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Reactivity of 2-Phosphonobutane-1,2,4-tricarboxylic Acid Esterification†

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In this study, 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTCA), a phosphorus-containing monomer, was used as raw materials to synthesize phosphate polyester polyol by esterification reaction. The esterification of PBTCA was investigated with different small primary alcohols by the change of acid value (A_v) and the products were characterized with Fourier transform infrared spectra and phosphorus nuclear magnetic resonance (^{31}P NMR). The results indicated that there were three types of phosphorus-containing esters formed in the esterification reaction system of PBTCA. Firstly, one of hydroxyl groups in the phosphonic group reacted with small molecules of primary alcohols and then the carboxylic acid groups at 1,4 sites reacted with primary alcohols to form esters. The effects of initial reactant molar ratio and water content of PBTCA on corresponding ester composition were examined.

Keywords: 2-Phosphonobutane-1,2,4-tricarboxylic acid, Esterification, Primary alcohols, ^{31}P NMR.

INTRODUCTION

A novel compound of 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTCA) was first synthesized by German H Geffers in early 1970s[1]. The molecular structure and ball-and-stick model of PBTCA were shown in Fig. 1. PBTCA consists of one phosphonic group and three carboxylic groups, which often used as chelating agents and scale inhibitors. PBTCA are not only chelating many metal ions, but also powerful inhibitors of mineral precipitation and growth. And more over PBTCA is environmentally friendly. So the PBTCA is widely used in desalination systems, cooling waters and in oil fields to inhibit scale formation[2-5].

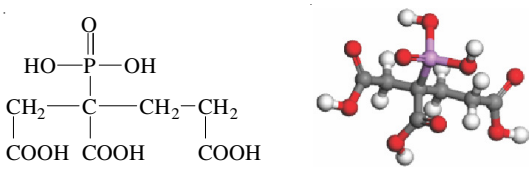

Fig. 1. Molecular structure and ball-and-stick model of PBTCA

The studies[6,7] of PBTCA have traditionally focused on chelating many metal ions and relevant application, for example, Appa Rao reported that a new three-component inhibitor system (PBTCA, with zinc ions and ascorbate) can protect carbon steel from corrosion in low chloride environment. However, PBTCA was less reported in the literature[8] to use as monomer to synthesize phosphate polyester polyol. The aim of the present work was to study the esterification of PBTCA reacted with different small primary alcohols. The effects of initial reactant molar ratio and water content of PBTCA on the esterification reaction were investigated.

EXPERIMENTAL

The 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTCA) was supplied by Jianghai Environmental Protection Co., Ltd (Changzhou, China) as a 50.4 wt % aqueous solution. Methanol, ethanol and *n*-butanol were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

Esterification reaction: The PBTCA was esterified with different small molecules of primary alcohols (methanol, ethanol, *n*-butanol) as following procedures: the methanol and dehydrate PBTCA (water content 14.3 %) were charged to a reaction vessel equipped with a heating mantle, agitator, condenser and thermometer they were mixed uniformly without heating and the original acid value number was measured. Then, the temperature was slowly raised to 70 ºC, the reaction was not terminated until an acid value unchanged by the sampling test. The

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final acid value was measured when the methanol and water were completely dehydrated. Similarly, the other esterification reactions can be carried out using ethanol and *n*-butanol, respectively. The esterification process between PBTCA and different small molecules of primary alcohols were showed in **Scheme-I**.

Measurements: Acid Value (A_v) is expressed as milligrams of NaOH required to neutralize the free acids in one gram of the samples. The acid value can be obtained by following eqn. 1.

$$A_v = \frac{40c(V_s - V_o)}{m} \quad (1)$$

where A_v is the acid value of sample (mg NaOH/g), V_s is the volume of sodium hydroxide used in sample (mL), V_0 is the volume of sodium hydroxide used in blank (mL), c is normality of sodium hydroxide (mol/L), m is grams of sample (g).

Fourier transform infrared spectra (FT-IR) were recorded by using a WQF-300 spectrometer (Beijing, China) with 32 scans and 4 cm^{-1} resolution at the range 4000-400 cm^{-1}.

The phosphorus nuclear magnetic resonance (^{31}P NMR) spectra of PBTCA and its esterification products dissolved in 0.5 mL D_2O (for signal lock) were recorded with a Bruker Avance 400 NMR spectrometer (162.0 MHz for ^{31}P) with proton decoupling using an acquisition time of 0.5 s, a 90º pulse length, 25.0 ºC probe temperature and using 85 % H_3PO_4 as external calibration.

