*Catalysis Letters Vol. 110, Nos. 1–2, August 2006 (© 2006)*
DOI: 10.1007/s10562-006-0091-1

# A new catalytic transesterification for the synthesis of *N*, *N*-dimethylaminoethyl acrylate with organotin catalyst

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Received 19 August 2005; accepted 11 April 2006

A new transesterification method for preparing *N*, *N*-dimethylaminoethyl acrylate (DMAEA) from methyl acrylate (MA) and dimethylaminoethanol (DMAE) was carried out in the presence of organotin catalyst. Among the catalysts examined, $(C_8H_{17})_2Sn(OCOC_{11}H_{23})_2$(TD) is the most active one for the reaction. The products were characterized by gas chromatography, IR spectroscopy, NMR spectroscopy and Mass spectroscopy. The effects of various reaction conditions such as the different catalysts, the reactants ratio, the amount of catalyst, the reaction time on the DMAE conversion, the selectivity to DMAEA and the DMAEA yield were investigated. Experimental results indicated that the sort of catalyst is vital to improving DMAEA yield. The reactants ratio could effect on the DMAE conversion, the selectivity to DMAEA and the DMAEA yield. The 96.28% conversion of DMAE was obtained over catalyst TD, the yield of DMAEA could reach 94.65%, the selectivity is 98.68%. A possible catalytic mechanism of transesterification of DMAE and MA with organotin catalysts was also presumed.

**KEY WORDS:** catalytic transesterification; *N*, *N*-dimethylaminoethylacrylate; organotin catalysts.

## 1. Introduction

*N*, *N*-Dimethylaminoethyl acrylate (DMAEA) is the most widely used in amino-containing (meth)acrylic monomer, which has non-toxicity and high reactivity for polymerization and modification; its derivatives comprise a novel class of water-soluble polymers, which have potential applications in wastewater treatment and sludge dewatering, in oil extraction and in paper production [1–3]. Water-soluble cationic polyelectrolytes based on aminoalkyl esters of (meth)acrylic acids and their derivatives, tertiary and quaternary salts, attract considerable interest, which is due to the possibility of widely varying their chemical nature and physicochemical characteristics and, on the other hand, to their wide use in various branches of national economy, industry, technology and medicine [2,4].

The most used procedure of (meth)acrylic esters production is transesterification in the presence of catalyst. Various catalysts currently have been applied to synthesize DMAEA in the transesterification, such as titanate esters [5–9], complexes of acetylacetone and metals (Cu, Ni or Zn) [10–12], K, Rb, or Cs carbonates [13,14], alkali metal phosphates ($Na_3PO_4$, $K_3PO_4$, $Rb_3PO_4$) [15], alkali metal bicarbonates ($KHCO_3$, $CsHCO_3$) and $RbHCO_3$ [16]. Organotins have been extensively employed as homogeneous catalysts for esterification [17] because they favor high conversion and very few by-products with production of fine chemicals.

In a previous work [18], we studied the transesterification of methyl acrylate (MA) with DMAE in a batch reactor using homogeneous titanates such as $Ti(OBu)_4$, $Ti(OCH_2CH_2CH_3)_4$ and $Ti[OCH(CH_3)_2]_4$, and Lewis acids such as $AlCl_3 \cdot 2H_2O$ and $Pb(AcO)_2 \cdot 3H_2O$. We also investigated that the homogeneous titanates catalysts led to a better efficiency than the heterogeneous Lewis acid catalysts, but the titanates catalysts caused side-reactions and impurities.

Now the amino-containing (meth)acrylic monomer are so widely used in the industrial fields. It is well known that the catalyst is a key part in the transesterification, but few of the scientific literatures about its studies of properties have been reported. In this work, the transesterification of MA and DMAE was studied with the aim to compare with the efficiency of catalysts such as $(C_8H_{17})_2Sn(OCOC_{11}H_{23})_2$(TD), $Sn(OCOCO)_4$ (oxalic acid tin), $Pb(AcO)_2 \cdot 3H_2O$, $Zn(OAC) \cdot 2H_2O$, $MgCl_2 \cdot H_2O$, $SnCl_2 \cdot 2H_2O$ and to optimize various reaction conditions such as the different catalysts, the reactants ratio, the amount of catalysts and the reaction time. The samples are analyzed by gas chromatography. The DMAEA product is characterized by IR spectroscopy, NMR spectroscopy, mass spectroscopy and elemental analysis.

