Hydrothemal Synthesis and Investigation of Aluminum Terephthalate

G.P. Panasyuk, L.A. Azarova, Mishal Khaddaj, I.L. Voroshilov, G.P. Boudova

N.S. Kurnakov Institute of General and Inorganic Chemistry,Russian Academy of Sciences. Leninskii prospect, 31,Moscow, GSP-1, 119991 Russia.
E-mail: panasyuk@igic.ras.ru Fax:+ 7(095) 9554852

Summary

A new method of obtaining crystalline aluminum terephthalate is developed. The transformation of the product of the autoclave treatment of terephthalic acid and solution $AlCl_3$ with the different methods of introduction to reaction and different ratios of reagents is investigated. The results of the physical and chemical analysis of the products are introduced.

Introduction & Experimental

The synthesis of various terephthalates in one of the interesting aspects of the further using of the products of decomposition of PET we manage to obtain ammonium terephthalate as well as terephthalates of elements of Groups I-IV.

TA derivatives are rather interesting products, and, in particular, TA ammoniac salts. The salts of TA and bivalent copper absorb oxygen, nitrogen, argon and xenon up to two moles of gas/1 mole of salt.

Earlier we obtained terephthalates of the elements of I-II groups [1]. Terephthalates of these elements can be obtained directly at temperatures not higher than 100^{o}C and normal pressure with interaction of a solution of ammonium terephthalate with the salts of the corresponding elements. Under analogous conditions we have obtained aluminum terephthalate in the amorphous state and it was identified on the basis of physical and chemical analysis (X-ray phase analysis, DTA, IR, element chemical analysis) [Panasyuk G.P., 2003].

For more specific identification it is necessary to obtain not amorphous but crystalline aluminum terephthalate. For obtaining this compound the method of hydrothermal synthesis was used.

The process was carried out in the autoclave in temperature interval of 200 – 390^{0}C and under pressure of 1.6 - 25 MPa. As initial substances we used crystalline terephthalic acid (TA) 99% purity, (production of "Across Organics" (Belgium), "Khemreactiv" (Russia)), as well as TA obtained from potyethyleneterephthalate (PET) [Panasyuk G.P., 2002], and aqueous solutions of aluminum chloride.

Initial reagents were placed into the autoclave in quartz-glass, steel and Teflon containers were maintained at constant temperature for 10 -72 hours.

Different molal TA/Al ratios from 0.5 to 2.6 were used. After treatment the autoclaves were cooled, the obtained product washed from chlorine ions, then dried and investigated by chemical and physical methods.

X-ray analysis was carried on diffractometer DRON-3M (Cu, Kα). Thermogravimetric analysis (TG) and differential thermal analysis (DTA)were carried on derivatograph MOM, with a heating rate of 6 deg./min.

Ammonium terephthalate

Ammonium terephthalate of can be obtained directly in the autoclave by treating post-consumer PET at 200^{0}C in the presence of NH_4OH and subsequent its excretion in the solid state. Heating to 150^{0}C leads to evaporation of ammonia, although the structure of ammonium terephthalate remains the same up to a content of nitrogen equal to 3.48 wt.%.

This allows us to consider ammonium salt as the compound of variable composition with general formula $(NH_4)_xH_{2-x}(OOCC_6H_4COO)$; $x = 1.7÷0.4$ [Panasyuk G.P.,2002]. This structure is formed when part of ammonium ions are not present, and the molecule is ready to accept other compounds to be absorbed in its structure, which enables such a salt to be used as the selective absorber, molecular sieve, etc.

Terephthalates of Group I-II

Obtained ammonium terephthalate is used further as an initial compound for synthesis of terephthalates of Groups I and II. The last were obtained by their precipitation from the reaction of ammonium solution of ammonium terephthalate with the solutions of salts of these elements. Precipitation of terephthalates of alkali metals (K, Na) was conducted in an excess of ammonium hydroxide. This fact does not prevent the formation of salts because of the high solubility of hydroxides of alkali metals under these conditions. With the conduction of terephthalates of Group II (Mg, Ca) relatively insoluble hydroxides are formed. These hydroxides interfere with terephthalates and this fact leads to considerable difficulties to obtain pure salts. Therefore the ammonium solution of ammonium terephthalate should be first neutralized by solution of HCl up to pH = 6 and then introduced for the substitution reaction.

