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Quantum Mechanical Computation and Experiments of Solvation Effect on Polymerization Reactions of Polyphosphazene

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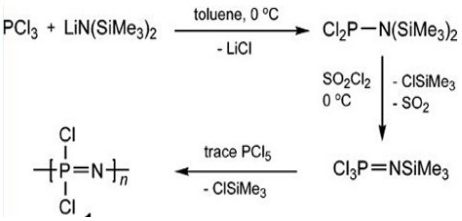
Highlights

- Interaction between $[PCl_6]^-$ anion and reactive cations in the polymerization of polyphosphazene has been simulated by quantum mechanical computation
- Calculated standard-state free energy of the polymerization in different solvents is in accord with corresponding dielectric properties.
- Using m-xylene as a solvent can better restrain the oligomerization and facilitate further improvements on polymerization of polyphosphazene.

1. Introduction

Polyphosphazenes are inorganic polymers based on the repeating unit $[N=PR_2]_n$, where R can be substituted by organic groups from $[N=PCl_2]_n$， with uses as high performance elastomers, polymeric electrolytes and biomedical materials. Recently, a living cationic polymerization to synthesis $[N=PCl_2]_n$ directly from PCl_3 using a one-pot route at ambient temperature in solvent presents great potential for large-scale and industrial polyphosphazene preparations.[1] Nevertheless, previous study shows that the [PCl6]$^-$ anion has hitherto been assumed to initiate oligomerization which leads to broad molecular weight distributions. In addition, different solvents can significantly alter the rates of the living cationic polymerization and quantum mechanical computation can be used to describe the solvation effect.



In our study, the interaction between $[PCl_6]^-$ anion and reactive cations in different solvents has been simulated by Gaussian09. Furthermore, selected solvents have been verified by experiments and the structures of products are investigated.

2. Methods

Computational methods. The electronic energy and the standard-state free energy of the polymerization in different solvents (dioxane, toluene, m-xylene and acetonitrile) have been computed with Gaussian 09 using the B3LYP/6-311G(d) functional. The structures of [PCl6]$^-$ anion and different polymerization degree reactive cations(n=1-3) were optimized using the same functional. The solvent properties required in the model were computed by PCM model. The ability of the conjunction between anions and cations was computed using transition-state theory, according to the following equation:

$$\Delta^{\ddagger}E^{el} = E^{el}_{(AB)^{\ddagger}} - E^{el}_{A} - E^{el}_{B}$$

$$\Delta^{\ddagger}\Delta G^{o,solv} = \Delta G^{o,solv}_{(AB)^{\ddagger}} - \Delta G^{o,solv}_{A} - \Delta G^{o,solv}_{B}$$

where E^{el} is the gas phase electronic energy, $\Delta G^{o,solv}$ is the standard-state free energy of solvation and $\Delta\ddagger$ indicates that an activation energy barrier is being calculated.

Experimental methods. $LiN(SiMe_3)_2$ (1.73g,10.3mmol) was dissolved in 40 mL of dioxane (toluene, m-xylene and acetonitrile, respectively), and the solution was cooled to 0°C. PCl_3(0.9mL,10.3mmol) was then added dropwise over 10 min. The resulting mixture was stirred for 30min at the same temperature followed by stirring at room temperature for 1h, giving a white suspension. SO_2Cl_2(0.85mL,10.5mmol) was then added dropwise over 10min to this suspension at 0°C. The reaction was allowed to proceed at 0°C for 1 h. PCl_5(106mg, 0.51mmol) was then added, and the resultant mixture was stirred overnight at room temperature. $[N=PCl_2]_n$ was observed from ^{31}P-NMR (toluene/$CDCl_3$).

3. Results and discussion

Figure.1 shows optimized ionic structures computed by Gaussian09 and the calculated average bond length of P-N and P-Cl of B1-B3 are fitted well with literature data(0.20nm and 1.65nm, respectively). This result means that the B3LYP/6-311G(d) functional can be used to calculate the electronic energy and the standard-state free energy of the polymerization in different solvents.

