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Jianmei Lu[a]; Shun-jun Ji[a]; Jianfei Wu[a]; Feng Guo[a]; Hui Zhou[a]; Weiquan Dai[a]; Xiulin Zhu[a]
[a] Department of Chemistry and Chemical Engineering, Suzhou University, Suzhou, P. R. China

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# STUDY OF MICROWAVE IRRADIATION POLYMERIZATION IN THE PRESENCE OF DIFFERENT CARRIERS

**Jianmei Lu,* Shun-jun Ji, Jianfei Wu, Feng Guo, Hui Zhou,
Weiquan Dai, and Xiulin Zhu**

Department of Chemistry and Chemical Engineering,
Suzhou University, Suzhou 215006, P. R. China

## ABSTRACT

The influence of the presence of an inorganic carrier in the polymerization systems was investigated in this paper. Ten polymerization systems that contained different inorganic carriers such as $Al_2O_3$, $SiO_2$ were studied. The ten polymerization systems are dibutyltin Maleate (DBTM) and allyl thiourea (AT), DBTM and stearic acid vinyl ester (SAVE), SAVE and maleic anhydride (MH), SAVE and acrylamide (AM), itaconic acid (IA) and AM, SAVE and IA, AM and MH, IA, sodium acrylate (AANa), AM. It was found that the activity of monomer can be changed in the presence of a carrier and furthermore, the different species of carrier influence the activity of same monomer differently in the polymerization.

*Key Words*: Inorganic carrier; $Al_2O_3$, $SiO_2$; Polymerization; Microwave irradiation

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*Corresponding author.

## INTRODUCTION

Some research [1–8] has been done with organic reactions in the presence of inorganic carriers. It was found that if the reaction system has no solvent, but a solid carrier, then its rate of reaction will be greater than the one that has only the solvent. At the same time, because of a lack of solvent, the previous system has two advantage—one is the different selectivity of reaction, and the other is it is cheaper. The influence of the inorganic carrier has not been reported in polymerization. In this work, ten polymerization systems in the presence of different carriers irradiated under microwave irradiation were studied. In the two copolymerizations of DBTM and AT, DBTM and SAVE, the inherent viscosity of polymer and the percent conversion in the presence of $Al_2O_3$ were both greater than the two which contained $SiO_2$, and the activity of polymeric monomer were also changed. The different species of carrier influence the polymerization differently. In order to confirm the influence of the carrier to polymerization, the other eight polymerization systems were studied.

## EXPERIMENTAL

### Base Material

$Al_2O_3$ (particle diameter = 0.236 μm), SAVE: analytically pure; $SiO_2$ (particle diameter = 0.208 μm), AT, AM, IA, MH, DBTM: chemically pure; AANa: prepared with acrylic acid.

### Procedure of Polymerization

Solid-phase polymerization under microwave irradiation was carried out in a special vial, the monomer (Note 1) was degassed with $N_2$ for 30 minutes, and the same original temperature was always required. The mixed monomers reacted at the best temperature (Note 2) and was always protected by $N_2$. The method of intermission irradiation was adopted during the course. After a given time, the mixture was poured into a precipitator (Note 3), and the polymer was separated out, filtering, washing, drying at a lower temperature under vacuum until it reached a constant weight. It was then weighed and the percent conversion was worked out.

[Note 1]: If the polymerization system contain carrier then it should be ground with monomer together

[Note 2]: The best temperature means the temperature closest to melting point of system but the monomer will be not melted.

[Note 3]: A ethyl acetate/methanol solution (1:1) is the precipitator of DBTM-SAVE system; methanol is the precipitator of the other systems.

## Measurement

### Determination of Reactivity Ratio [9]

Solid-state polymerization was carried out in the special vial, irradiated after a given time at the power of 430 w, the reaction was ended by adding a hydroquinone inhibitor into the solid system. The percent conversion was controlled below 10%. The composition of the copolymer was determined by a liquid chromatogram (Shimadzu model LC-6A. Chromatographic column condition: filler – cyan column, size – 4.6 × 150 mm, velocity of flow – 0.8 mL/min). The reactivity ratios were worked out by the Lewis and Mayo equation.

### Determination of Inherent Viscosity

The polymer inherent viscosity was determined by one-point method separately at 30.0 ± 0.5°C conditions as follow: DBTM-AT system, inner diameter of Umstatter viscometer is 0.35 mm, 20:1 chloroform-acetic acid solution; DBTM-SAVE system, the inner diameter is 0.7 mm, 3:1 benayl alcohol-chloroform solution.

