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Zwitterions of 1-Poly(oxyethylene)-2-imidazoline Derivatives as Anti-Electrostatic Agent for Polyamide Fiber

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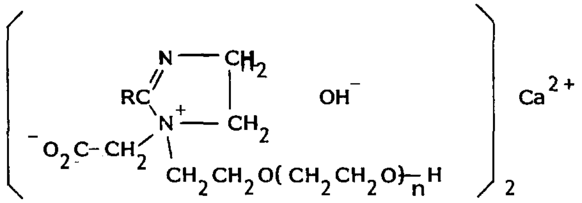
Summary

This paper describes a group of anti-electrostatic agents **1** for polyamide fiber(Nylon 6). Agents **1** are calcium imidazolinium-carboxylates having poly(oxyethylene) chain and long alkyl group($C_{11}H_{23}$ and $C_{17}H_{35}$). Eight derivatives of **1** were prepared by a four-step one-pot synthesis shown in Scheme **1**. Nylon 6 fibers and films containing some of **1** (1.0 and 2.0 wt%) show improved anti-electrostatic property. The performance of **1** was increased by the increase of the length of poly(oxyethylene)chain.

Introduction

Anti-electrostatic modification of synthetic fibers is still one of important unsolved problems in synthetic fiber technology(EL-SHAHED et al 1981). This paper describes a group of anti-electrostatic agents for polyamide(Nylon 6), which are calcium salts of imidazolinium carboxylic acids **1** having poly(oxyethylene) chain and long alkyl group. They were prepared by a four-stage one-pot synthesis.



1a(n); R=$C_{11}H_{23}$ n=0. 10, 30, 50

1b(n); R=$C_{17}H_{35}$ n=0. 10. 30, 50

These agents are characterized by the three attaching groups, i.e., (1) a long alkyl group R which is the so-called "anchor component" having high compatibility with polyamide, (2) a poly(oxyethylene) chain and (3) a zwitterionic group. The poly(oxyethylene) chain and zwitterionic group possess strong affinity toward moisture (water) which is responsible for anti-electrostatic property. In addition, they are salts of Ca, whose decreased solubilities are advantageous for attaining the resistance toward washing.

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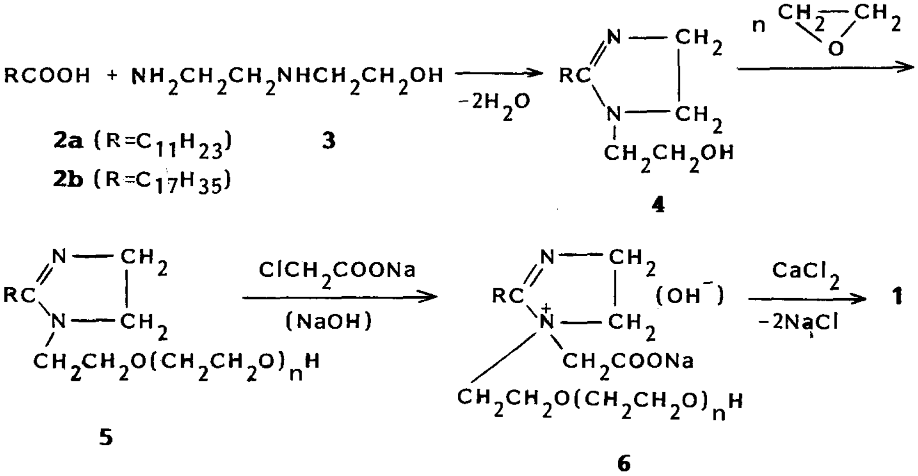
Anti-electrostatic property of Nylon 6 containing **1** (1.0 and 2.0 wt%) was examined in the forms of fiber and film.

Experimental

Preparation of Calcium Salt of 1-Carboxymethyl-1-poly(oxyethylene)-2-undecyl-2-imidazolinium hydroxide **1a**. A series of the agents **1** were prepared in a one-pot synthesis according to a series of reactions shown in Scheme I.

Scheme I



A typical example is as follows.

