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Study of Organic Aluminum Compounds Catalysts in Poly(ethylene terephthalate) Synthesis

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This paper presents a series of organic aluminum compounds as new polycondensation catalysts in poly(ethylene terephthalate) (PET) synthesis. Their catalytic activity in the esterification process is monitored by measuring the amount of water generated, while intrinsic viscosity is used as the index in the polycondensation process. Aluminum alkoxide shows higher activity than the other catalysts, but they can not be used as esterification catalyst. Aluminum β-ketoesters can be used as esterification and polycondensation catalyst and their activity is similar to aluminum alkoxide. The result shows that the activity of aluminum β-diketones and β-ketoesters is related to the ligand of β-diketones and β-ketoesters. Ethylene glycol aluminum was synthesized and applied in poly(ethylene terephthalate) synthesis. From this study, ethylene glycol aluminum was proved to be the real catalyst for using organic aluminum compounds as catalysts in poly(ethylene terephthalate) synthesis.

Key Words: Organic aluminum compound, Catalyst, Polycondensation, Poly(ethylene terephthalate).

INTRODUCTION

Poly(ethylene terephthalate) is a semicrystalline polymer possessing excellent chemical resistance, thermal stability, melt mobility, sinnability, low cost and good mechanical properties[1-3]. To get high molecular weight poly(ethylene terephthalate) by the reaction of terephthalic acid with ethylene glycol, the presence of a catalyst is essential. Poly(ethylene terephthalate) synthesis was performed by the usual two steps: esterification and polycondensation. The catalyst is not essential in esterification, but the polycondensation reaction could not perform without catalyst. So the main work is to find more efficient catalyst of polycondesationn in poly(ethylene terephthalate) synthesis. A large number of catalysts were reported on the catalytic aspects of the formation of poly(ethylene terephthalate), such as compounds of Sb, Ti, Sn and Ge[4-6]. These catalysts appeared to possess a similar activity towards polycondensation reaction, but they all appeared to be different disadvantage. Sb and Sn compounds were toxic[7,8]. So it is urgency to find new kinds of catalysts in poly(ethylene terephthalate) synthesis. Aluminum compounds are low toxic, but the main problem is finding aluminum compounds which possessed similar activity comparing with compounds of Sb, Ti, Sn and Ge.

In this study, organic aluminum compounds were used as catalysts in poly(ethylene terephthalate) synthesis. Pure terephthalic acid was esterified with ethylene glycol, then the produced oligomers were polycondensated in the second step under high vacuum in the presence of various organic aluminum compounds. Aluminum β-diketones or β-ketoesters are not sensitive to water, so they are the catalyst in both esterification and polycondensation. Aluminum alkoxide is used as polycondensation catalyst because they are sensitive to water. The results show that aluminum alkoxides appear to be more efficient than others. Aluminum β-ketoesters and aluminum acetylacetonate are also efficient in poly(ethylene terephthalate) synthesis. In mechanism tests, the process of esterification was examined. Additionallly, specific strategy for designing the real catalytic material in the polycondensation reaction has been also discussed. The result shows that ethylene glycol aluminum is produced for using aluminum chelates as catalyst and it is the real catalytic material.

EXPERIMENTAL

Ethylene glycol and terephthalic acid, which were used without further purification, were supplied by China Resource Company. The catalysts and reagents were of commercial grade and were used without further purification.

Detection method: Intrinsic viscosity measurements were performed using an Ubbelohde viscometer at 25 ºC in a mixture of phenol/1,1,2,2-tetrachloroethane (60/40, w/w). Intrinsic viscosity was calculated using Moore eqn.[9] carboxyl end-group content (-COOH) of the resins was determined according to Pohl's method[10] by titrating a solution of the resin in phenol/chloroform with standard KOH in ethanol in the presence of bromophenol blue as indicator. After the polymer samples were saponified by sodium hydroxide and methanol, the content of DEG was measured on Shanghai Precision & Scientific Instrument Co. Ltd. gas chromatographic instrument[4]. The esterification water was measured by the internal standard method on GC instrument and the internal standard substance was pentanediol[11]. FT-IR spectra were recorded with an infrared spectrophotometer (Nicolet 560). NMR data was obtained from AVANCE II 500 MHz (Bruker company), using CD_3OD or $CDCl_3$ mixture with TFA (95:5, by weight) as the solvents. Colour measurements were performed on Beijing Kangguang WSD-3C whiteness tester.

