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Articles

Solubilities of Bis(4-methylphenyl)phosphine Sulfide and Bis(4-carboxyphenyl)phenylphosphine Oxide in Acetic Acid

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The solubilities of bis(4-methylphenyl)phosphine sulfide (BMPPS) and bis(4-carboxyphenyl)phenylphosphine oxide (BCPPO) in acetic acid were measured. The concentration of the solution was determined by sodium hydroxide with phenolphthalein as indicator. The solubilities of BMPPS were measured over the range of 64−104 °C, and the solubilities of BCPPO were measured over the range of 66−106 °C with uncertainties of 3% and 2%, respectively.

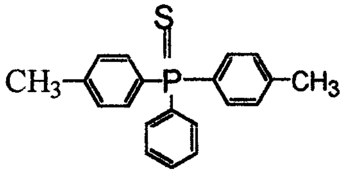
Introduction

Copolymers containing phosphine oxide demonstrate good flame-retarding behavior.[1,2] One of the most important polyester products, flame retardant poly(ethylene terephthalate) (FR-PET), manufactured via direct esterification and polycondensation of ethylene glycol (EG) and terephthalate (TPA) with trivalent phosphine oxide as a comonomer, exhibits improved flame-retarding ability, good fiber-forming properties, and high glass transition temperature.[3]

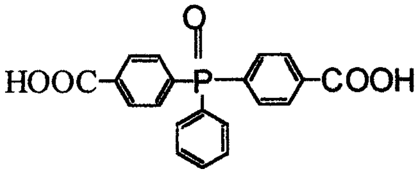
As a dicarboxylic trivalent phosphine oxide monomer, bis(4-carboxyphenyl)phenylphosphine oxide (BCPPO) is a halogen-free flame-retarding agent that eliminates toxicity caused by halogens upon decomposition. The flame-retarding behavior and other properties of FR-PET with BCPPO as comonomer were investigated extensively by Wang et al.[4] The results showed significantly improved thermostability, increased molecular weight, and increased intrinsic viscosity compared with PET resin.

The preparation of BCPPO was previously conducted by direct oxidation of bis(4-methylphenyl)phosphine sulfide (BMPPS) with $KMnO_4$ in two steps.[2] The first step was oxidation of BMPPS in a pyridine solution with excessive $KMnO_4$. The oxidation product in the first step was a white solid. In the second step, the solid was dissolved in aqueous KOH solution and oxidized with a slight excess of $KMnO_4$. In the first step, the reaction mixture was a highly viscous thick mixture, which led to considerable separation difficulties of the oxidized product.

BCPPO:



BMPPS:



Therefore, it is of interest to improve the oxidation process of BMPPS to eliminate difficult separation operations in an industrial application. It is possible to prepare BCPPO by direct oxidation of BMPPS with pure oxygen or air in acetic acid solution under suitable conditions. To accomplish this oxidation process, reliable solubility data of BMPPS and BCPPO in acetic acid are of primary importance.

Experimental Section

Chemicals and Reagents. Both BMPPS and BCPPO were synthesized and characterized according to the literatures.[1−3] The results are as follows: for BMPPS, molar mass = 170.208 $g \cdot mol^{-1}$ and melting point T_m = 154.1 °C; for BCPPO, molar mass = 366.29 $g \cdot mol^{-1}$ and melting point T_m = 337.4 °C. The acetic acid, sodium hydroxide, and phenolphothalein are all analytical reagents from Beijing Chemical Factory. The molar mass of acetic acid = 60.05 $kg \cdot kmol^{-1}$ with a purity of 99.9%. The aqueous NaOH solution was prepared with concentration of n = 2.5686 $mol \cdot L^{-1}$.

Apparatus. The apparatus for the solubility measurement is the same as described in the literature.[2] The equilibrium cell was a sealed 120 mL glass measuring flask. The flask was immersed in a constant-temperature water bath for temperatures <100 °C, and for temperatures >100 °C a glycerine bath was used. The bath temperature control uncertainty is within ±0.1 °C. A magnetic stirrer was utilized for solution preparation. The precision of the analytical balance was 0.1 mg. The mass of samples taken for titration ranged from 19.18 g to 27.94 g.