In a four-neck 500 ml flask equipped with a condenser, a vacuum stirrer, a thermomether, and a two-way stop-cock was heated an equimolar mixture of lauric acid (**2a**, 20g) and 2-(2-aminoethylamino)ethanol (**3**, 10.5g) at 120°C under nitrogen. After 10 hr the by-product water was thoroughly removed *in vacuo* to give **4** almost quantitatively. Then, the two-way stop-cock was replaced by a gas-inlet tube, through which ethylene oxide was introduced into the reaction mixture. The condenser was cooled with ice water. In the flask containing **4** (unisolated) was added 0.1 mol % amount of KOH (0.011g), and gaseous ethylene oxide was introduced at a rate of ca. 44 g/hr with vigorous stirring at 120°C. The average degree of polymerization, i.e., the average number of oxyethylene unit per molecule, reached 50 after 12 hr. After stirring at 120°C for additional one hour, a pale yellow polymeric material **5** was obtained. In the next step, the gas-inlet tube was replaced by a stopper, and 12g of sodium chloroacetate in 100 ml of water was added to **5**. Then the mixture was maintained at 80°C for 12 hr at pH 10 with contineous addition of aqueous NaOH. Then, an aqueous solution (30 ml) of 5.6g of $CaCl_2$ was added to the cooled reaction mixture to deposit the final product **1a** as a viscous oil. The product **1a** was washed twice with a small amount of water, and dried *in vacuo*. The total yield was 83% on the basis of the used amount of lauric acid. The fundamental structure of **1a** was established by the following data: ^1H NMR($CDCl_3$) δ 0.7-1.7 (broad $C_{11}H_{23}$), 3.0-3.3 (m, $N-CH_2-C$), 3.4-3.8 (m, $C-CH_2-\overset{+}{N}-CH_2-C$), 3.8 (s, OH) 3.95 (s, CH_2CO_2), 4.5 (s, OCH_2CH_2O); IR (film) 3400 (ν_{O-H}) 2910, 2830, 1620 ($\nu_{C=N}$), 1590 ($\nu_{CO_2^-}$), 1400, 1070 (ν_{C-O}). From the integral ratio of the NMR signal at δ4.5 to that at 0.7-1.7 the number of oxyethylene units (degree of polymerization) was calculated at 50. The elemental analyses data (Table I) were in good agreement with the calculated values (Table I). Other agents of **1** as well as those having no poly(oxyethylene) chain (n=0) (MARUMO 1965) were prepared by similar ways. Synthetic and analytical results are shown in Table I.

Blend Spinning and Film Molding. To Nylon 6 chips (relative viscosity of 2.64 in 96% H_2SO_4, provided by Unitica Co. Ltd. (Japan)), **1** was added, and the mixture was well blended at 60°C, which was then dried throughly at 100°C *in vacuo*. Melt spinning was carried out at 260°C with a single-screw (25 mmø) extruder equipped with a spinneret having 30 holes of 0.9 mmø. The as-spun filaments thus obtained were submitted to a 4.5-fold cold-drawing. Using the cuttings of the above as-spun filaments, film samples with 0.1 mm thickness were molded by a hot-press (240°C, 30 atm).

Measurements of Anti-electrostatic Property. Three conventional methods were employed at 20°C under 45% relative humidity (RH). The first method was the accumulate static electricity (ASE) of film, which was measured by a Rotary Satic Tester (Koa-Shokai Co., Japan). The electrostatic voltage by surface friction was recorded when the sample film was rubbed by a cotton fabric rotating at 750 rpm under 200 g/cm^2 load for 30 sec. The second method was the surface area resistivity (Rs) of film, which was measured by using an instrument of Denpa Kogyo Co. (Japan) (Type 2010 (SM-10)). The third one was the half-life time ($t_{1/2}$) of leakage of electrostatic charge (SHASOUA 1958) of filament. An instrument having a trade name of "Static Honest Meter" (s-4104 shishido-shokai Co., Japan) was used.

Washings. Washing test was made in a 0.2% soap solution at 80°C using a standard launder meter (Suga Test Instrument Co., Japan). One washing cycle was 30 minutes.

Results and Discussion

Spinnability. Nylon 6 blended with **1** was melt spun. The draft ratio (melt draw ratio) at spinning (FURUKAWA et al, 1971) of Nylon 6 remained unchanged by blending with **1**. The strength of filaments of the blends after drawing was in the range of 4.7-5.0 g/denier, while that of a control sample of Nylon 6 was 5.9 g/denier. The films molded by hot-press were almost transparent and slightly yellow. The surface showed no sticky touch. All these results are taken to show that agents **1** are highly compatible with Nylon 6.

Anti-electrostatic Property. The results of the three measurements of anti-electrostatic property are shown in Table II.

