

Preparation of Polystyrenylphosphonous Acid of Low Polymerization Degree and Influence of Initiators upon the Free Radical Reaction Mechanism

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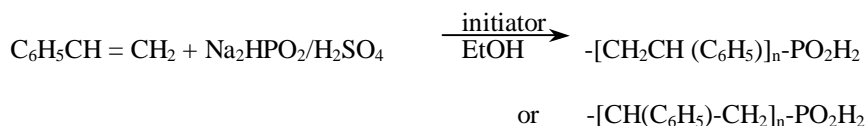
Abstract: The polystyrenylphosphonous acid (PSPA) of low polymerization degree was prepared with one step reaction. The reaction mechanism was changed with different initiators. For the reaction with AIBN or BPO as the initiator, there are 2 or 3 series of radical reaction chains and 5 or 9 series of polystyrenyl products. The main products are PSPA without or with the fragment of the initiator $\text{H}[\text{CH}(\text{C}_6\text{H}_5)\text{-CH}_2]_n\text{-PO}_2\text{H}_2$ and $\text{C}_6\text{H}_5\text{CO}_2\text{-}[\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)]_n\text{-PO}_2\text{H}_2$ respectively.

Keywords: Polystyrenylphosphonous acid (PSPA), low polymerization degree, 2, 2'-azobisisobutyronitrile (AIBN), benzoyl peroxide (BPO), reaction mechanism.

Organophosphorus chemistry plays an important role in chemical engineering, pesticide, medicine and catalysis^{1,2}. In recent years, after extensive research and widespread application, synthesis and preparation of new organophosphorus compounds have attracted increasing research interest. Polystyrene is a very important and versatile matrix or precursor of various kinds of functional polymer. Usually, introducing of phosphonic $\text{-PO}_3\text{H}_2$ or phosphinic $\text{-PO}_2\text{H}_2$ group into polystyrene matrix through at least two or three reaction steps.

The phosphonic acid derivatives of organophosphorus compounds including polystyrenylphosphonic acid may be used as chelating resin and preparation of zirconium or titanium phosphatephosphonate which is a new kind of matrix or precursor of mixed organic-inorganic polymer functional material³.

Herein we report the preparation of PSPA with low polymerization degree in one step of free radical reaction with styrene, sodium phosphinate, sulfuric acid and free radical initiator in ethanol for the first time:



Experimental

0.5 mol $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ (53.0 g), 0.15 mol styrene (15.6 g), 300 mL of ethanol, and 14 mmol of AIBN or BPO were mixed with stirring, 13.2 mL of concentrated sulfuric acid was added dropwise. The reaction mixture was heated to refluxing and stirred for 6 hr, then another 9.5 mmol of AIBN or BPO was added, and the reaction mixture was kept refluxing and stirring continuously for additional 12-16 hr. The white solid was filtered out, ethanol in the filtrate was evaporated, and 80 mL of water was added into the residue. The resulting solution was extracted with ethyl acetate (3×30 mL), and the combined organic phase was dried over anhydrous sodium sulfate. The ethyl acetate was evaporated, the resulting thick liquid residue was the product PSPA.

The product PSPA was characterized by IR and MS, and the average polymerization degree of the product was determined with terminal group analysis method.

Results and Discussion

Except of the IR absorption peaks of the polystyrenyl and phosphinic group, the IR spectrum of the product A which is initiated with AIBN shows the presence of CN group (2226 cm^{-1} , very weak and small peak), and the IR spectrum for product B which is initiated by BPO, indicates the presence of PhCOO group (1710 cm^{-1} , the signal is stronger than that of CN group).

Usually, the yield of product B is more than that of product A by 25 - 35 percent, and the product A is more sticky than the product B, which means that the average molecular weight and average polymerization degree of product A are larger than that of product B. The results of the terminal group analysis indicate: the average polymerization degree of the product A is about 10 - 40 and 5 - 15 for product B.