For Na both mono- and di-substituted terephthalates salts were obtained, where as for potassium only monosubstituted sal is formed. Individual diffractograms were obtained for each terephthalate. Upon heating different terephthalates behave themselves similarly: endothermic effects, related to the loss of crystallization water (where it is present), and exo-effects, one of them is noticed at temperature higher than 500^0C and related with the process of decomposition of terephthalates. Further thermo-oxidizing destruction leads to the formation of carbonates, which are transformed at temperatures above 800^0C into oxides (Na_2O, K_2O, CaO, MgO). Only for di-substituted sodium terephthalate the end product is sodium carbonate.

Aluminum Terephthalate

In the case of aluminum terephthalate the use of above mentioned method leads to the formation of amorphous compound.

To obtain crystalline aluminum terephthalate (Fig. 1) hydrothermal method was applied. TA (both commercial and obtained from post-consumer PET) and a solution of aluminum chloride were introduced into steel, teflon or quartz container, which was placed in the autoclave. The TA:Al ratio varied in the range 0.5÷2.6. Experiment conditions are represented in Tab. 1 . In all cases crystals of aluminum terephthalates with the following formula $Al_2(C_6H_4(COO)_2)_3.2H_2O$ are formed (chemical element analysis confirm the presented formula (see Tab. 2).

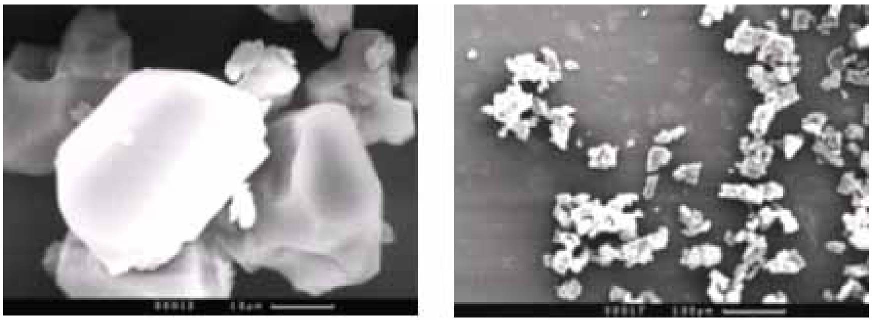


Fig. 1 - Electron microscopic photos of aluminum terephthalate

Table 1

Reaction conditions between terephthalic acid and aluminum chloride in the autoclave and X-ray phase analysis results

N	Container material	Treatment conditions	TA:A1	T°C	Time, hrs	Product (X-ray results)
1	Teflon		1.80	200	16	$TA+A1C1_3{\cdot}6H_2O$
		After heating to 950^0C				γ-$A1_2O_3$
2	Teflon		1.80	200	72	TA+A1-Terephthate +$A1_2O_3$.3H20
3	Teflon		0.56	200	72	TA+ A1-Terephthate
		Insoluble in DMSO residue				A1-Terephthate
4		After heating to 950^0C				γ-$A1_2O_3$
5	Steel		1.80	200	36	A1-Terephthate + small amount of impurities
6	Steel		1.60	200	36	A1-Terephthate
7	Quartz		1.80	200	36	A1-Terephthate +TA
8	Quartz		1.60	200	36	A1-Terephthate +TA
9	Quartz		0.80	300	36	A1-Terephthate
10	Quartz		0.95	300	36	A1-Terephthate + $A1_2O_3$..$3H_2O$
		After heating to 750^0C				amorphous compound
11	Quartz	TA from PET	2.6	300	36	A1-Terephthate
12	Steel		1.8	390	72	A1OOH-boehmite

Table 2

Element composition of terephthalate

Container	C	H	O	A1
Steel	49.62	2.49	39.05	8.84
Teflon	50.21	2.52	39.24	8.03
Quartz	49.56	2.70	38.73	9.01
$Al_2[C_6H_4(COO)_2]_3.2H_2O$ (theoretical calculation)	49.48	2.74	38.48	9.27

Values of interplanar spacing for aluminum terephthalate from X-ray phase analysis are represented in Table 3.