Synthesis of poly(ethylene terephthalate): Poly(ethylene terephthalate) was synthesized in 1 L stainless-steel batch reactor starting from the terephthalic acid and ethylene glycol in a molar ratio of TPA/EG=1:1.2, employing different catalyst. The syntheses were carried out in two steps: esterification and polycondensation. In the first step, the temperature was raised to 260 ºC under nitrogen atmosphere and maintained there until more than 90 % of the theoretical amount of water was distilled off. In the second step, the pressure was reduced (about 70 Pa), in order to facilitate the removal of EG in excess and the temperature was kept at 280 ºC. After the polycondensation reaction was completed, the product was unloaded into cold water with a pressure of nitrogen and dried 12 h in a vacuum oven at 100 ºC and reduced pressure. ^{1}H NMR (δ [ppm], $CDCl_3$-TFA (95:5 by wt), 20 ºC): 3.59-3.45 (m, 2H, $-CH_2-$), 6.91 (m, 4H, phenyl), 10.30 (s, 1H, -COOH).

Synthesis of catalyst: Aluminum β-ketoesters: An amount of 2.0 g (0.01 mol) of aluminum isopropoxide was dissolved in 100 mL of cyclohexane at room temperature followed by slow addition of 0.03 mol β-ketoesters (methyl acetoacetate, ethyl acetoacetate, *iso*-propyl acetoacetate and *tert*-butyl acetoacetate) under stirring. The clear reaction solution was then stirred at room temperature for 18 h. The volatiles were removed *in vacuo* and the resulting colourless solid washed with dichloromethane[12,13]. Aluminum methylacetoacetate: ^{1}H-NMR (δ [ppm], C_6D_6, 20 ºC): 4.97 (s, 3H, -CO-CH-CO-), 3.69/3.66/3.64/3.63 (s, 9H, $-O-CH_3$), 1.86/1.85/1.80/1.79/1.73 (s, 9H, CH_3-CO-). ^{13}C NMR (δ [ppm], d_8-toluene, 20 ºC): 189.3/188.9 (-CO-), 176.0/175.8 (-CO-O-), 85.7/85.5/85.4 (-CO-CH-CO-), 52.6/52.5/52.4/52.3 ($-O-CH_3$), 26.7 (CH_3-CO-). Aluminum ethylacetoacetate: $_1$H NMR (δ [ppm], C_6D_6, 20 ºC): 4.94/4.93 (s, 3H, -CO-CH-CO-), 4.17-4.01 (m, 6H, $-O-CH_2-CH_3$), 1.85/1.84 (s,9H, $-CH_3$-CO-), 1.23/1.22/1.20/1.19 (t, 9H, $-O-CH_2-CH_3$). ^{13}C NMR (δ [ppm], d_8-toluene, 20 ºC): 189.1/189.0/188.8/188.7 (-CO-), 175.6/175.4 (-CO-O-), 86.1/86.0/85.8 (-CO-CH-CO-), 61.82/61.78/61.72 ($-O-CH_2-CH_3$), 26.7 (CH_3-CO-), 15.2/15.1 ($-O-CH_2-CH_3$). Aluminum isopropylacetoacetate: $_1$H NMR(δ [ppm], C_6D_6, 20 ºC): 4.50-4.86 (m, 6H, -O-CH-), 1.85/1.84 (s, 9H, CH_3-CO-), 1.42-0.83 (m, 18H, $-O-CH-(CH_3)_2$). ^{13}C NMR (δ [ppm], d_8-toluene, 20 ºC): 188.9/188.7/188.5/188.4 (-CO-), 175.22/175.20/175.08/175.00 (-CO-O-), 86.5/86.4/86.1 (-CO-CH-CO-), 69.54/69.47/69.39 ($-O-CH-(CH_3)_2$), 26.7/26.3 (CH_3-CO-), 22.7/22.6/22.5/22.4 ($-O-CH-(CH_3)_2$). Aluminum tertbutylacetonate: $_1$H NMR(δ [ppm], C_6D_6, 20 ºC): 4.93/4.88/4.81 (s, 3H, -CO-CH-CO-), 1.83/1.82/1.80 (s, 9H, CH_3-CO-), 1.43/1.42 (s, 27H, $-O-CH-(CH_3)_3$). ^{13}C NMR (δ [ppm], d_8-toluene, 20 ºC): 187.9/187.8/187.7 (-CO-), 175.65/175.54/175.49/175.27 (-CO-O-), 87.35/87.26/86.97 (-CO-CH-CO-), 82.25/82.18/82.05/82.02 ($-OC-(CH_3)_3$), 29.3/29.2 ($-OC-(CH_3)_3$), 26.8/26.7/26.6 (CH_3-CO-).