The MS instrument could demonstrate up to 1000 m/z peaks, but less than 600 m/z peaks were given here. The dominant m/z peaks of MS and corresponding fragments for product A are:

The strong peaks: m/z 64 (PO_2H^-), 77 (C_6H_5^-), 90 ($\text{C}_6\text{H}_5\text{CH}^-$), 104 ($\text{PhCH}=\text{CH}_2$), 170, 274, 378, 482 [$\text{H}-(\text{PhCHCH}_2)_n-\text{PO}_2\text{H}_2$ $n=1, 2, 3, 4$]; The middle peaks: m/z 237, 341, 445 [$(\text{CH}_3)_2\text{C}(\text{CN})-(\text{CH}_2\text{CHPh})_n-\text{PO}_2\text{H}_2$ $n=1, 2, 3$]; The weak peaks: m/z 173, 277, 381, 485 [$(\text{CH}_3)_2\text{C}(\text{CN})-(\text{CH}_2\text{CHPh})_n-\text{H}$ $n=1, 2, 3, 4$]; 210, 311, 417, 522 [$\text{H}-(\text{CH}_2\text{CHPh})_n-\text{H}$ $n=1, 2, 3, 4$]; 240, 448 [$(\text{CH}_3)_2\text{C}(\text{CN})-(\text{CH}_2\text{CHPh})_n-(\text{CN})\text{C}(\text{CH}_3)_2$ $n=1, 3$].

The main m/z peaks of MS and corresponding fragments for product B are:

The strong peaks: m/z 64 (PO_2H^-), 77 (C_6H_5^-), 90 ($\text{C}_6\text{H}_5\text{CH}^-$), 104 ($\text{PhCH}=\text{CH}_2$), 290, 394, 498 [$\text{PhCO}_2-(\text{CH}_2\text{CHPh})_n-\text{PO}_2\text{H}_2$ $n=1, 2, 3$]; The middle peaks: m/z 170, 274, 378, 482 [$\text{H}-(\text{PhCHCH}_2)_n-\text{PO}_2\text{H}_2$ $n=1, 2, 3, 4$]; The weak peaks: m/z 182, 390 [$\text{H}-(\text{PhCHCH}_2)_n-\text{Ph}$ $n=1, 3$]; 210, 311, 417, 522 [$\text{H}-(\text{CH}_2\text{CHPh})_n-\text{H}$ $n=1, 2, 3, 4$]; 246, 350 [$\text{Ph}-(\text{CH}_2\text{CHPh})_n-\text{PO}_2\text{H}_2$ $n=1, 2$]; 302, 406, 510 [$\text{PhCO}_2-(\text{PhCHCH}_2)_n-\text{Ph}$ $n=1, 2, 3$]; 329, 434 [$\text{PhCO}_2-(\text{PhCHCH}_2)_n-\text{H}$ $n=2, 3$]; 346, 450, 554 [$\text{PhCO}_2-(\text{PhCHCH}_2)_n-\text{O}_2\text{CPh}$ $n=1, 2, 3$]; 362, 466 [$\text{Ph}-(\text{PhCHCH}_2)_n-\text{Ph}$ $n=2, 3$].

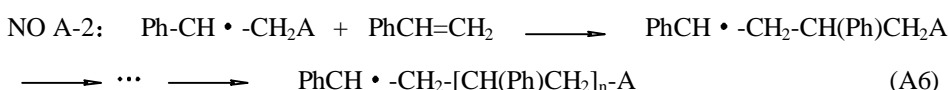
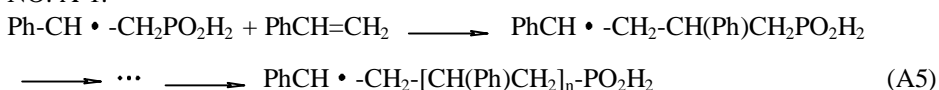
According to the above MS data, it is deduced that the free radical reaction mechanisms were different with two initiators. For the reaction with AIBN as the initiator, there are two series of radical reaction chains:

Chain initiate:



Chain propagation:

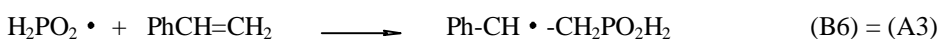
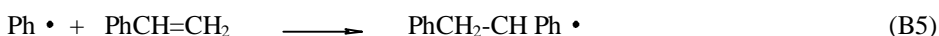
NO. A-1:



