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A New Catalyst System for the Aldol Type Condensation of Silyl Enol Ethers and Ketene Silyl Acetals

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The aldol reaction is one of the most fundamental and important carbon-carbon bond formation reaction in organic synthesis. In 1973, the reaction of carbonyl compounds with silyl enol ether promoted by Lewis acid such as $TiCl_4$ was reported for the first time[1]. Over the years, so much effort has been devoted to the development of catalysts which efficiently promote the coupling reaction of carbonyl compounds with silyl carbon nucleophiles that various catalysts were developed for example, trityl cation[2], fluoride ion[3], $BiCl_3$[4], phosphonium salts[5], and various lanthanide salts[6].

In the course of our investigation to explore new catalyst, a novel catalyst system, TMSCl-$InCl_3$, was developed for the reaction of O-trimethylsilylmonothio acetals with triethyl silane and some silyl carbon nucleophiles. But, this catalyst was not so effective for the reaction of carbonyl compounds with silyl carbon nucleophiles[7]. Therefore it was necessary to develop more effective catalyst for the aldol type reactions.

We screened some combination of weak Lewis acids ($InCl_3$, $SnCl_4$, $ZrCl_4$, $SbCl_3$, and $SiCl_4$) and metal salts ($AgClO_4$, LiOTf, AgOTf and $AgSbF_6$) in the reaction of benzaldehyde and 1-trimethylsilyloxy-1-cyclohexene. From this results, the combined use of $InCl_3$ and $AgClO_4$ is most effective for coupling reaction than any other combinations. Although $InCl_3$ itself has a poor activity as promoter, the combined use of $InCl_3$ with the equimolar amount of $AgClO_4$ gave rise to the impressively rapid and clean reaction. Until now, some catalyst system, $TrClO_4$[2], and Cp_2MCl_2-$AgClO_4$[8] (M=Ti, Zr, Hf) were used in the aldol reaction or glycosidation reactions. But, as far as we know, $InCl_3$-$AgClO_4$ catalyst system was used in the aldol reaction by us for the first time.

Reactions of benzaldehyde and 3-phenylpropanol with some silyl enol ethers and ketene silyl acetals in the presence of $InCl_3$-$AgClO_4$ catalyst system (10 mol%) are demonstrated in Table 1.

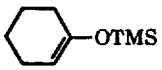
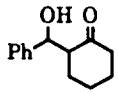
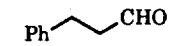
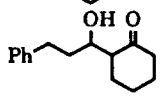
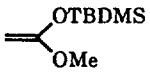
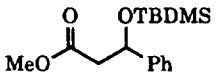
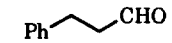
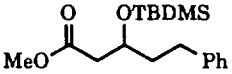
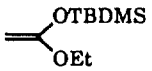
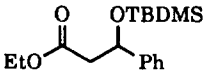
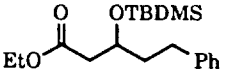
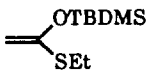
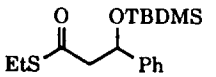
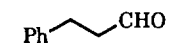
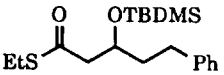
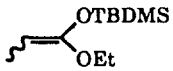
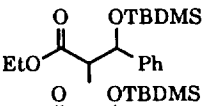
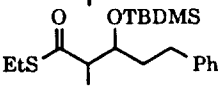
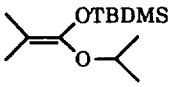
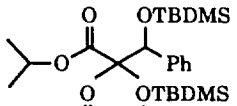
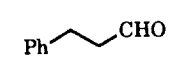
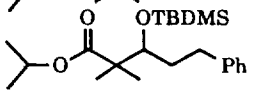
In all cases, the reactions proceeded smoothly at low temperature and the corresponding aldol adducts were obtained in fairly good yields.

In conclusion, the combination of $InCl_3$-$AgClO_4$ is shown to be an effective catalyst for the aldol type carbon-carbon bond forming reaction of aldehydes with various silyl nucleophiles. The application of this catalyst to the other reactions are underway.

Typical procedure: Indium (III) chloride (0.03 mmol) was placed in a 30 m*l* flask and dried *in vacuo* by heating for

Table 1. The Reaction of Aldehyde with Some Silyl Nucleophiles

$$\text{R-CHO} + \text{Nucleophile} \xrightarrow[CH_2Cl_2]{InCl_3\text{-}AgClO_4(10\ mol\%)} \text{product}$$

Entry	Nucleophile	Aldehyde	Product	Temp (℃)	Time (hr)	Yield (%)[a]
1		Ph–CHO		−23	0.5	95
				−23	3	58
2		Ph–CHO		−78	2	96
				−78	4	83
3		Ph–CHO		−78	1.5	93
				−78	6	76
4		Ph–CHO		−78	6	94
				−78	6	74
5		Ph–CHO		−78	1	92
				−78	4	84
6		Ph–CHO		−78	1	97
				−78	7	31

[a] Isolated yield

30 min. Anhydrous $AgClO_4$ (0.03 mmol) and dichloromethane (2 m*l*) were added at 0℃ and stirred for 30 min at room temperature. Reaction mixture was cooled down to −78℃. Benzaldehyde (0.3 mmol) in dichloromethane (2 m*l*) and silyl nucleophile (0.36 mmol) in dichloromethane (2 m*l*) were dropwise successively. After being stirred at that temperature for the given time, the reaction mixture was quenched with saturated sodium bicarbonate solution. The aqueous layer was extracted with dichloromethane (10 m*l*×3) and combined organic layer was washed with brine and dried with sodium sulfate. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel to yield the corresponding adduct.