Table 3- Interlayer distance (d, Å) and intensity (I, %) of aluminum terephthalate crystals (X-ray phase analysis data)

d, Å	8,59	5,79	4,98	4,17	3,68	3,30	2,84	2,76	2,21
I, %	76	54	100	76	68	79	34	14	14

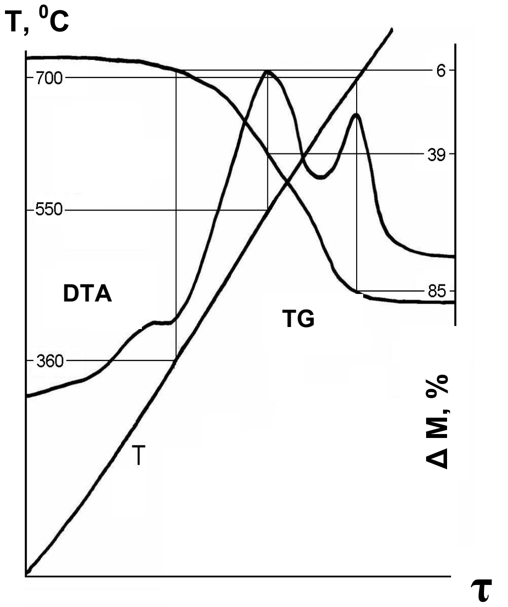


Fig. 2. DTA and TG of $Al_2[C_6H_4(COO)_2]_3.2H_2O$

Thermo-gravimetrical analysis shows here two exo-effects typical for terephthalates at 550^0C (related with oxidizing thermal destruction of organic ligand) and 730^0C (combustion of organic residue). Intensive loss of weight reaches 85% at 730^0C. X-ray analysis of the product obtained after heating to 950^0C shows the presence of wide reflexes, corresponding to γ-Al_2O_3.

IR spectra of aluminum terephthalate, obtained in the autoclave, and of the samples thoroughly heated at 500, 600, 900^0C shows, that the valence vibrations of CO, CH, CC, OH, AlO bonds partially keep existing after treating at 500^0C. The valence vibrations of OH group (v_{OH}) in the initial product has two strips at 3609 and 3443 cm^{-1} but only one at 3420 cm^{-1} after treatment at 600^0C. Besides a deformation vibration of water molecule (δ_{HOH}) at 1631 cm^{-1} remains in the spectrum even after treatment at 900^0C. The presence of this vibration is caused, probably, by the process of polycondensation. During the decomposition aluminum terephthalate upon thermal treatment $Al(OH)_3$ is formed. Further heating of aluminum hydroxide leads to the disappearance of structural water and to the formation of γ-Al_2O_3.

IR spectra of investigated terephthalates are represented on fig. 2. For all terephthalates there are wide intensive bands of absorption in the range of 3410-3472 cm^{-1} which belong to stretching vibrations of OH-groups v(OH). Shift of the bands towards the low frequency area of the spectrum is related with significant molecular interaction. In spectra of calcium, magnesium and aluminium terephthalates there are bands in the range 1612-1621 cm^{-1}, belonging to deformation vibrations of water molecules δ(HOH). That confirms the presence of crystallization water in these salts. Disodium terephthalate has no bands in the range of hydroxyl groups stretching vibrations. In terephthalic acid the bands at 1682 cm^{-1} belong to the stretching vibrations of v(C=O) [Arenas J.F.,1980]. For hydrogen terephthalates there is shift of this band towards the low frequency area of spectrum.