In general, transesterification reactions are catalyzed by both acids and bases [10]. The purpose of this study is to develop an effective and inexpensive catalyst for the transesterification of MA and DMAE to give DMAEA. This paper is the first to report the good catalytic performance of a $(C_8H_{17})_2Sn(OCOC_{11}H_{23})_2$(TD) catalyst in this type of transesterification reaction, with liquid phase reactants.

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## 2. Experimental

### 2.1. Materials

Methyl acrylate with purity of 99.5% was purchased from Shanghai Chemical Reagent Co., China; DMAE was purchased with purity of 99.0%. The catalysts used were of laboratory reagent grade and obtained from Beijing Stable Chemical Co., Ltd. The standard DMAEA sample with purity of 99.6% was from ATOFINA in France.

### 2.2. Experimental set-up

The catalytic transesterification of MA and DMAE was carried out in a reactor of capacity 1000 mL. The reactor was equipped with an electrically heated jacket, a turbine agitator, a variable speed magnetic drive and a distilling column. The temperature and the speed of agitation were controlled by means of a WMZK-01 controller. The two thermometers were located on top of the distilling column and at the bottom of the reaction vessel, respectively. The distilling column was also provided with cooling water.

### 2.3. Experimental procedure

Into a flash equipped with a stirrer, a thermometer and a distilling column are charged 516.5 g (6.0 mol) of MA, 213.6 g (2.4 mol) of DMAE, 2.583 g of phenothiazine as a polymerization inhibitor and 10.68 g of organotin as a catalyst. The mixture is heated with stirring until it boils and the bottom temperature is 87 °C. The azeotropic mixture of methanol formed as a by-product and MA as a starting material is refluxed for about 0.5 h, and the reaction mixture is then reacted while part of the azeotropic mixture is withdrawn from the system at a reflux ratio of 5:1. By this means, the reaction equilibrium was broken and the reaction was accelerated to develop towards the desired direction. During the reaction, the temperature at the top of the distilling column is kept at 65–75 °C. The transesterification reaction is completed in 7–8 h. After the separation of the distillate, heating was resumed and the apparatus was put on gradual reduced pressure. The unreacted MA and DMAE were distilled over rapidly, the main portion of this fraction being collected at 25–55 °C, at −1.3 to −2.6 kpa. The final product DMAEA is distilled at 80–85 °C and −0.26 kpa.

### 2.4. Instruments and conditions of analysis

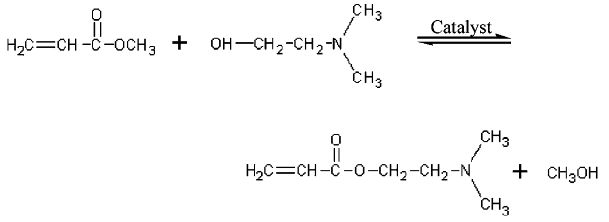
The instruments used in this work was carried out a FTLA2000-104 FTIR spectrometer (Normal scanning speed, resolution power: 4 $cm^{-1}$, 500–4000 $cm^{-1}$, KBr), spectrum of the product was determined by a FULI-9790 GC chromatograph (FID; SE-54 capillary column; 50–250 °C, 40/min; injecting temperature, 250 °C; detecting temperature, 280,$$C), the mass spectra of the sample was examined by a TRACE GC-MS spectrometer (PEG-20000 capillary column; 50–240 °C, 10 °C/min, injecting temperature is 250 °C. Helium as carry gas with speed of 1.0 mL/min; EI, 70 eV; $m/z$ range: 33–500 $m/z$), and a INOVA-400 NMR spectrometer (400 MHz, solvent is $DCCl_3$).

## 3. Results and discussion

### 3.1. Influences of different catalysts

The ester exchange reaction of MA with DMAE conversion towards dimethylaminoethyl acrylate (DMAEA) over different catalysts are according to scheme 1.

In selecting of catalysts, it was found that the highest conversion is TD catalyst, which was 96.28%. These results are consistent with the ease with which the transition organotin alkoxides are formed from reactants. Especially, TD was one of the efficient catalyst for transesterification of MA with DMAE and it exhibited better selectivity and higher yield of DMAEA and higher conversion of DMAE than such catalysts as shown in table 1. The selectivity of DMAEA based on DMAE over ZT could reach 98.68% while others conversion was only 78–90%, respectively. Furthermore, the yield of DMAEA could reach 94.65% when TD is chosen as the catalyst for the transesterification. Overall,



Scheme 1. Chemical reaction equation for methyl acrylate (MA) and dimethylaminoethanol (DMAE).