## RESULTS AND DISCUSSION

## Copolymerization of DBTM and AT

### Reactivity Ratios of Two Monomers Under Microwave Irradiation

The Lewis and Mayo composition equation is represented as follows:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \times \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} \tag{1}$$

$M_1$ – the concentration of AT in the system,
$M_2$ – the concentration of DBTM in the system,
$r_1$ – reactivity ratio of AT,
$r_2$ – reactivity ratio of DBTM.

If $b = [M_1]/[M_2]$, $a = d[M_1]/d[M_2]$, then Equation 1 could be changed as:

$$b \times \frac{a-1}{a} = -r_2 + r_1 \times \frac{b^2}{a}$$

$$\text{or} \quad \frac{a-1}{b} = r_1 - r_2 \times \frac{a}{b^2} \tag{2}$$

Various composition of monomers (value of $b$) were copolymerized under microwave (controlling conversion <10%). The relative value of "$a$" is:

$$a = \frac{d[M_1]}{d[M_2]} = \frac{[M_1]_0 - [M_1]}{[M_2]_0 - [M_2]} \tag{3}$$

Here, $[M_1]_0$ and $[M_2]_0$ are the concentration of AT and DBTM before reaction, which are two compositions of monomers. $[M_1]$ and $[M_2]$ are the concentrations of AT and DBTM after reaction, which were measured respectively by Liquid chromatogram.

The lines (Figs. 1, 2, and 3) were obtained with $(a-1)b/a$ as longitudinal coordinates, $b^2/a$ as a horizontal ordinate. $r_1$ was the linear slope, $-r_2$ was the linear intercept. Detail results are shown in Figs. 1–3 and Table 1.

From the figures and Table 1, they showed that in the three reactions $r_1 r_2 < 1$ that was to say DBTM and AT were easy to co-polymerize, but the reactivity ratio was different in a wide degree because of different carriers. Compared with the system that contained no carrier, the influence of the existing of carrier displayed that $Al_2O_3$ or $SiO_2$ are not only inorganic carriers but also have some function just like catalyst. Furthermore, their influence to reactivity ratio of monomer differently also proved that carriers had a certain function as catalyst which will affect the character of polymer directly.

## The Influence Resulted from the Quantity of Carrier

The influence of carrier's species and quantity to the percent conversion or inherent viscosity showed as Figs. 4 and 5.

From Fig. 4, it is shown that the percent conversion increased noticeably after the adding of a carrier. It proved that the carrier had a certain function as a catalyst, which was also identical to previous conclusions. In addition, the percent conversion of the system that contained $Al_2O_3$ was obviously higher than the one which contained $SiO_2$. Although the quantity of two carriers was increasing, the trends of two curves of percent conversion don't agree with each other: the percent conversion of the system which contained $Al_2O_3$, increased along with the increase of the carrier quantity. However, the system which contained $SiO_2$ has a maximum – the percent conversion reached a maximum when $SiO_2$ was about 80% (mass) of monomers. It displayed that, in the two systems, the function of $Al_2O_3$ was stronger than the one of $SiO_2$ system.

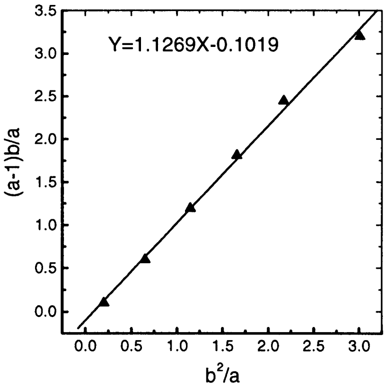

***Figure 1.*** Solid phase and no initiator, no carrier.

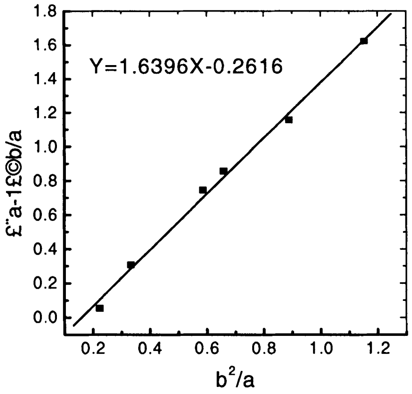

***Figure 2.*** Solid phase and no initiator, $SiO_2$ as carrier.

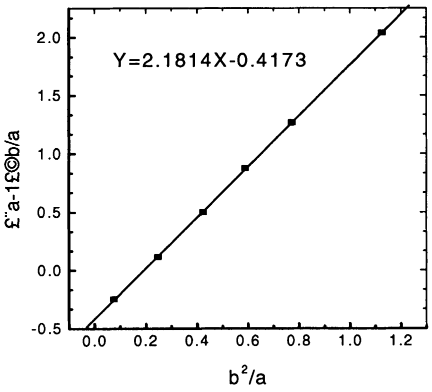

***Figure 3.*** Solid phase and no initiator, $Al_2O_3$ as carrier.

*Table 1.* Reactivity Ratio of Copolymerization System—DBTM and AT

| Carriers | Solid Phase (No Initiator, No Carrier) | Solid Phase (No Initiator, $SiO_2$ Carrier) | Solid Phase (No Initiator, $Al_2O_3$ Carrier) |
|---|---|---|---|
| $R_{AT}$ | 1.127 | 1.640 | 2.181 |
| $R_{DBTM}$ | 0.102 | 0.262 | 0.417 |

Carrier: 160% (wt) of monomers.