Aluminum dibenzoylmethanate: An amount of 0.01 mol aluminum nitrate nonahydrate was dissolved in 10 mL of ethanol and the solution of dibenzoylmethane 6.72 g in 25 mL trichloromethane was slowly added. Then pH was adjusted to 7 by adding ammonia water. After 5 h of stirring the product precipitated from the reaction solution was filtered, washed with ethanol and a white solid was obtained[14]. ^{1}H NMR (δ [ppm], $(CD_3)_2CO$, 20 ºC): 8.16/8.15(m, 12H, phenyl), 7.56-7.43 (m, 18H, phenyl), 7.22(s, 3H, -CO-CH-CO-). ^{13}C NMR (δ [ppm], $(CD_3)_2CO$, 20 ºC): 186.2 (-CO-), 139.7 -129.1 (phenyl), 95.1 (-CH-).

Aluminum benzoylacetone: An amount of 0.01 mol aluminum nitrate nonahydrate was dissolved in 50 mL of water and the solution of benzoylacetone 4.8 g in 75 mL methanol was slowly added. Then pH was adjusted to 7 by adding ammonia water. After 9 h of stirring the product precipitated from the reaction solution was filtered. The received product was washed with ethanol and a white solid was obtained[15]. ^{1}H NMR(δ [ppm], $(CD_3)_2CO$, 20 ºC): 7.95-7.94 (m, 6H, phenyl), 7.51-7.39 (m, 12H, phenyl), 6.42-6.38 (m, 3H, -CH-), 2.87-2.84 (s, 9H, $-CH_3$). ^{13}C NMR(δ [ppm], $(CD_3)_2CO$, 20 ºC): 194.75-194.47 (-CO-), 184.1-183.8 (CH_3-CO-), 139.3-128.8 (phenyl), 98.3 (-OC-CH-CO-), 27.9 (CH_3-CO-).

Ethylene glycol aluminum: Aluminum isopropoxide was added to ethylene glycol at room temperature. The mixture was the heated under reflux at 190 ºC. The solution was cooled and toluene was added. The product precipitated out as a white solid. Then the white solid sample was dried in vacuum at room temperature[17]. The product was characterized by NMR. ^{1}H NMR(δ [ppm], CD_4O, 20 ºC): 3.3168/3.603(d, 12H, $-CH_2-$), 4.948 (t, 1H, -OH). ^{13}C NMR (δ [ppm], CD_4O, 20 ºC): 49.59 (CD_4O), 62.91 ($-CH_2-$).