Table 1
Catalytic performance of synthesis of DA using different catalysts in transesterification reaction[a]

| Catalyst | DMAE conversion (%) | Selectivity to DMAEA (%) | DMAEA yield (%) |
|---|---|---|---|
| $Pb(AcO)_2 \cdot 3H_2O$ | 78.69 | 85.75 | 65.45 |
| $Zn(OAC) \cdot 2H_2O$ | 84.25 | 86.45 | 75.3 |
| $SnCl_2 \cdot 2H_2O$ | 82.56 | 82.56 | 67.25 |
| $MgCl_2 \cdot H_2O$ | 88.23 | 88.06 | 75.3 |
| $Sn(OCOCO)_4$ | 90.22 | 91.65 | 82.24 |
| TD | 96.28 | 98.68 | 94.65 |

[a] Reaction conditions: time 8 h, temperature 87 °C, MA 516.5g (6.0 mol), DMAE 213.5 g (2.4 mol), catalyst 21.4 g ($m_{cat}$:$m_{DMAE}$ = 1:10), inhibitor (phenothiazine) 2.583 g ($m_{inhibitor}$:$m_{MA}$ = 1:200). Methanol is azeotropically distilleout with MA.

the catalyst TD more significant selectivity to DMAEA and conversion of DMAE than others.

### *3.2. Influence of the reactants ratio*

The influence of the reactants ratio on the transesterification reaction is shown in figure 1. It can be known that the conversion of DMAE, the yield of DMAEA and the selectivity to DMAEA are heightened with the increasing of the $n_{MA}/n_{DMAE}$ value. When the molar ratio of MA/DMAE is lower, the DMAE concentration will be become higher because MA was azeotropically distilleout with methanol in reaction system, which dose not favor the conversion of DMAE. Along with the $n_{MA}/n_{DMAE}$ value changing from 1.2 to 2.5, the conversion of DMAE, the yield of DMAEA, and the selectivity to DMAEA are increased sharply. However, they are enhanced slowly between 2.5 and 3.0. The reason is that the higher $n_{MA}/n_{DMAE}$ initial molar ratio would result in lower DMAE concentration and it will reduce the reaction rate. Therefore, the $n_{MA}/n_{DMAE}$ initial molar ratio 2.5 was selected in view of recycling of the azeotropic mixture and utilization of the materials.

### *3.3. Influence of the amount of the catalyst*

Figure 2 presents catalytic activities of different catalyst amounts. As shown in this figure, along with the increasing of the amount of TD, the conversion of DMAE to produce DMAEA and the yield of DMAEA were enhanced gradually. However, when the value of $m_{DMAE}/m_{cat}$ is less than 20 wt.%, the conversion of DMAE and the yield of DMAEA increase slightly. The reason is that higher catalyst concentration can cause the consuming of DMAE and DMAEA by Michael Addition Reaction catalyzed by the excess ZT. Therefore, the $m_{DMAE}/m_{cat}$ 20 was selected. The experiment results show that the amount of the catalyst is upwards of 10.68 g ($m_{DMAE}/m_{cat}$ is 20), the yield of DMAEA and the conversion of DMAE reach 94.59 and 96.38%, respectively.

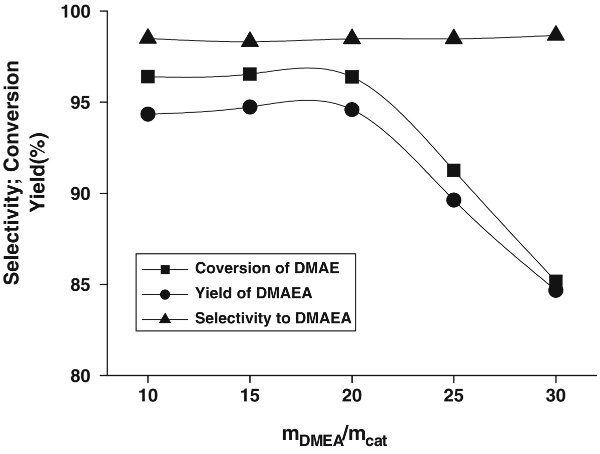


Figure 2. Effects of the amount of catalysts on the reaction. Reaction conditions: time 8 h, temperature 87 °C, MA 516.5 g (6.0 mol), DMAE 213.5 g (2.4 mol), catalyst (ZT), inhibitor (phenothiazine) 2.583 g ($m_{inhibitor}$:$m_{MA}$ = 1:200). Methanol is azeotropically distilleout with MA.