The value of v(C=O) for ammonium hydrogen terephthalate, potassium hydrogen terephthalate and sodium hydrogen terephthalate are 1704, 1702 and 1745 cm^{-1} respectively. All bands are quite intensive, that is related to significant weakening of C=O bond and in accordance with known structural data [Cobbledick R.E., 1972, Keisuko Miyakubo, 1994]. In disodium, calcium and in magnesium terephthalates the absorption in this area is practically absent, and that is due to the transformation of C=O bond to C-O-Me bond.

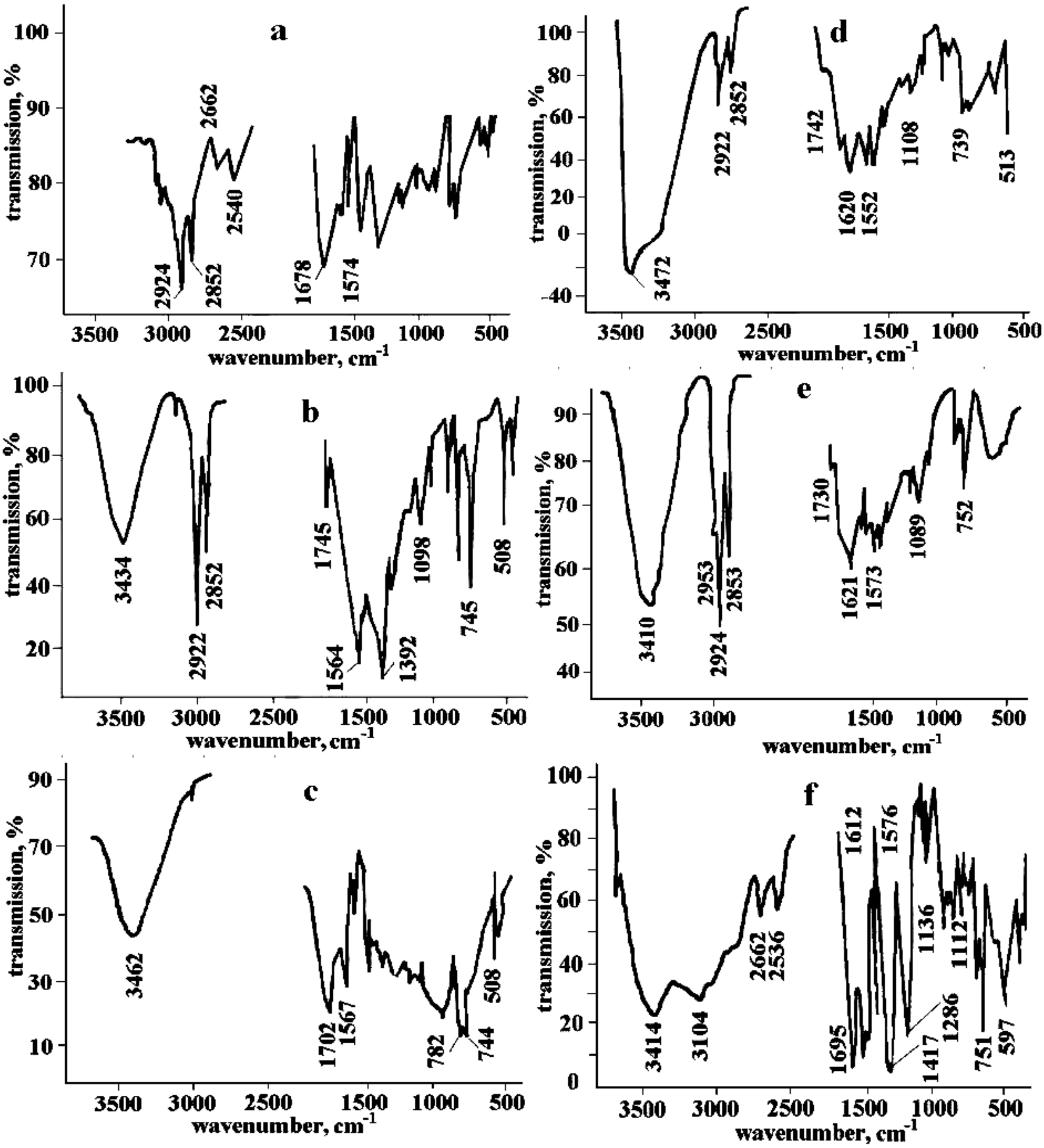


Fig. 3. IR spectra of terephthalates:

