Triptycene	0.50	111
Benzylidene ethylene glycol	0.50	111
Octylidene sorbitol	0.50	110
Sorbitol tris(benzene boronate)	0.50	107
None—control	0.00	109

The nucleators were dispersed in polypropylene following the melt-mixing procedure. Crystallization temperatures were measured with DSC.

[a] (16/84 "*S*/*R*").

and purification dramatically. In this method, we tumble-mixed the nucleator with powdered polypropylene, extruded the mixture through a capillary rheometer, cut, and re-extruded. We then measured the crystallization temperature of the extrudate with a differential scanning calorimeter.

Fifteen compounds were synthesized, and the crystallization temperatures of the nucleator/polypropylene mixtures were determined using the method described above. Results are listed in Table I.

Table II T_{cc} as a Function of tns Concentration

Tns %	T_{cc} of Polypropylene (°C)
0.00	110
0.10	112
0.25	112 + 124
0.40	123
0.50	124
0.60	121
0.75	121
1.00	119

Trinaphthylidene sorbitol (tns) (87/13 "*S*/*R*") was dispersed in polypropylene using the melt-mixing procedure. The recrystallization temperatures were measured with DSC.

Table III Polypropylene's Crystallization Rate

% (Additive)	Crystallization Rate ($t_{.05}^{-1}$ min^{-1} × 1000)
0.00	15
0.50 (dibenzylidene sorbitol)	88
0.50 (tns)[a]	208

[a] Note that polypropylene's crystallization rate is greatly enhanced by addition of tns (87/13 "*S*/*R*").

Since trinaphthylidene sorbitol (tns) yielded the highest crystallization temperature, we scaled-up the synthesis and purification. Mass spectrometry and nuclear magnetic resonance spectroscopy (NMR, $CDCl_3$) indicated that the large-scale product was > 95% pure. This product was blended with polypropylene and made into polypropylene plaques. The plaques, however, contained agglomerates of tns and had very low crystallization temperatures. The tns was not functioning as a nucleator.

Careful analysis indicated that the large-scale and small-scale products contained different ratios of tns isomers. This fact was not evident in the original NMR data, because trace amounts of acid in the NMR solvent, chloroform-*d*, isomerized the two tns samples to the same isomer ratio. The isomer ratio indicated in the spectra was not indicative of the true isomer ratios of the products. Isomerization was evident even in chloroform-*d* that was run through alumina to remove trace amounts of acid.

The isomer ratio could be readily determined, however, employing NMR with pyridine-*d*5 as the solvent and/or employing reversed-phase high-performance liquid chromatography (HPLC, no chloroform). The structures of the two diastereomers were tentatively assigned after comparison of the NMR spectra with that of the tribenzylidene sorbitol

Table IV The Effect of Isomer Ratio on the T_{cc}

T_{cc} (± 1, °C)	Isomer Ratio ("*S*/*R*")
122	100/0
124	95/5
124	87/13
121	80/20
116	55/45
110	52/48
113	0/100

diasteromers.[4] The two diastereomers differ only at the methine carbon attached to the oxygens on carbons 5 and 6 of the sorbitol moiety. This methine carbon can either be in the "*R*" or "*S*" conformation. The conformations at the other stereocenters remain constant (Figs. 1–3).

A study of the synthetic reaction showed that sorbitol reacts with naphthaldehyde, forming a monoacetal. This monoacetal reacts with an additional naphthaldehyde to form a diacetal. This diacetal quickly reacts to form the triacetal, tns. The "*S*" diastereomer forms first. This "*S*" conformer is the "active" compound. Since acetal formation is a reversible, acid-catalyzed reaction, the triacetal can reverse to the diacetal and monoacetal. As the reaction mixture is further heated, a second diastereomer, "*R*", begins to form.

The "*R*" diastereomer is not a nucleator and interferes with the activity of the first diastereomer. This is not due to a dilution effect of the active form, for when we doubled the percent of nucleator using a 52/48 mixture of isomers, we still did not see nucleation. Therefore, the "*R*" diastereomer not only is ineffective, but it also renders the first diastereomer ineffective in a mixture.

