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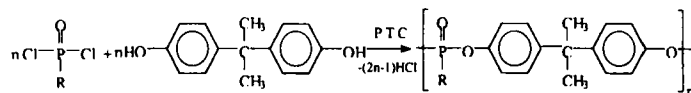
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Synthesis of Phosphorus Containing Polymers by Phase Transfer Catalysis (PTC). I. Comparative Study between Liquid-Liquid and Liquid-Vapor Systems

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Polyphosphonates were synthesized by interfacial alkaline polycondensation of bisphenol A (BA) with phenyldichlorophosphonate (PPD) and cyclohexyldichlorophosphonate (CPD) in liquid-liquid^[1] (l-l) and liquid-vapor^[2] (l-v) systems.



Different base concentrations, molar ratios (PPD/BA or CPD/BA) and temperatures were applied and the yield (η) and inherent viscosity (η_{inh}) of the products were determined. In both systems the best results were obtained with 1-2 M aqueous solutions NaOH (i.e. with 1.5 M NaOH, for $R=C_6H_5$, in l-l, $\eta=60\%$ and $\eta_{inh}=0.80$ dl/g, in l-v, $\eta=65\%$, $\eta_{inh}=0.95$ dl/g; and for $R=C_6H_{11}$, in l-l, $\eta=55\%$, $\eta_{inh}=0.72$ dl/g; in l-v, $\eta=60\%$, $\eta_{inh}=0.90$ dl/g).

Concerning to the molar ratios (varied in either direction from unity) better results were found with an excess of phosphonic dichloride (with PPD:BA=0.75, in l-l, $\eta=45\%$ and $\eta_{inh}=0.58$ dl/g, in l-v, $\eta=48\%$, $\eta_{inh}=0.62$ dl/g; with PPD:BA=1.30, in l-l, $\eta=65\%$, $\eta_{inh}=0.78$ dl/g; in l-v, $\eta=70\%$, $\eta_{inh}=0.95$ dl/g; with CPD:BA=0.75, in l-l, $\eta=40\%$ and $\eta_{inh}=0.57$ dl/g, in l-v, $\eta=52\%$, $\eta_{inh}=0.65$ dl/g; with CPD:BA=1.30, in l-l, $\eta=65\%$, $\eta_{inh}=0.75$ dl/g; in l-v, $\eta=68\%$, $\eta_{inh}=0.94$ dl/g).

The influence of the temperature are as follows: in l-l, the yields and inherent viscosities increase with decrease of the temperature, whereas, in l-v will show an increase in yield and inherent viscosity as the temperature is increased. (i.e., at $T=0^\circ C$, for $R=C_6H_5$, in l-l, $\eta=72\%$ and $\eta_{inh}=0.85$ dl/g; and for $R=C_6H_{11}$, in l-l, $\eta=70\%$, $\eta_{inh}=0.82$ dl/g; at $T=25^\circ C$, for $R=C_6H_5$, in l-l, $\eta=40\%$ and $\eta_{inh}=0.48$ dl/g; and for $R=C_6H_{11}$, in l-l, $\eta=32\%$, $\eta_{inh}=0.30$ dl/g; at $T=35^\circ C$, for $R=C_6H_5$, in l-v, $\eta=30\%$ and $\eta_{inh}=0.42$ dl/g; and for $R=C_6H_{11}$, in l-v, $\eta=25\%$, $\eta_{inh}=0.38$ dl/g; at $T=60^\circ C$, for $R=C_6H_5$, in l-v, $\eta=75\%$ and $\eta_{inh}=0.72$ dl/g; and for $R=C_6H_{11}$, in l-v, $\eta=70\%$, $\eta_{inh}=0.70$ dl/g).

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