RESULTS AND DISCUSSION

Esterification reaction: Fig. 2 shows the peaks at 2900, 1714 and 1412 cm^{-1}, which can be assigned to O-H, C=O and C-OH characteristic groups of pure PBTCA, respectively. The peak at 1204 cm^{-1} is assigned to the P=O group and the other peaks at 1020 and 927 cm^{-1} are assigned to the P-OH group. By contrast, the C=O stretching frequency of PBTCA was shifted from 1714 to 1730 cm^{-1} and the new peaks at 1170 and 1000 cm^{-1} are assigned to the C-O-C group. These suggests that the O=C-O-C bands are formed between PBTCA and primary alcohols. Weak bands observed in the spectra 927 and 1020 cm^{-1} and a new peak appeared at 1170 cm^{-1} can be interpreted in terms of an interaction of P-OH with the primary alcohols to form P-O-C bonds. Therefore, the FT-IR spectra suggest that the phosphonic groups and carboxyly groups of PBTCA were involved in esterification.

Fig. 3 indicated that four phosphorus-containing products were synthesized in the esterification of PBTCA and different primary alcohols. Based on the ^{31}P NMR of the esters of PBTCA and methanol (ab. MeOH-PBTCA), which was measured again after adding PBTCA in the same tube, only the integration at

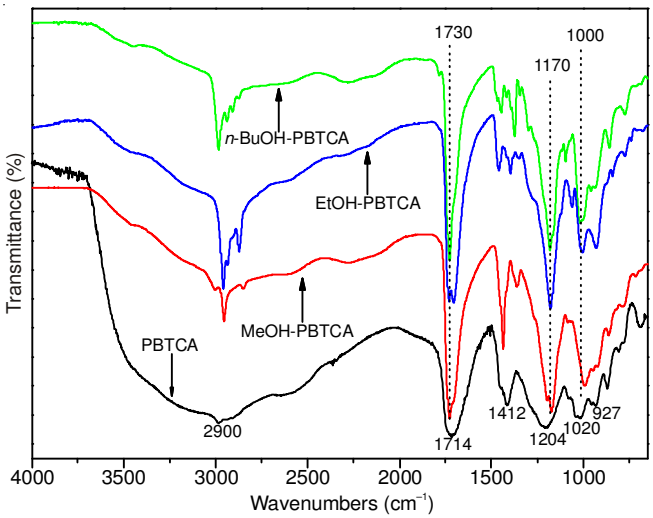


Fig. 2. FT-IR spectra of PBTCA and its esterification products

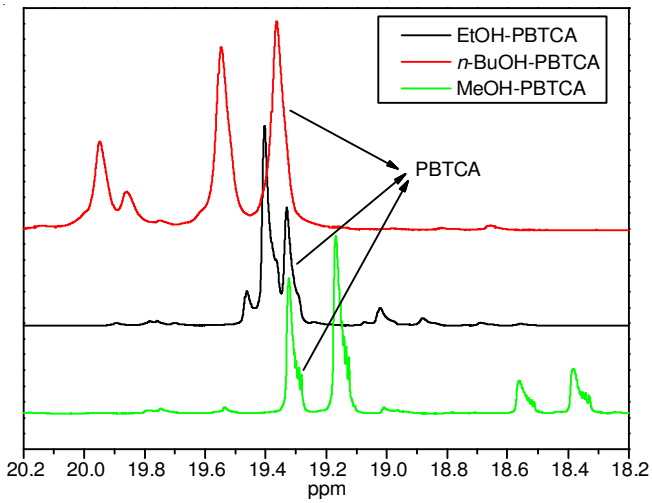
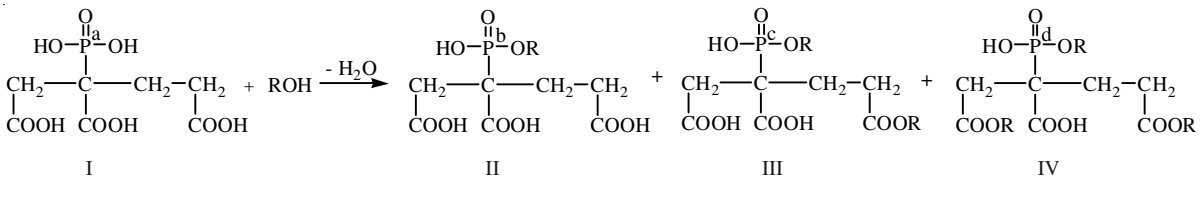


Fig. 3. ^{31}P NMR of the esters of PBTCA and primary alcohols

δ = 19.3 ppm increased. This indicated that the peak at 19.3 ppm was the chemical shift of PBTCA. Thus, three different phosphorus-containing esters were obtained in the esterification of PBTCA with different small molecules of primary alcohols.