TABLE-1
EFFECT OF DIFFERENT ALUMINUM COMPOUNDS ON PET SYNTHESIS

Catalyst	Symbol	Intrinsic viscosity (dL/g)	-COOH (µmol/g)	DEG (mol/t)	Sample colour		
					L^*	a^*	b^*
Aluminum methylacetoacetate for 60 min	$Al(meac)_3$	0.82	66.36	8.5	60.4	1.0	14.5
Aluminum ethylacetoacetate for 60 min	$Al(etac)_3$	0.81	67.96	7.2	65.2	0.8	13.0
Aluminum isopropylacetoacetate for 60 min	$Al(ipac)_3$	0.79	69.80	7.8	61.4	2.2	14.1
Aluminum tertbutylacetonate for 60 min	$Al(tbuac)_3$	0.80	63.40	6.3	65.9	1.2	12.9
Aluminum acetylacetonate for 54 min	$Al(AAc)_3$	0.83	71.50	6.9	60.5	1.5	12.0
Aluminum benzoylacetonate for 60 min	$Al(BAc)_3$	0.65	69.25	5.4	61.4	0.7	15.6
Aluminum dibenzoyl methane for 60 min	$Al(DBA)_3$	0.59	64.10	7.9	55.7	0.9	10.9

TABLE-2
EFFECT OF DIFFERENT METAL ACETOACETATES ON PET SYNTHESIS

Catalyst	Intrinsic viscosity (dL/g)	-COOH (μmol/g)	DEG (mol/t)
Aluminum acetylacetonate for 54 min	0.83	71.50	6.9
Ferric acetylacetonate for 60 min	0.60	63.9	9.3
Titanium acetylacetonate for 45 min	0.88	67.96	4.5
Zirconium acetylacetonate for 60 min	0.56	65.3	8.6
Calcium acetylacetonate for 60 min	0.50	61.6	7.5
Zinc acetylacetonate for 60 min	0.52	58.5	9.8

TABLE-3
EFFECT OF DIFFERENT ALUMINUM ALKOXIDES ON PET SYNTHESIS

Catalyst	Intrinsic viscosity (dL/g)	-COOH (μmol/g)	DEG (mol/t)	Sample colour		
				L^*	a^*	b^*
Aluminum methoxide for 42 min	0.86	29.3	8.5	60.4	0.2	14.2
Aluminum ethoxide for 45 min	0.84	25.0	7.2	60.8	0.8	15.6
Aluminum isopropoxide for 45 min	0.86	19.3	8.1	55.7	0.3	10.9
Aluminum tert-butoxide for 48 min	0.85	21.5	6.1	59.9	2.3	16.8
Ethylene glycol aluminum for 39 min	0.87	23.0	8.2	53.8	0.1	9.0
Aluminum phenoxide for 1 h	0.56	28.9	9.4	60.4	0.5	14.6
8-Hydroxyquinoline aluminum for 60 min	0.59	25.7	7.8	63.4	2.0	15.3
Ethylene glycol antimony for 45 min	0.86	29.3	9.3	60.4	0.2	16.2
Titanium glycolate for 30 min	0.89	26.6	6.8	73.4	3.0	29.3

RESULTS AND DISCUSSION

Catalytic activity of different catalyst: For chemical reaction, poly(ethylene terephthalate) is influenced by many conditions. In this paper, different kinds of catalysts were studied. Tables 1-3 were the results of different aluminum compounds. As a model initiator from this family of compounds we have chosen different aluminum β-diketones and β-ketoesters. They were prepared in accordance with the method described by Gnanasoundari[12] and Lichtenberger[13].

In order to compare the catalytic acitivity, different aluminum β-diketones and β-ketoesters were used both as esterification and polycondensation catalyst because they are not sensitive to water. Samples were tested for the intrinsic viscosity after reaction. The carboxyl contents were determined only for the base polymer according to the Pohl's method[10]. The results were presented in Table-1 and Fig. 1.