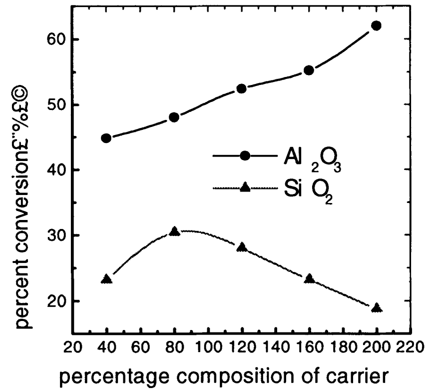

***Figure 4.*** Relation between the quantity of carrier and percent conversion of polymerization microwave irradiation energy: $9.03 \times 10^4$J. DBTM:AT = 1:1.

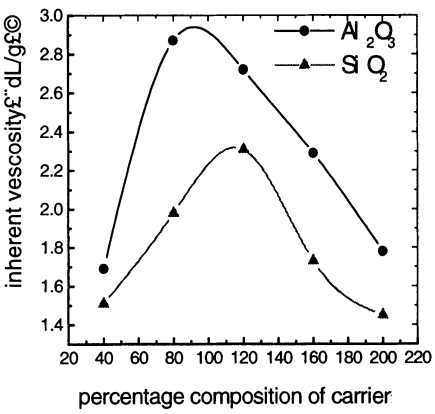

***Figure 5.*** Relation between the quantity of carrier and inherent viscosity of polymer microwave irradiation energy: $9.03 \times 10^4$J. DBTM:AT = 1:1.

The influence of the carrier quantity to inherent viscosity of the polymer is shown in Fig. 5. The inherent viscosity of the polymerization system which contained the carrier was higher than the one of the system which contained no carrier (no carrier, no initiator, then the maximal inherent viscosity was 1.82 dL/g. A maximum appeared both in the $Al_2O_3$ and $SiO_2$ systems, the polymer inherent viscosity of $Al_2O_3$ system was higher than the one of $SiO_2$ system and it showed again that the function of $Al_2O_3$ was stronger than the $SiO_2$.

## Copolymerization System of DBTM and SAVE

The influence resulting from the carrier quantity was investigated. In this system, the percent conversion and inherent viscosity of polymer were both affected when the inorganic carrier was added in. It was identical to the DBTM-AT system. The detail results are shown in Figs. 6 and 7.

Figure 6 shows that a maximum appeared both in the two cases when the quantity of carrier increased: if $Al_2O_3$ was adopted as a carrier, and about 160% (mass) of monomers, the percent conversion had a maximum 41.9%. If $SiO_2$ was adopted as a carrier, and about 120% (mass) of monomers, the percent conversion had a maximum 30.5% which was obviously lower than the $Al_2O_3$ system. It proved again that the carrier had not only the function of a carrier, but also it can obviously promote the polymerization. Furthermore, the function of $Al_2O_3$ was stronger than the $SiO_2$.

Figure 7 shows that when the carrier quantity was increased, the two curves of inherent viscosity are different. If $Al_2O_3$ was adopted as a carrier and about 80% (mass) of monomers, the inherent viscosity had a maximum 4.62 dL/g, and if $SiO_2$ was adopted as a carrier, the inherent viscosity

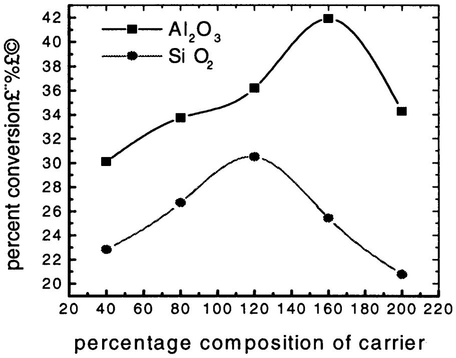

***Figure 6.*** Relation between the quantity of carrier and percent conversion of polymerization microwave irradiation energy: $21.93 \times 10^4$ J. DBTM:SAVE = 1:1 (mol ratio).