$n_{PBTCA}/n_{methanol}$ effect on the esterification reaction: Fig.4 indicated that three phosphorus-containing esters were synthesized with various proportions by changing the $n_{PBTCA}/n_{methanol}$ in esterification. The results inferred that hydroxyl group on the phosphonic group of PBTCA was firstly esterified and then, the 1,4-carboxyly groups followed, as the literature reported[9], resulting in three phosphorus-containing esters (compound **II**, **III** and **IV**, **Scheme-I**). Theoretical acid value of the component of **I**, **II**, **III** and **IV** are 592.6, 422.5, 268.5 and 128.5 mgNaOH/g,



R= $-CH_3$, $-C_2H_5$, $-(CH_2)_3CH_3$

Scheme-I: Reaction of PBTCA and different small molecules primary alcohols

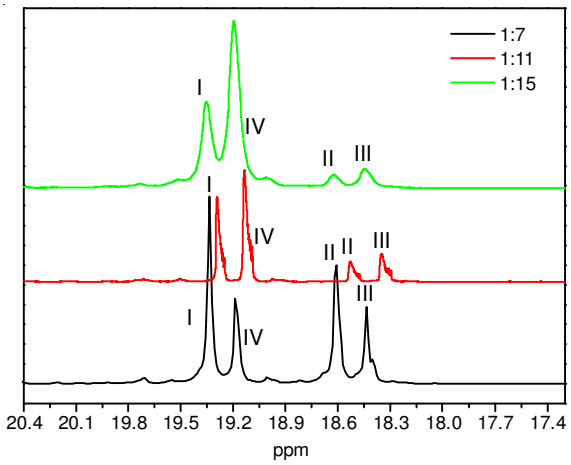


Fig. 4. ^{31}P NMR of the esterification products for different $n_{PBTCA}/n_{methanol}$

respectively. Each peaks of corresponding esters were confirmed by optimal combination as showed in Fig. 4. Component content *vs.* chemical shift of ^{31}P NMR and acid value for different $n_{PBTCA}/n_{methanol}$ are given in Tables 1 and 2, respectively.

TABLE-1
COMPONENT CONTENT *vs.* CHEMICAL SHIFT FOR DIFFERENT $n_{PBTCA}/n_{methanol}$

Chemical shift (ppm) of ^{31}P NMR	Component content (%) in **Scheme-I**	$n_{PBTCA}/n_{methanol}$		
		1: 7	1:11	1:15
19.3	**I**	36.2	31.1	29.9
18.6	**II**	27.5	10.0	4.8
18.4	**III**	16.7	13.7	7.2
19.2	**IV**	19.6	45.2	58.1

TABLE-2
ACID VALUE FOR DIFFERENT $n_{PBTCA}/n_{methanol}$

$n_{PBTCA}/n_{methanol}$	1:7	1:11	1:15
Final acid value(mgNaOH/g)	389.5	305.7	277.0
Theoretical acid value(mgNaOH/g)	400.9	321.6	291.6

Water content of PBTCA effect on the esterification reaction: From Fig. 5 and Tables 3 and 4, all the three phosphorus-containing esters were synthesized by changing the water content of PBTCA in esterification reaction. Each peak of corresponding esters was further verified.

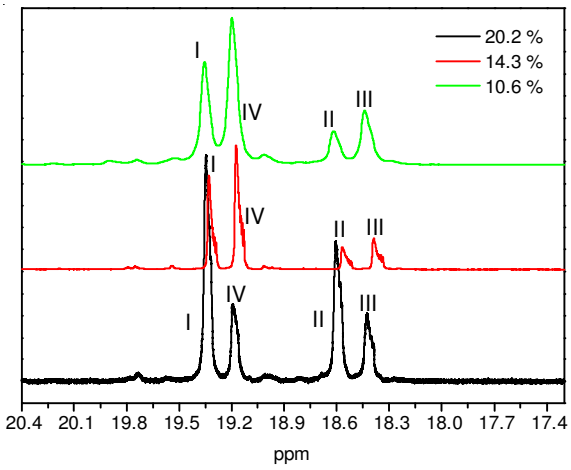


Fig. 5. ^{31}P NMR of the esterification products for different water content

TABLE-3
COMPONENT CONTENT *vs.* CHEMICAL SHIFT FOR DIFFERENT WATER CONTENT OF PBTCA

Chemical shift (ppm) of ^{31}P NMR	Component content (%) in **Scheme-I**	Water content of PBTCA (%)		
		20.2	14.3	10.6
19.3	**I**	40.3	31.1	28.8
18.6	**II**	29.4	10.0	10.4
18.4	**III**	15.0	13.7	17.3
19.2	**IV**	15.3	45.2	43.5

TABLE-4
ACID VALUE FOR DIFFERENT WATER CONTENT OF PBTCA

Water content of PBTCA (%)	20.2	14.3	10.6
Final acid value (mgNaOH/g)	403.2	305.7	296.7
Theoretical acid value (mgNaOH/g)	423.1	321.6	317.0

Conclusion

The phosphonic groups and carboxyly groups of PBTCA were involved in esterification. All components of corresponding esters were confirmed by acid value and ^{31}P NMR. The content of each component of phosphorus-containing esters can be changed by different primary alcohols, $n_{PBTCA}/n_{methanol}$ and the PBTCA with different water content.

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