Table I. Syntheses of **1**

	Yields(%)	n[a)]	mp. (°C)	Elemental Analyses			
				Ca^{2+} Contents(%)		N Contents(%)	
				Calcd	Found	Calcd	Found
1a(0)	95	0.0	50	5.51	5.50	7.71	7.70
(10)	89	10.1	28	2.49	2.44	3.49	3.49
(30)	91	30.3	28	1.19	1.09	1.66	1.65
(50)	83	50.0	28	0.78	0.78	1.09	1.03
1b(0)	97	0.0	78-80	4.47	4.45	6.26	6.25
(10)	89	10.2	40-42	2.25	2.27	3.16	3.14
(30)	88	31.6	liq.	1.13	1.13	1.58	1.56
(50)	80	52.3	liq.	0.76	0.77	1.06	1.05

a) Calculated by ^{1}H NMR.

Table II. Anti-electrostatic Property of Nylon 6 Containing **1** (20°C, 45% RH)

Agents	1.0 wt%			2.0 wt%		
	ASE[a] (Volts)	Rs[b] (Ω)	$t_{1/2}$[c] (sec)	ASE[a] (Volts)	Rs[b] (Ω)	$t_{1/2}$[c] (sec)
Blank[d]	5000	4.0×10^{13}	>50	5000	4.0×10^{13}	>50
1a(0)	1250	5.5×10^{12}	8.0	1000	3.2×10^{12}	5.5
(10)	1000	8.0×10^{11}	5.2	880	5.5×10^{11}	4.0
(30)	700	2.5×10^{11}	4.8	540	8.4×10^{10}	2.8
(50)	420	7.0×10^{10}	2.0	300	3.5×10^{10}	2.0
1b(0)	1480	7.6×10^{12}	8.0	1170	2.5×10^{12}	5.5
(10)	1200	2.5×10^{12}	6.7	980	8.8×10^{11}	2.8
(30)	600	5.5×10^{11}	5.0	600	6.5×10^{10}	2.2
(50)	380	6.4×10^{10}	3.2	320	5.0×10^{10}	2.2

a) Accumulate static electricity of film.
b) Surface area resistivity of film.
c) Half-life time of leakage of electrostatic charge of filaments.
d) Unblended Nylon 6.

It is clearly shown that **1** reduces both ASE and Rs of film. The $t_{1/2}$ value of filament was also much decreased.

On the basis of these results, the following general conclusions are given. (1) The performance of **1** was increased as the length of poly(oxyethylene) chain was increased. Satisfactory results were obtained with **1a,b(50)**, i.e., the agents having the degree of polymerization of poly(oxyethylene) chain of 50. (2) The increase of the amount of **1** from 1.0 to 2.0 wt% showed only a slight improvement. (3) The difference of the effect of alkyl group between $C_{11}H_{23}$ and $C_{17}H_{35}$ was not observed. However, when R was smaller than C_8H_{17}, the derivatives became incompatible with Nylon 6. The corresponding Mg salts of **1** were prepared in a similar way ($MgCl_2$ instead of $CaCl_2$ was used in the final reaction of synthesis). The performance of anti-electrostatic property of Mg analogues were quite similar to that of Ca agents.

Previously, a poly(oxyethylene) derivative such as **7** have been reported (STEIGER 1958) as an anti-electrostatic agent. However, the performance was not satisfactory. Thus, the present study has shown that the combination of poly(oxyethylene) chain and a zwitterionic group is very effective.

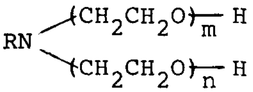


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Table III shows the change of $t_{1/2}$ of the Nylon 6 filament containing **1a** or **1b** (1.0 wt%) by repeated laundering. It can be seen that anti-electrostaitic property is retained after many washing cycles. This wash-resistance may be ascribed to the decreased solubility of Ca salts. Thus, permanent antistatic modification of Nylon 6 fiber has been attained by a small amount of **1**.

Table III. Change in Half-Life Times of Blend Filament of Nylon 6 with Launderings (20°C, 45% RH)

Agents[a)]	Washing Cycles[b)]			
	0	10	20	30
1a(10)	5.2sec	5.0sec	5.2sec	5.2sec
(30)	4.8	4.8	5.2	5.5
(50)	2.0	2.5	2.5	3.0
1b(10)	6.7	6.5	6.5	7.0
(30)	5.0	5.3	5.5	5.5
(50)	3.2	3.2	3.2	3.0

a) 1.0 wt%.

b) By 0.2% soap solution at 80°C. One cycle is for 30 min.

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