a- disodium terephthalate;
b- sodium hydrogen terephthalate;
c- potassium hydrogen terephthalate;
d- calcium terephthalate;
e- magnesium terephthalate;
f- aluminum terephthalate.

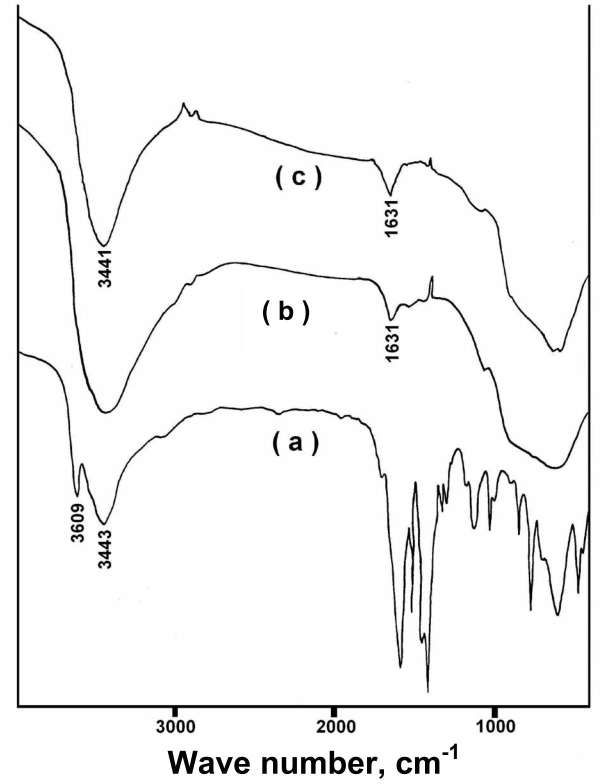
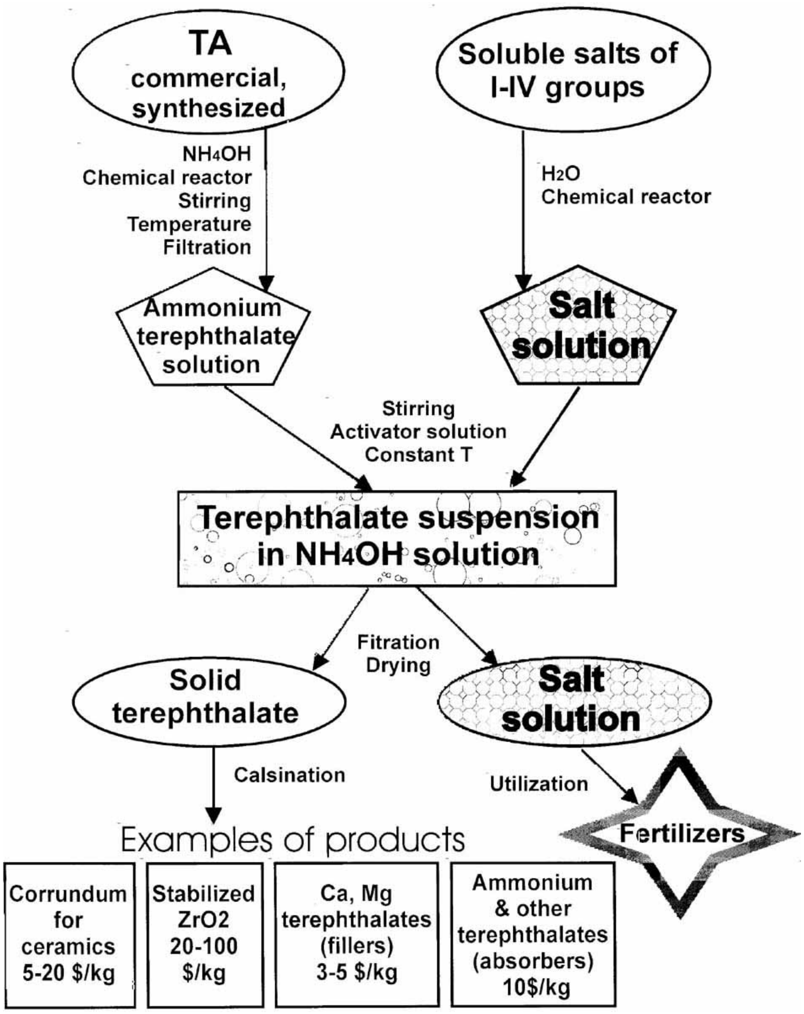