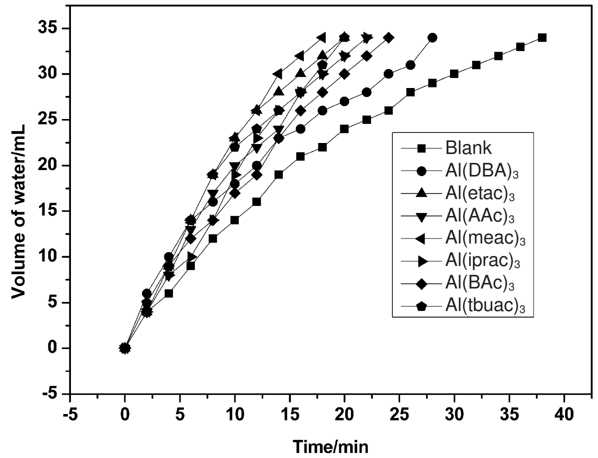


Fig. 1. Volume of water versus the time in the esterification process

As shown in Table-1, intrinsic viscosity distribution of poly(ethylene terephthalate) samples synthesized with aluminum chelates was found to be different to each other. Diethyl glycol (DEG) and carboxyl end-group content are similar. It can be seen that aluminum acetylacetate was the best one in the seven catalysts and intrinsic viscosity was the best one of the seven catalysts; however, the intrinsic viscosity of the other catalysts is lower, which showed that different catalysts had different catalystic activity on the polycondensation reaction.

The catalytic activity of aluminum dibenzoyl methane is the lowest. This phenomenon could be caused by two reasons. Firstly, the steric hindrance of different ligands is different. When the steric hindrance is higher, the catalytic activity is lower. Secondly, Lewis acidity of aluminum is different when the ligand is different. Each aluminum atom in aluminium β-diketones molecule becomes highly electrophilic because of the stronger electron- attracting inductive effect of the conjoint O atoms and thereby improves the Lewis acidity of the active center (Al atom). There is also Al-O bond and electron attracting effect in aluminium β-diketones molecules, but it is not so strong because of the weaker inductive effect of the higher steric hindrance ligand (β-diketones) that results in the lower Lewis acidity of active center (Al).

Measurements of the distillation rate of water in the first step of the reaction make it possible to evaluate the catalytic activity of the catalysts employed. The data of the volume of produce water *versus* reaction time presented in Fig. 1. allow us to compare the activities of the catalysts employed. Different aluminum catalysts appeared to be much more efficient as compared with no catalyst.

As it is shown in Fig. 1. the produced water rate for using aluminum compounds as catalysts is faster than the uncatalyzed rate. Among aluminum β-ketoesters, the produced water rate of aluminum methylacetoacetate is the fastest. The reason is that all the usage of aluminum β-ketoesters is 0.1 g and the molecular weight of aluminum methylacetoacetate is the highest. So the mole of aluminum methylacetoacetate is the highest. Among aluminum β-diketones, the produced water rate of aluminum acetylacetate is the fastest. Others are lower than it and also lower than aluminum β-ketoesters. The reason is the same to aluminum β-ketoesters.

In order to find the effect of different metal acetylacetonate on poly(ethylene terephthalate) synthesis, six compouds were used. The catalytic activity is different significantly. The result shows that there is no significant law. Titanium acetylacetate and zirconium acetylacetonate are tetravalent salt, but calcium acetylacetonate and zinc acetylacetonate are divalent salt. Aluminum acetylacetonate and ferric acetylacetonate are trivalent salt and the catalytic activity of titanium acetylacetonate and aluminum acetylacetonate is higher than others. This phenomenon may be caused by the electrophilic ability. Different metal acetylacetonate has appropriate Lewis acidity. Each metal atom in metal acetylacetonate molecule becomes highly electrophilic because of the stronger electron-attracting inductive effect of the conjoint O atoms and improves the Lewis acidity of the active cente. The electrophilic ability for different metal is different significantly and it is bigger for the higher valent metal.

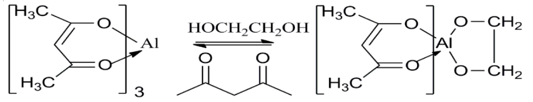
In order to detect other aluminum organic compound acitivity, different aluminum alkoxides were used. As can be seen from the results presented in Table-3, intrinsic viscosity distribution of poly(ethylene terephthalate) samples synthesized with aluminum alkoxides was found to be very close to each other. DEG and carboxyl end-group content are also similar. The intrinsic viscosity data (Table-3) illustrates that the catalytic activity of titanium glycolate is higher than ethylene glycol aluminum and ethylene glycol antimony and it is similar between ethylene glycol aluminum and ethylene glycol antimony. This phenomenon could be caused by the coordinative ability of Ti to create some kinds of coordinative network in the polymer melt that results in enhanced values of melt viscosity; Al and Sb are unable to form such network and, as a consequence, lead to lower values of intrinsic viscosity, which can be considered a further advantage in their application.