The crystallization temperature of polypropylene containing tns of several isomer ratios is indicated in Table IV. Ratios as low as 85/15 (active/nonactive) are effective in nucleating polypropylene. We are working on a theory to explain our results.[5]

Our third hurdle in this project was overcoming the agglomeration present in the tns/polypropylene plaques. Tns was agglomerated into visible, white specks in the plaques. We can speculate on three causes of this agglomeration: (1) poor melt-mixing in the extruder, (2) tns self-affinity, or (3) tns incompatibility with polypropylene.

Consistent with tns self-affinity, tns forms needlelike crystals that do not separate in mineral oil. The needles stay together in a haystacklike formation. These formations are best visualized with a microscope. In addition, when tns crystals are ground with a mortar and pestle, the needles form thin sheets.

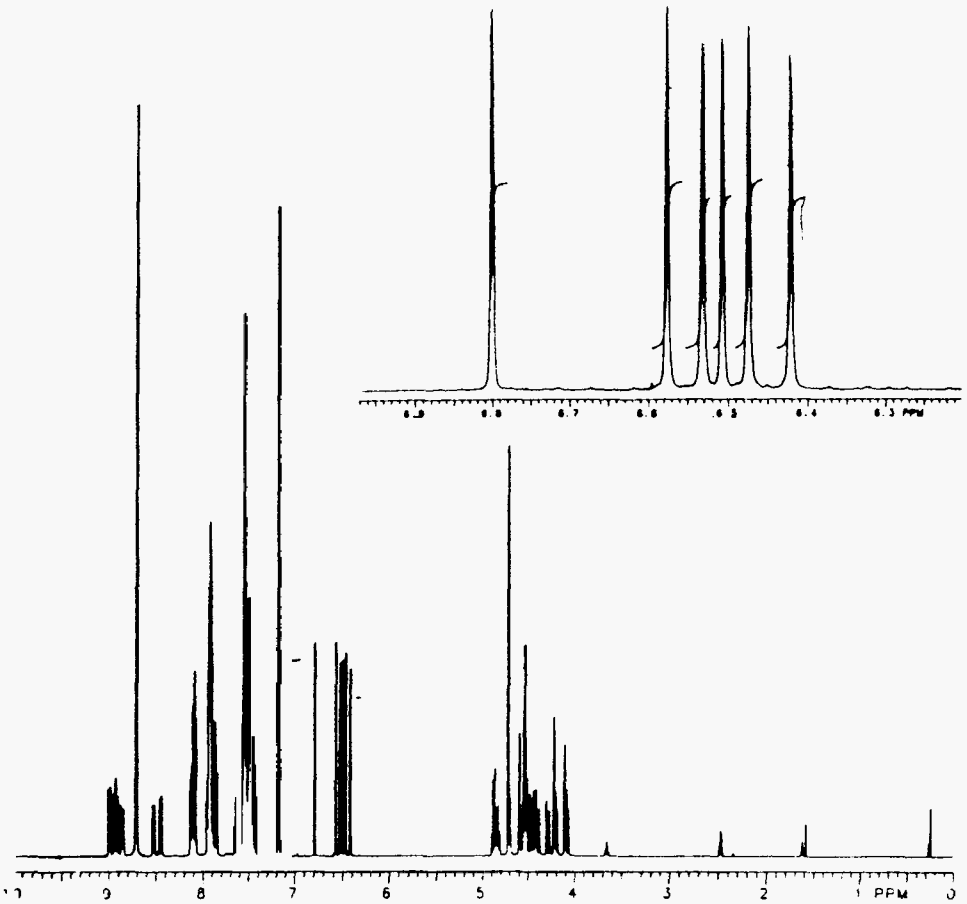

Figure 2 Proton NMR of trinaphthylidene sorbitol (tns) (52/48; "*S*/*R*").

