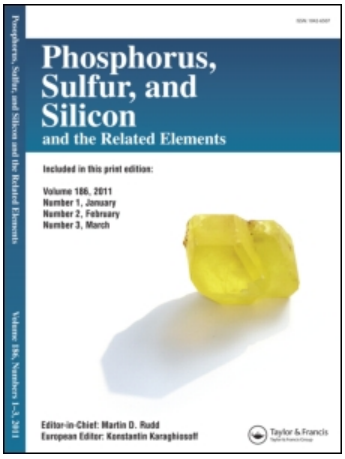

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MECHANISM OF POLYMER PHOSPHATE CLASSES ANION STRUCTURE FORMATION

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The purpose of this work is to determine the influence of the cation nature, Me/P ratio and the conditions of synthesis on the molecular mass distribution of linear and cyclic anions and the rate of branching the structure in glasslike phosphates. More than ca. 2000 samples with the average chain length ($\bar{n}$) from 2 to 800 have been examined by a set of methods including chromatography, ultracentrifugation, measuring of light scattering, etc. Sometimes original methods were designed. Quantitative comparision of the results with the well-known models has been carried out. It was established that (without taking into account the cycles) the chain contents of the glasses goes back to the model "flexible chain" diminishing the degree of the ionicity Me-O bonds, e.g. in the row Cs-Rb-K-Na-Li-Ca-Mg--Zn-Cu. For the sodium phosphate glasses ($n < 15$) the "diphosphate" model is the most applicable while changing the "a"-parameter: $a = 0.98 + 6O\bar{n}^{-3}$. The mass portion (W) of the cycles, as a rule, increases with the growth of the flexibility of chains and $\bar{n}$, so $W\ Na_3P_3O_9 = 0.052\cdot(1-2/\sqrt{\bar{n}})$. We used a model which takes into account the cycle-formation. The branching of chains at $Me/P \geqslant 1$ is due to mutual transformation of the structural units: 2 middle ⟸ end + + branched. At rather low water vapour partial pressure over the initial melt only end groups in P-OMe form should be taken into account. Thus, the branching number depends on the ratio Me/P, but not on $\bar{n}$. The equilibrium constant decreases with the increase of the degree Me-O bond ionicity and is: $K-1\cdot10^{-6}$, $Na-4.8\cdot10^{-6}$, $Li-7.2\cdot10^{-5}$, $Ca-2.9\cdot\cdot10^{-4}$, $H-1.8\cdot10^{-3}$. This constant (K) value determines maximum possible $\bar{n}$, so at Me/P=1: $\bar{n}_{glass}=2/\sqrt{K}$, $\bar{n}_{solution}=1/\sqrt{K}$.