It is worthwhile to note that when titanium compounds are used for the production of poly(ethylene terephthalate), the polymer becomes markedly yellowish[17-19]. From b* values of colour measurement of poly(ethylene terephthalate) samples of this work (Tables 1 and 3), the poly(ethylene terephthalate) sample of titanium glycolate showed a clear visible yellow discolouration (b* = 29.3) due to titanium glycolate adding. A visible yellow discolouration showed the samples with b* values > 4.5 and all the other samples showed sensilbe discolouration. But the samples of aluminum organic compounds are whiter than the sample of titanium glycolate and b* values are lower.

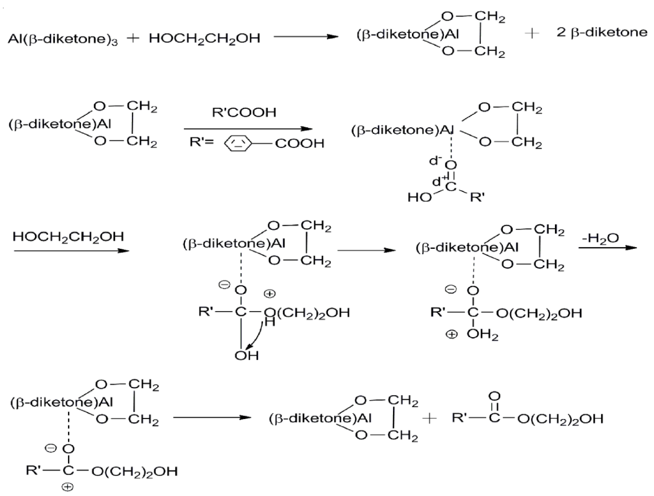
Mechanism: In order to find the real catalytic material, blank test was done. Eight aluminum compouds (2.0 mol) were reacted with ethylene glycol (200 mL) in a reactor equipped with a nitrogen inlet, a condenser and a mechanical stirrer. The temperature is 200 ºC. The conversion of ligand was listed in Table-4. Data presented in Table-4 showed that these aluminum compounds were reacted with EG and the corresponding ligands were produced. It was detected by GC. We choosed aluminum acetylacetonate as a example and Rosca[20] reported zinc acetylacetonate mechanism. We proposed aluminum acetylacetonate according to it and the reaction mechanism was listed in **Scheme-I** and **II**. The aluminum chelates with β-diketones or β-ketoesters reversible exchange of β-diketones or β-ketoesters with ethylene glycol at the Al atom. It can be concluded that aluminum glycoxide may be the real catalytic material.

TABLE-4
The reaction of catalyst (2.0 mol) and EG (200mL) at 200 ºC

No.	Catalyst	Ligand produced (%)
1	Aluminum methylacetoacetate	31.8
2	Aluminum ethylacetoacetate	29.3
3	Aluminum *iso*-propylacetoacetate	26.5
4	Aluminum *tert*-butylacetoacetate	33.5
5	Aluminum acetylacetate	25.9
6	Aluminum ethoxide	45.5
7	Aluminum *iso*-propoxide	49.1
8	Aluminum *tert*-butoxide	40.3