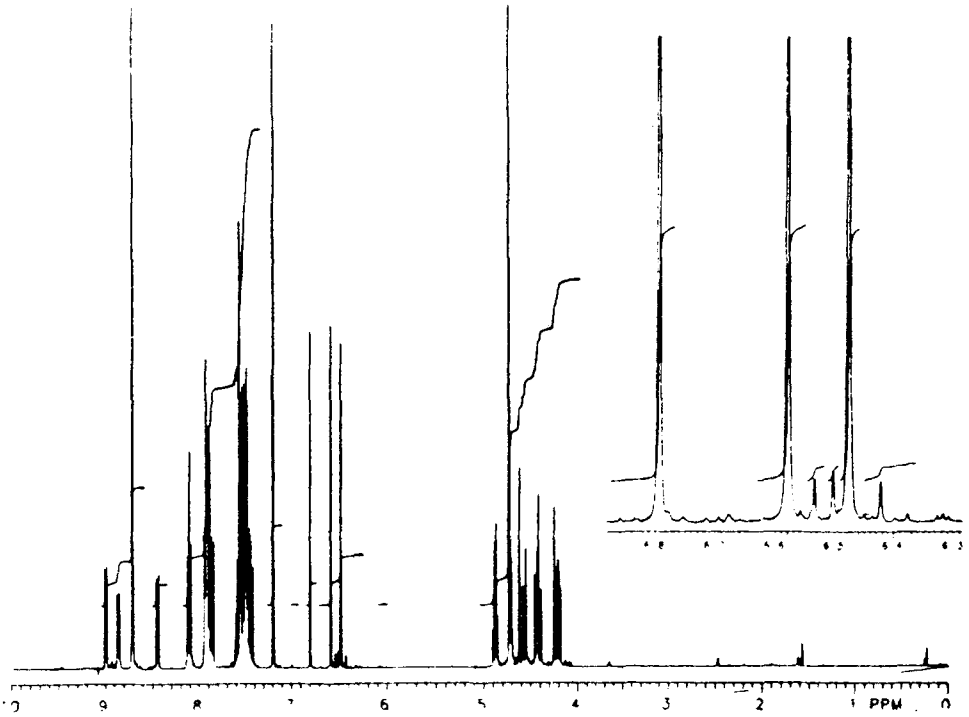

Figure 3 Proton NMR of trinaphthylidene sorbitol (tns) (94/6; "*S*/*R*").

Poor tns dispersion can be addressed by processing changes, hardware changes, or by chemical dispersing agents. For example, one could change the processing conditions to include several extrusions instead of one. One could also change the extruder hardware to include a mixing screw, etc., to improve the mixing in the melt. For the third option, one could add a chemical agent to the tns that would aid in its dispersion in polypropylene. Hardware or processing changes are likely the best way to address dispersion on a commercial process. We opted, however, to study chemical dispersants, because the dispersion tests could be easily done in our laboratories and because many dispersant candidates could be screened within a period of several days.

To screen dispersants for tns in polypropylene, we adapted a method currently used for alumina dispersant testing. In the adapted method, tns, a dispersant candidate, and mineral oil were added to vials. The solutions were mixed well and allowed to settle. We measured the degree of settling vs. time. Dispersant candidates that settled the tns quickly were further evaluated at varying concentrations. From these tests, we determined seven samples that settled tns quickly and five samples that prevented the settling of tns.

We dissolved these dispersants and tns in acetonitrile/pentane, evaporated the solvents, and added the powdered mixture to powdered polypropylene. The resulting mixture was extruded to make plaques. Our results show that, in general, the dispersants that settle tns the fastest work the best as dispersants. This is consistent with the results seen in the testing of dispersants for alumina. Using these dispersants, we improved the tns dispersion and produced a nucleated polymer. The tns/dispersant/polypropylene plaques contained no visible agglomerates. The dispersants that worked best include stearic acid (0.5, 2, 25%); dioctylsulfosuccinate, sodium salt (2%); and polyethylene glycol (0.5%) (Fig. 4). Further studies should be directed toward improving the dispersion of tns through processing and hardware changes to improve the clarity of the polypropylene.

CONCLUSIONS

In conclusion, we synthesized and tested 15 nucleators. We found trinaphthylidene sorbitol (tns), tri(4-methyl-1-naphthylidene)sorbitol, tri-(4-methoxy-1-naphthylidene)sorbitol, and dibenzylidene xylitol to be good nucleators for polypropylene.[6] One diastereomer of tns ("*S*") nucleates polypropylene. A second diastereomer of tns ("*R*") does not nucleate polypropylene and, in fact, interferes with the nucleating ability of the first diastereomer. Twice as much of a 52/48 mixture of diastereomers still