Fig. 4. IR spectra of terephthalates:
$Al_2[C_6H_4(COO)_2]_3.2H_2O$
a – after treatment at 500^{0}C
b – after treatment at 600^{0}C
c – after treatment at 950^{0}C

IR spectra for aluminum terephthalate, obtained upon autoclave treatment, then heated to 500, 600 and 950^{0}C are illustrated in Fig.4. Here we can find peaks belonging to $\nu_{(OH)}$, $\nu_{(CO)}$, $\nu_{(CC)}$, $\nu_{(OCO)}$, $\nu_{(AlO)}$. After heating to product to 500^{0}C the valence OH vibrations at 3609 and 3443 cm^{-1} $\nu_{(OH)}$ do not disappear. Although after reaching 600^{0}C only one them is distinguished (3420 cm^{-1}), besides, deformation vibration of water molecule $\delta_{(HOH)}$- 1631cm^{-1} is noticed, probably due to the polycondensation of the hydroxyl groups. We can propose that upon thermal treatment of aluminum terephthalate aluminum hydroxide is formed, and the later is transformed to γ-$A1_2O_3$ above 500^{0}C. This process is accompanied by of structural water. These vibrations remain noticed up to 950^{0}C. Unhydrated α-$A1_2O_3$ is formed only at 1200^{0}C. Wide reflexes in the X-ray diagrams of γ-$A1_2O_3$ and the unsharp character of the IR spectra in the range 830-570 cm^{-1} are due to the non-ideal crystallic structure of this compound

After heating aluminum and zirconium terephthalates (similarly obtained also by us) at 600^{0}C amorphous oxides of these elements are formed with particle size of 200-300 nm. Further thermal treatment of these compounds up till 1000^{0}C leads to the formation of crystalline forms of these oxides. In this case a gamma form of Al_2O_3 is obtained consisting of well shaped fine crystalline corundum with isometric habitus and particle size of 0.5-0.8 microns. For ZrO_2 such treatment leads to the formation of monoclinic crystals with particle size of 0.5 microns. The use of yttrium oxide in the synthesis of zirconium terephthalate enables us to obtain tetragonal zirconium oxide. From the above mentioned oxides, using the method of slip casting and pressing, we obtain ceramics with high durability
It is possible to say in conclusion, that fine-crystalline oxides CaO, MgO with the particle size of 5-300 microns can be used for manufacturing special ceramics, fire-proof materials.
Sub-micron particles of obtained Al_2O_3 may represent special interest and perspective applications.
The transformation of TA to terephthalates and oxides is demonstrated in the following scheme:

The Scheme of Synthesis of Terephthalates and Oxides of Elements of Groups I-IV



Conclusions

The chemical compound and structure of terephthalates is in favor of their using as fillers for various plastics. Also it is quiet interesting to expose terephthalates to thermal treatment at high temperature to obtain corresponding oxides in fine crystalline form. During this work we obtained fine-grained oxides of calcium, magnesium and aluminum, which can find wide application.

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