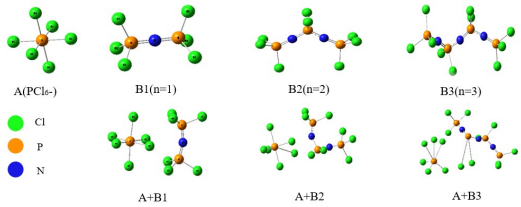


Figure 1. Optmized structures of A($[PCl_6]^-$) anion and B1-B3(reactive cations polymerization degree n=1-3, respectively)

According to Figure.2(a), the electronic energy and the standard-state free energy increase with increasing dielectric constant of solvents and it is estimated that the interaction between anions and cations decreases with the increasing value of dielectric constant. In addition, Figure.2(b) shows that the standard-state free energy increase with the increase of polymerization degree. This coincides with the assumption that oligomerization happens in the early stages of the polymerization due to the appearance of $[PCl6]^-$ anion. [2]

(a)

Solvent	ΔE^{el}	$\Delta G^{o,solv}$	dielectric constant
gas		-94.79	
dioxane	-41.27	-32.14	2.10
toluene	-25.58	-13.02	2.24
m-xylene	1.32	1.46	2.78
acetonitrile	-5.77	13.87	37.50

(b)

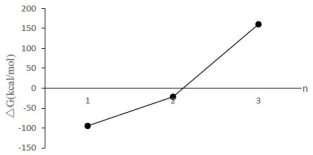
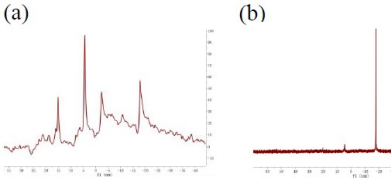


Figure 2. (a)Calculated electronic energy, standard-state free energy and dielectric constant in different solvents, (b)Relation between polymerization degree and standard-state free energy

$[N=PCl_2]_n$ prepared in different solvents have been observed with different response values from ^{31}P-NMR (-17.6 ppm), which fit well with the standard-state free energy in different solvents except acetonitrile(Figure.3). The experimental results show that m-xylene has better effect on polymerization of polyphosphazene, which means quantum mechanical computation can be used to guide solvent selection.

(a) (b) (c) (d)



(e)

Solvent	$\Delta G^{o,solv}$	response value
dioxane	-32.14	60
toluene	-13.02	6800
m-xylene	1.46	25000
acetonitrile	13.87	0

Figure 3. ^{31}P-NMR results in different solvents(a) Dioxane,(b)Toluene(c) M-xylene (d) Acetonitrile (e) Standard-state free energy and response value in different solvents

4. Conclusions

Solvation effect has great influence on the interaction between $[PCl_6]^-$ anion and reactive cations, which has been simulated by Gaussian09 and supported by experiments. Besides, m-xylene shows better effect on restraining oligomerization in the process. Our work facilitates further improvements on polymerization of polyphosphazene and can guide solvent selections of other living cationic polymerization system.

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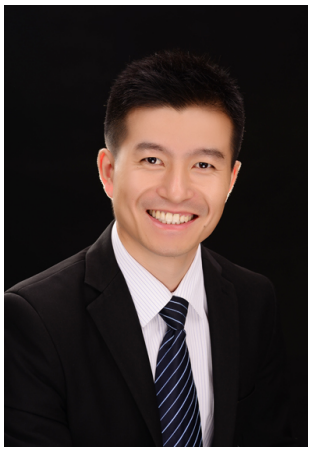
Keywords
Polyphosphazene, living cationic polymerization, solvation effect, quantum mechanical computation

Curriculum Vitae



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Research Description

- Polymerization reaction engineering
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- Computational Fluid Dynamics (CFD) and numerical simulation
- Polymers processing with Supercritical Fluids
- Design and process optimization and intensification
- Bio-based polymers engineering and tissue engineering scaffolds
- Microcellular injection molding and micro foaming

Honors

- Sino-French Outstanding Young Investigator, 2017
- Shanghai Rinsing-Star Award, 2016
- Hou Debang Chemical Science and Technology Award for Young Investigator, 2016
- Best paper award, Conference on Chemical Engineering and Technology (China), 2016
- China patent award, Seventeenth China Patent Award, 2016
- Second Prize of Ningxia Award for Science and Technology Progress, 2015
- Excellence Award in China Industry-University-Research Institute Collaboration, 2016
- First Prize of Shanghai Technological Invention Award, 2014
- Shanghai Outstanding Young Teacher, 2012

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[5] Kinetics of Epoxidized Vegetable Oil and A Green Hardener Based on Non-Isothermal DSC Method, ***ISCRE (International Symposium on Chemical Reaction Engineering) 2016***, 2016.06.12-15, Minneapolis, USA **(Poster)**

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[11] Experimental and Numerical Study of Foaming Injection Molding of Polypropylene / nano-Calcium Carbonate Composites by Supercritical Carbon Dioxide. ***ANTEC 2014***, 2014.04.28-30, Las Vegas, USA **(Oral)**

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