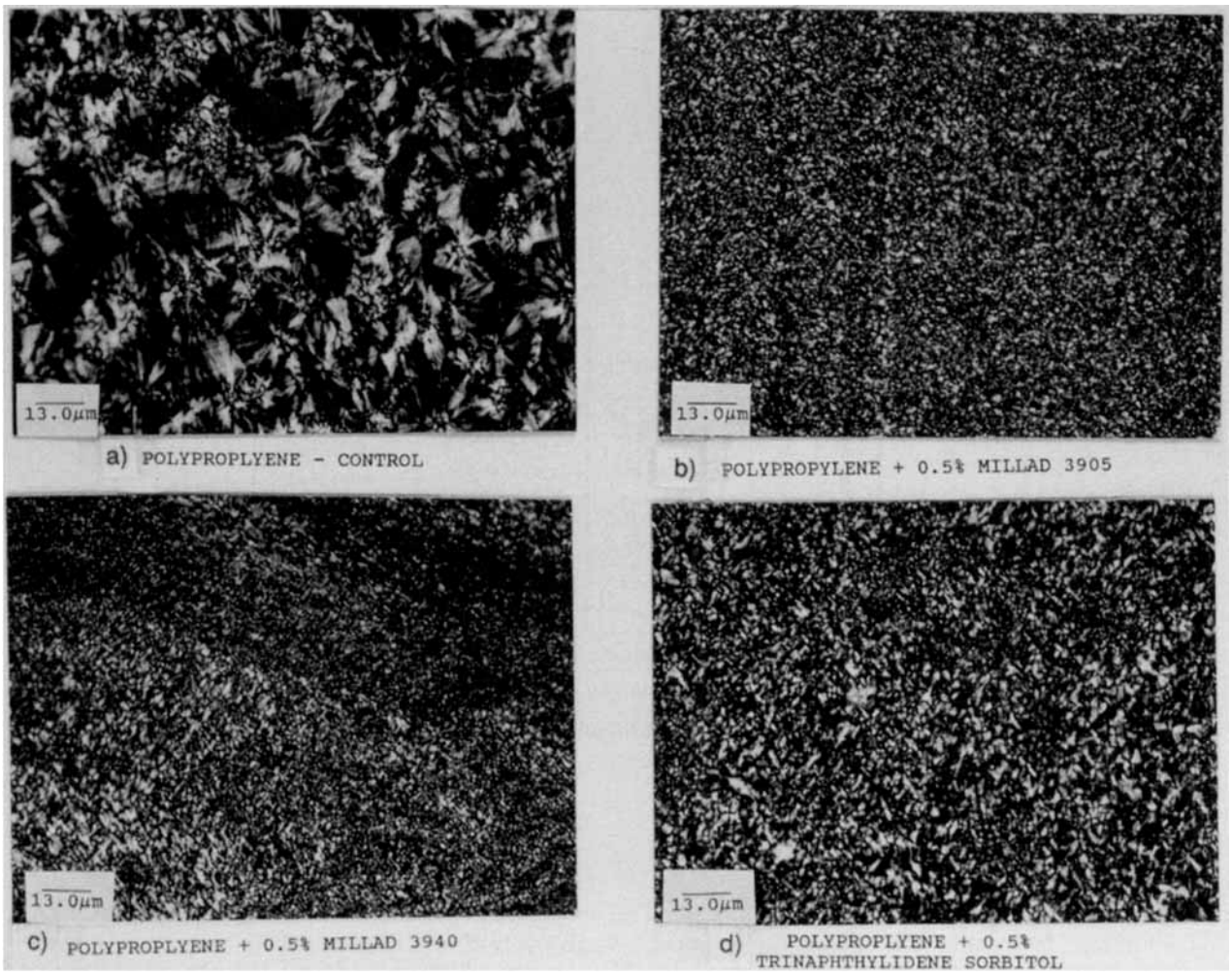

Figure 4 Spherulites. Polypropylene was melted and cooled in a press. Photos were taken under a polarized light: (a) control; (b) dibenzylidene sorbitol (0.5%); (c) di-(*p*-methyl benzylidene)sorbitol (0.5%); (d) trinaphthylidene sorbitol (tns) (0.5%, no dispersant).

does not nucleate polypropylene. In the synthesis of tns, the "*S*" diastereomer forms first. This "*S*" conformer is the active compound. As the reaction mixture is further heated, the inactive "*R*" diastereomer forms.

Dispersants can be used to aid the dispersion of tns in polypropylene. Dispersants candidates were screened with a method adapted from one used for alumina. The dispersants that worked best include stearic acid (0.5, 2, 25%); dioctylsulfosuccinate, sodium salt (2%); and polyethylene glycol (0.5%).

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