Chain termination include a few reactions such as recombination, disproportionation, and the main termination reaction is recombination, according to the reference⁴. Thus, the product A which was initiated with AIBN is formed with five series of polystyrenyl compounds, they are: $(\text{CH}_3)_2\text{C}(\text{CN})\text{-[CH}(\text{C}_6\text{H}_5)\text{-CH}_2\text{]}_n\text{-PO}_2\text{H}_2$ and $(\text{CH}_3)_2\text{C}(\text{CN})\text{-[CH}_2\text{-CH}(\text{C}_6\text{H}_5)\text{]}_n\text{-PO}_2\text{H}_2$ (AII), $\text{H- [CH}(\text{C}_6\text{H}_5)\text{-CH}_2\text{]}_n\text{-}(\text{CH}_3)_2\text{C}(\text{CN})$ (AIII), $\text{H- [CH}(\text{C}_6\text{H}_5)\text{-CH}_2\text{]}_n\text{-H}$ (AIV), $(\text{CH}_3)_2\text{C}(\text{CN})\text{-[CH}_2\text{-CH}(\text{C}_6\text{H}_5)\text{]}_n\text{-}(\text{CH}_3)_2\text{C}(\text{CN})$ (AV), $\text{H}_2\text{O}_2\text{P- [CH}(\text{C}_6\text{H}_5)\text{-CH}_2\text{]}_n\text{-H}$ (AI), and among them the main product is the PSPA without the fragment of the initiator (AI). The amount of the polystyrene with or without the fragment of the initiator (AIII), (AIV) and (AV) is about 5-8 % of the product A.

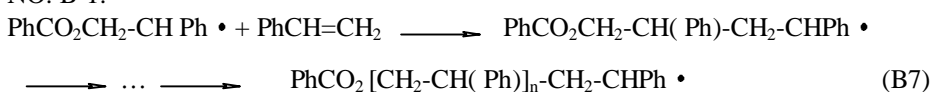
For the reaction initiated with BPO, there are three series of radical reaction chains:

Chain initiate:

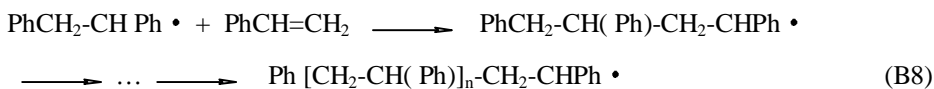


Chain propagation:

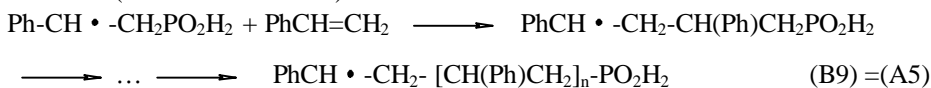
NO. B-1:



NO. B-2:



NO. B-3: (as same as NO. A-1)



Chain termination also takes several reactions such as recombination, disproportionation, and the main termination reaction is recombination too. Thus, the product B with BPO as the initiator is composed of nine series of polystyrenyl compounds, they are: Ph[CH(C₆H₅)-CH₂]_n-PO₂H₂ and Ph-[CH₂-CH(C₆H₅)]_n-PO₂H₂ (BI), PhCO₂-[CH(C₆H₅)-CH₂]_n-PO₂H₂ and PhCO₂-[CH₂-CH(C₆H₅)]_n-PO₂H₂(BII), H-[CH(C₆H₅)-CH₂]_n-PO₂H₂ (BIII=A1), PhCO₂-[CH₂-CH(C₆H₅)]_n-H(BIV), PhCO₂-[CH(C₆H₅)-CH₂]_n-O₂CPh (BV), Ph-[CH₂-CH(C₆H₅)]_n-H(BVI), Ph-[CH(C₆H₅)-CH₂]_n-Ph(BVII), PhCO₂-[CH(C₆H₅)-CH₂]_n-Ph (BVIII), H-[CH(C₆H₅)CH₂]_n-H (BIX=AIV), and among them the main product is the PSPA with the fragment of the initiator (BII). The total amount of the polystyrene with or without the fragment of the initiator (BIV) to (BIX) is also about 5 - 8% of the product B.

References

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