Scheme-I. Aluminum acetylacetonate reacted with EG



Scheme-II: Aluminum compound mechanism for polycondensation process

The reaction mechanism in **Scheme-II** can be divided into four steps. Firstly, β-diketones or β-ketoesters of aluminum β-diketones or β-ketoesters exchange with ethylene glycol at the Al atom. Secondly, aluminum β-diketones or β-ketoesters have appropriate Lewis acidity. Each aluminum atom in aluminum β-diketones or β-ketoesters molecule becomes highly electrophilic because of the stronger electron-attracting inductive effect of the conjoint O atoms and thereby improves the Lewis acidity of the active center (Al atom). Thus, the O atom in carbonyl group of terephthalic acid is easier to coordinate on the aluminum center and then accelerate the reaction. Thirdly, the C atom in carboxyl group of terephthalic acid, which is coordinate to the aluminum center, becomes highly electrophilic and thereby the hydroxyl of ethylene glycol is easier to coordinate on the carboxyl C atom. Meanwhile, the hydroxyl H atom coordinates on hydroxyl of carboxyl and water is produced. Lastly, Al-O bond is not so strong because of the weaker inductive effect of ligand (β-diketones or β-ketoesters) that results in the lower Lewis acidity of active center (Al).

The produced functional group removes from Al atom and it is the end of one circle. The **Scheme-II** listed the esterification process and the polycondensation process is similar.

FT-IR and ^{1}H NMR of poly(ethylene terephthalate): The FT-IR spectrum of poly(ethylene terephthalate) produced by the esterification of ethylene glycol and terephthalic acid is shown in Fig. 2. The FT-IR spectrum of poly(ethylene terephthalate) coincided with work of Serio *et al.*[21]. Fig. 2 shows the FT-IR of poly(ethylene terephthalate). The characteristic absorption peaks were ester conformation and benzene ring. The bands at 1240 cm^{-1} and 1090 cm^{-1} are due to stretching vibration of C-O. The absorptions at 1720 cm^{-1} and 727 cm^{-1} were assigned to the band of the carboxyl and benzene ring. The absorbencies of the signals at 3430 and at 872 cm^{-1} were due to the end-group. ^{1}H NMR spectrum of the sublimate in $CDCl_3$-TFA (95:5 by wt) mixture is shown above. The multiplet observed in the δ 3.45-3.59 ppm region has been assigned to the protons of methylene groups present in poly(ethylene terephthalate)[22]. The singlets observed at δ 6.91 and 10.30 ppm have been assigned to the protons of the phenyl groups and terminal carboxyl groups.

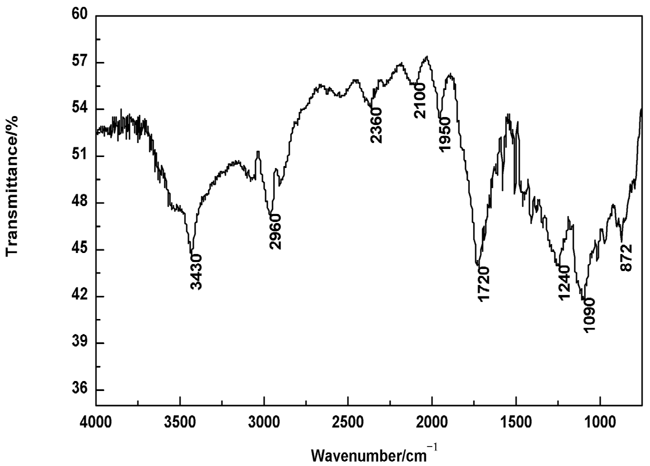


Fig. 2. FT-IR of poly(ethylene terephthalate)

Conclusion

A series of experiments were done to study the effects of new organic aluminum compound catalysts on the polycondensation reaction. As shown earlier, aluminum ethylene glycol was demonstrated as the one of the best aluminum organic compounds used, which could improve the polycondensation time and the colour is whiter than titanium glycolate. Its catalytic activity is similar to antimony ethylene glycol. It could not be used as esterification catalyst because it is sensitive to water.

Aluminum β-diketones and aluminum β-ketoesters can be used esterification and polycondensation catalyst because they are not sensitive to water. Among these compound aluminum acetylacetonate and aluminum β-ketoesters are more efficient and their catalytic mechanism are disscussed. Aluminum β-diketones or β-ketoesters do not give any rise to environmental problems and is available at reasonable cost.

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