Solubility Measurement. At each selected temperature, an excessive amount of BMPPS or BCPPO was added to 100 g of acetic acid and constant stirring was applied.

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At an interval of 30 min, the stirrer was stopped and then the solution was kept still for 30 min; the excessive solid could be observed to settle in the lower portion of the equilibrium cell. The clear upper portion of the solution was withdrawn from the cell to another measuring flask and weighed with analytical balance; the flask was then immersed in the same bath. The concentration of the solution was determined by sodium hydroxide titration with phenolphthalein as indicator.

If the total mass of the sampled solution is represented as m/g and the mass of BMPPS or BCPPO in the solution is assumed as m_1/g, the mass of HAC as m_2/g, the volumetric consumption of NaOH solution for titration as V/mL with concentration of n mol·L^{-1}, then

$$m_1 + m_2 = m \qquad (1)$$

with known m. From the quantitative reactions of NaOH with HAC and BCPPO, two additional equations can be obtained, that is

$$m_2/60.05 = nV/1000 \qquad (2)$$

for BMPPS (no reaction between BMPPS and NaOH) and

$$2m_1/366.29 + m_2/60.05 = nV/1000 \qquad (3)$$

for BCPPO with known n and V. Both m_1 and m_2 can be solved from these combined equations of mass balance and quantitative reactions. Molar fraction solubility can be determined accordingly.

Repeated processes were performed for different dissolution times to determine how long it would take to reach equilibrium. It was found that 150 min would be enough for both BMPPS and BCPPO in pure acetic acid within the measuring temperature ranges. For each measuring temperature, the titration operation was conducted three times and an averaged value was taken.

Correlation

The mole fraction solubilities of BMPPS and BCPPO were correlated as a function of temperature (T) by adopting a second-order polynomial:

BMPPS

$$s = 0.2956 - 8.221 \times 10^{-3}(T/°\text{C}) + 6.132 \times 10^{-5}(T/°\text{C})^2 \qquad (4)$$

BCPPO

$$s = 1.026 \times 10^{-2} - 2.221 \times 10^{-4}(T/°\text{C}) + 1.873 \times 10^{-6}(T/°\text{C})^2 \qquad (5)$$

Table 1. Measured *s* and Smoothed *s* (Calculated) Mole Fraction Solubility of BMPPS and BCPPO in Acetic Acid

		10^3s (measured)				
	T/°C	1	2	3	av	10^3s (calcd)
BMPPS	64	20.02	20.32	19.07	19.81	(20.64)
	72	21.84	22.49	21.74	22.02	(21.59)
	79	30.18	30.64	30.81	30.55	(28.86)
	84	38.79	38.89	37.91	38.53	(37.74)
	89	47.64	48.38	48.12	48.06	(49.68)
	96	69.80	69.25	70.29	69.77	(71.54)
	104	105.1	105.5	104.9	105.2	(103.9)
BCPPO	66	3.854	3.805	3.903	3.854	(3.761)
	73	3.952	3.903	3.903	3.919	(4.029)
	84	4.586	4.732	4.732	4.683	(4.821)
	90	5.494	5.624	5.462	5.527	(5.444)
	95	6.111	6.062	6.305	6.159	(6.066)
	99	6.677	6.693	6.758	6.710	(6.631)
	106	7.711	7.695	7.582	7.663	(7.764)

The measured solubility and the smoothed data based on eq 4 for BMPPS in the temperature range of 64−104 °C and based on eq 5 for BCPPO in the range of 66−106 °C are presented in Table 1. The absolute average deviation (AAD%) of the measured solubility to the smoothed data is defined as

$$\text{AAD\%} = \frac{1}{N}\sum_i |s_i^{\text{exptl}} - s_i^{\text{calcd}}|/|s_i^{\text{exptl}}| \times 100$$

where the superscript exptl stands for experimental and calcd stands for calculated values, respectively. The absolute average deviations of the measured solubility to the smoothed data of BMPPS and BCPPO in Table 1 are 3% and 2%, respectively.

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