### *3.4. Influence of the reaction time*

Figure 3 indicates the influence of reaction time on the transesterification reaction. Conversion of DMAE, yield of DMAEA, and selectivity to DMAEA are enhanced with the increasing of the reaction time. The

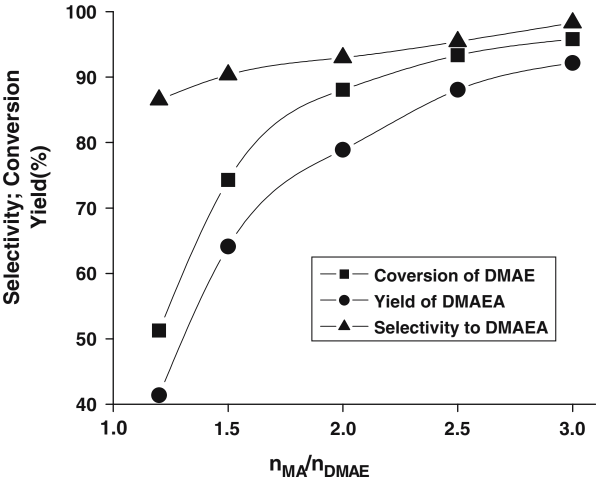


Figure 1. Effect of the ratio of reactants on the reaction. Reaction conditions: time 8 h, temperature 87 °C, MA 516.5 g (6.0 mol), DMAE 213.5 g (2.4 mol), catalyst (TD) 21.4 g, inhibitor (phenothiazine) 2.583 g ($m_{inhibitor}$:$m_{MA}$ = 1:200). Methanol is azeotropically distilleout with MA.

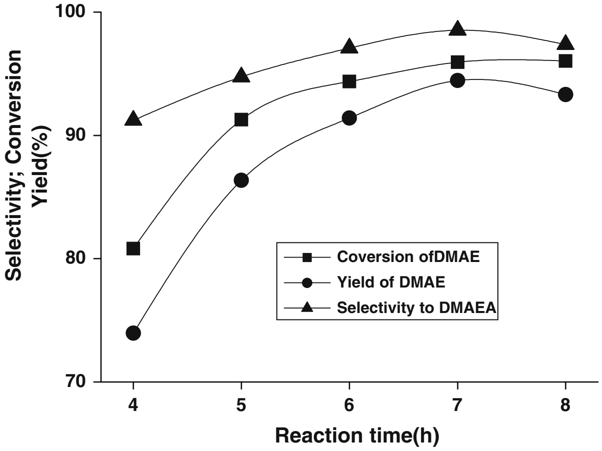


Figure 3. Effect of the reaction time on the reaction. Reaction condition: temperature 87 °C, MA 516.5 g (6.0 mol), DMAE 213.5 g (2.4 mol), catalyst (TD), inhibitor (phenothiazine) 2.583 g ($m_{inhibitor}$:$m_{MA}$ = 1:20.0). Methanol is azeotropically distilleout with MA.

reaction time changes from 4 to 8 h, meanwhile, conversion of DMAE, yield of DMAEA, and selectivity to DMAEA are increased sharply. However, yield of DMAEA, and selectivity to DMAEA are decreased slowly between 7 and 8 h. The reason is that the conversion of DMAE, the yield of DMAEA, and the selectivity to DMAEA increases at a higher reaction rate to synthesize DMAEA due to the higher raw material concentration in the process of time before 7 h. Along with the increasing of DMAEA concentration, the side reaction will occur to form the Michael addition by-products owing to the higher reaction activity of DMAEA. Between 7 and 8 h, the forming rate of DMAEA is almost balanced with the consuming rate of DMAEA by its Michael addition reaction. After 8 h, the consuming rate is faster than the forming rate of DMAEA and, selectivity to DMAEA and DMAEA yield decline. Therefore, the reaction time 7 h was selected.

### *3.5. Reactant and product analysis*

The analysis of the liquid-phase samples for the quantitative estimation of reactants and the products formed during the course of transesterification was carried out using gas chromatography (GC). The DMAEA product is characterized by IR spectroscopy, NMR spectroscopy, mass spectroscopy, and elemental analysis. The DMAEA product of reaction shows buff liquid with yield of 95.0% and purity of 99.5% (figure 4 and table 2). Elemental analysis for DMAEA product ($C_7H_{13}O_2N$), value of theory: C 58.72, H 9.15, N 9.78; value of practice: C 58.54, H 9.11, N 9.79.