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Thermally Stable Polymaleimide and Poly[maleimide-*co*-(methyl methacrylate)] Containing N-(4-Nitrophenyl)-L-prolinol Units for Second-order Nonlinear Optics

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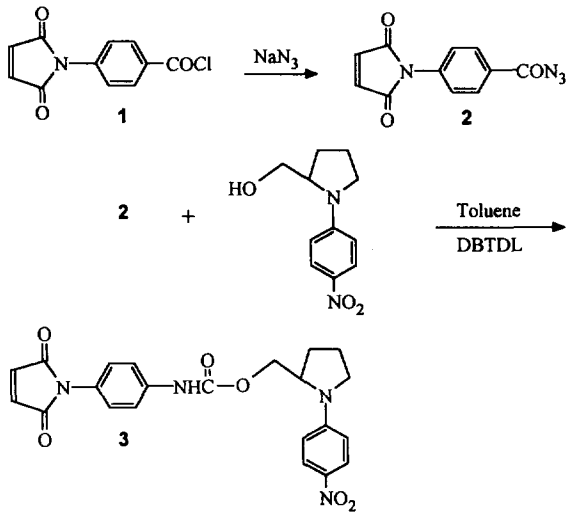
Side chain polymers with nonlinear optical properties have been intensively studied in recent years as potential candidates for application in electro-optic (EO) and photonic devices.[1-3] Ease of processability, high damage threshold, fast response, and large nonlinear optical (NLO) coefficients are the advantages to utilize them in NLO devices such as frequency doubler, light modulators, and logic gates. A number of new polymers and the related fabrication technology to realize the practical NLO devices have been developed so far. However, the fast relaxation of the poled dipolar alignment of the NLO chromophores is still a problem with these second-order NLO polymers and recent research efforts are more concentrated on the enhancement of the thermal stability.

In this work, we prepared N-phenyl maleimide coupled with N-(4-nitrophenyl)-L-prolinol (NPP) through a urethane linkage as a monomer (**3**). Monomer **3** was polymerized and copolymerized with methylmethacrylate (MMA). The polymers of N-phenyl maleimide and its derivatives have been known to exhibit high glass transition temperatures (T_g) due to the rigid imide rings in the backbones.[4,5] In addition to their inherent backbone rigidity, the polymers of monomer **3** possess urethane bonds, which would promote interactions between the polymer chains or the side chain chromophores through inter- or intramolecular hydrogen bondings, and therefore were expected to show a great enhancement of thermal stability of EO activity.

This synthesis of monomer **3** was carried out according to Scheme 1. Compound **1** was prepared by following the procedures in the literature.[6] To a solution of compound **1** (2.08 g, 8.8 mmol) in methylene chloride (35 mL) was added dropwise a solution of sodium azide (0.72 g, 10 mmol) in



Scheme 1.

water (25 mL) at 0℃. After stirring for 4h at the same temperature, the solution was washed with ice water three times and then dried over anhydrous $MgSO_4$. After filtration and evaporation, the product was isolated by column chromatography on silica gel (methylene chloride) to give N-(4-azidocarbonylphenyl)maleimide (**2**), mp. 120-121℃ (43% yield).[7] The azide of the acid is known to decompose thermally to the corresponding isocyanato compound. A solution of compound **2** (5 g, 20.6 mmol) and NPP (4 g, 18.0 mmol) in toluene (150 mL) was refluxed for 48h in the presence of dibutyltin dilaurate (DBTDL) (0.1 mL). In the reaction, the isocyanato compound formed was not isolated and subjected to react *in situ* with NPP. The precipitates were collected by filtration and purified by recrystallization from methanol to yield monomer **3**, mp 201-202℃ (46% yield).[7]

A mixture of monomer **3** (0.2 g, 0.5 mmol) and AIBN (1.6 mg) in N,N-dimethylformamide (DMF) (0.35 mL) was charged into a polymerization tube (5 mL). After freeze-thaw treatments under nitrogen, the tube was sealed. The polymerization was carried out at 80℃ for 24h. The resulting polymer was isolated by precipitation into methylene chloride and purified by reprecipitation from DMF into methylene chloride twice (76% yield). The copolymer was obtained in a similar manner. From monomer **3** (0.2 g, 0.46 mmol) and MMA (0.05 mL, 0.46 mmol) was obtained 0.12 g of the polymer (48% yield). The mole ratio of MMA units to maleimide units in the copolymer was determined to be 65 : 35 by ^{1}H-NMR spectroscopy.[8]

Intrinsic viscosities of the homopolymer and the copolymer were measured in DMF at 30℃ to be 0.14 and 0.20 dL/g, respectively.

DSC thermograms were recorded under nitrogen atmosphere in order to investigate the glass transition temperature (T_g) of each polymer. In the case of the copolymer, very weak transition was observed around 160-163℃. The homopolymer did not show any distinctive transition below 250℃.

The filtered polymer solutions in dimethylformamide were spincoated at 1500 rpm onto indium tin oxide glass and dried overnight in a vacuum oven to give optically transparent films. The films were poled using the corona poling technique in a wire-plane geometry.[9,10] During poling, the polymer films