Compared with value of theory, it was found that the results of practice are in good agreement. IR spectra of the DMAEA product is the same as DMAEA sample spectra (figure 5). Figure 6 showed the mass comparison spectra of the DMAEA product (b) and the standard sample (a). The $^1$H NMR method was then used to determine the DMAEA. Results (figure 7) show the same sharp singlet at 2.3, 2.6 and 4.3 ppm due to the

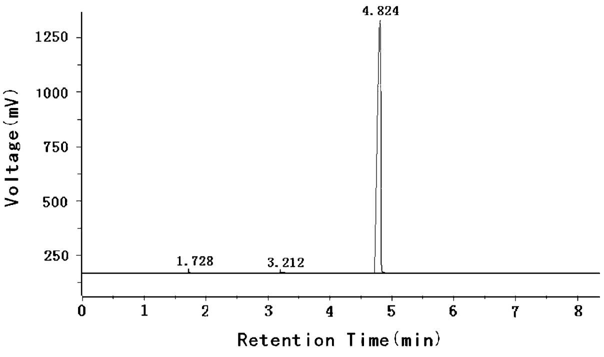


Figure 4. The gas chromatography (GC) spectrum of the product.

Table 2
Analysis results of chromatography (GC)

| Peak | Component | Ret. time (min) | Peak area (%) |
|---|---|---|---|
| 1 | MA | 1.728 | 0.0013 |
| 2 | DMAE | 3.212 | 0.0034 |
| 3 | DMAEA | 4.824 | 0.9953 |

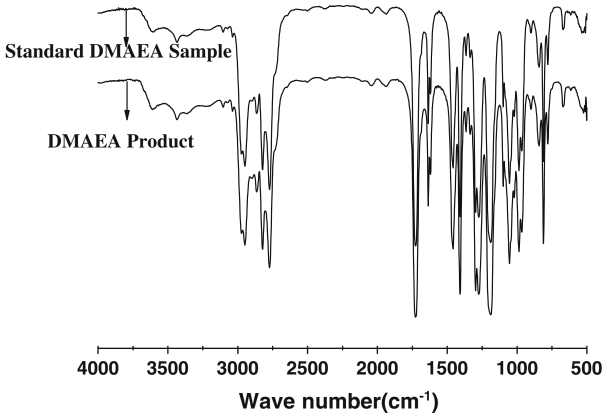


Figure 5. IR comparison spectra of the DMAEA product and the standard sample.

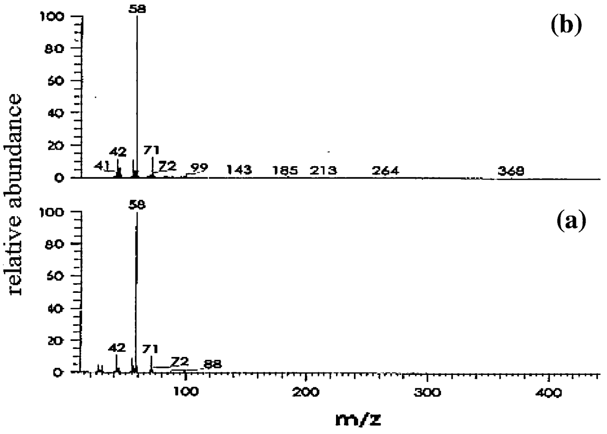


Figure 6. The mass comparison spectra of the DMAEA product (b) and the standard sample (a).

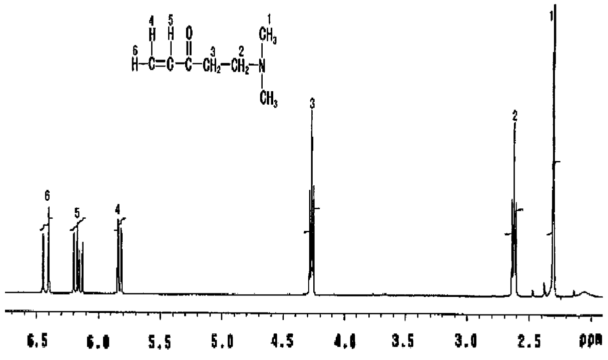
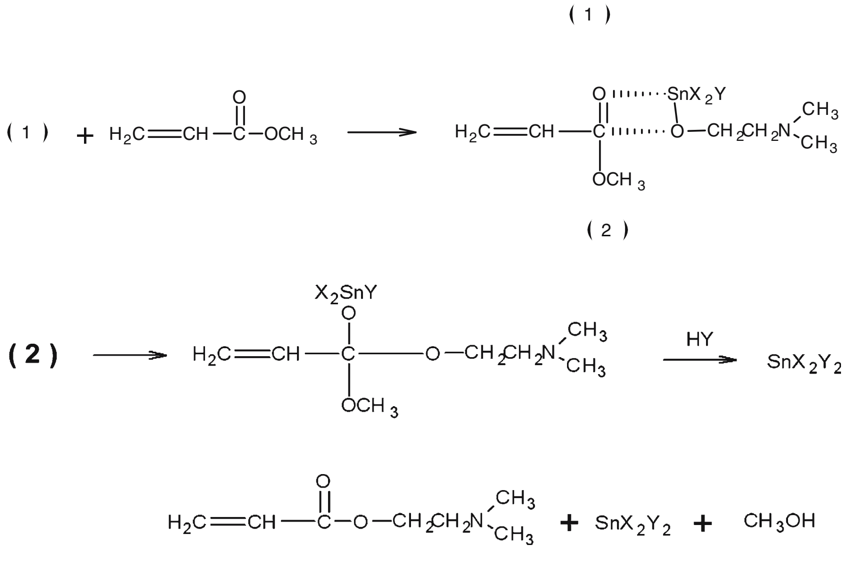


Figure 7. $^1$ HNMR spectrum of the DMAEA product.

Table 3
IR spectra analysis of sample

| Wave number ($cm^{-1}$) | The types of vibration |
|---|---|
| 2948.9 | C–H inversion symmetry flex vibration of $CH_3$– |
| 2864.1 | C–H inversion symmetry flex vibration of –$CH_2$– |
| 2821.7 | C–H flex vibration of Amine N–$CH_3$ |
| 2771.5 | C–H flex vibration of Amine N–$CH_3$ |
| 1726.2 | C=O flex vibration of ester |
| 1458.1 | C–H inversion symmetry flex vibration of $CH_3$– |
| 1372.5 | Tertiary amine C–N flex vibration |
| 1349.1 | Tertiary amine C–N flex vibration |
| 1188.1 | C–O–C inversion symmetry flex vibration of ester |
| 1099.3 | C–O–C inversion symmetry flex vibration of ester |



Scheme 2. Mechanism of transesterification of DMAE and MA with organotin catalyst.

products' –$CH_3$ and two –$CH_2$– groups. Peaks at 5.8, 6.2 and 6.4 ppm indicated the C=C groups' H, which also characterize the DMAEA chemical structure. The MS and $^1$H NMR spectra of the product DMAEA were in good accordance with the standard spectra.

Table 3 showed IR spectra analysis of datum. In the transesterification reaction, spectra analysis of samples are all the same as pure DMAEA one, and analysis results indicate that the target product is dimethylaminoethyl acrylate (DMAEA).

### *3.6. Mechanism for catalytic transesterification reaction*

A possible catalytic mechanism for the transesterification reaction between DMEA and MA over Di-*n*-octyltin dilaurate (TD) catalyst is depicted in scheme 2.

Firstly, through the reaction of DMEA and the catalyst. It's easy to obtain the transition product (1); secondly, product (1) reacts with another compounds methyl acrylate MA to synthesis the complexing agent of four rings (2). As four rings is characteristic of tensile force and non-stabilization, which makes the transition product acyclic, the target product DMAEA and $CH_3OH$ were formed, therefore a catalytic cycle was accomplished.

## 4. Conclusion

It is found that the catalyst (TD) has an excellent catalytic activities and selectivity for synthesis of DMAEA by transesterification of MA with DMAE. The 96.28% conversion of DMAE was obtained over catalyst (TD), the yield of DMAEA could reach 94.65%, The selectivity is 98.68%, which is superior to the advanced catalysts in the scientific literatures. The optimized reaction conditions are $n_{MA}/n_{DMAE}$ molar ratio is 2.5, $m_{DMAE}/m_{cat}$ is 20, reaction time is 7 h. Gas chromatography, IR spectroscopy, NMR spectroscopy, Mass spectroscopy and Elemental analysis showed *N*, *N*-Dimethylaminoethyl acrylate chemical structural. A possible catalytic mechanism of transesterification of DMAE and MA with organotin catalysts was also presumed.

## Acknowledgments

This research was supported by Scientific Foundation of Ministry of Science and technology P.R. China. (No. 2002380).

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