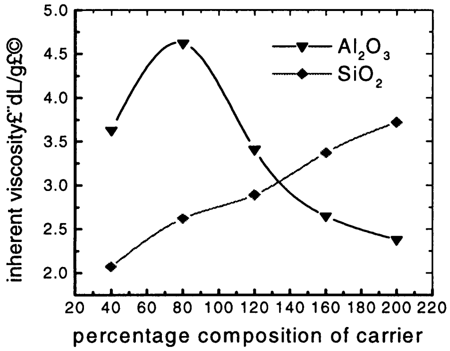

*Figure 7.* Relation between the quantity of carrier and inherent viscosity of polymer microwave irradiation energy: $21.93 \times 10^4$ J. DBTM:SAVE = 1:1.

increased along with the increase of quantity of carrier, and the maximum was 3.72 dL/g in this experiment range. It proved that the carrier also had the function of special catalysis.

## Copolymerization of SAVE and MH

Figure 8 shows that the inherent viscosity of the polymer containing $Al_2O_3$ is greater than the one which contained $SiO_2$.

## Copolymerization System of SAVE and AM

Figure 9 shows that the inherent viscosity of the polymer containing the carrier $SiO_2$ is greater than the one which has the carrier $Al_2O_3$.

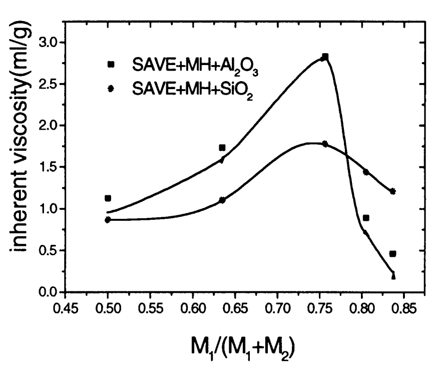

*Figure 8.* Influence of carrier to inherent viscosity $M_1$-maleic anhydride $M_2$-vinyl stearate.

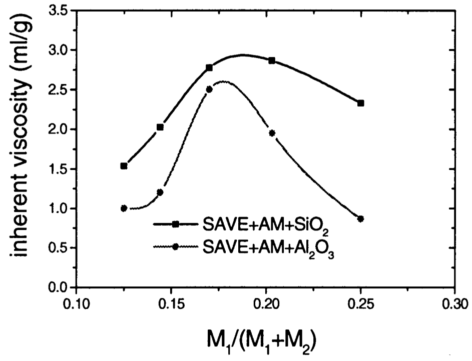

*Figure 9.* Influence of carrier species to polymer property $M_1$-maleic anhydride $M_2$-vinyl stearate.

## Copolymerization of IA and AM

Figure 10 shows that the inherent viscosity of the polymer containing the carrier $Al_2O_3$ is greater than the one which has the carrier $SiO_2$.

## Copolymerization of SAVE and IA

Figure 11 shows that the inherent viscosity of the polymer which contains the carrier $Al_2O_3$ is greater than the one which has the carrier $SiO_2$.

## Copolymerization of AM and MH

Figure 12 shows that the inherent viscosity of polymer which has the system which has the carrier $Al_2O_3$ is greater than the one which has the carrier $SiO_2$.

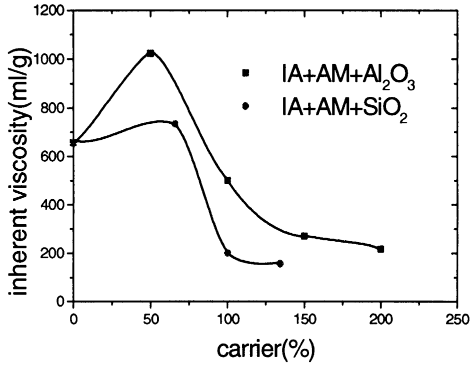

*Figure 10.* Relation between carrier species and polymer inherent viscosity.

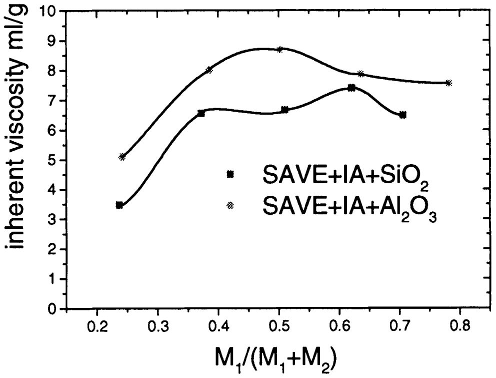

***Figure 11.*** Influence of carrier species to polymer inherent viscosity $M_1$-itaconic acid $M_2$-vinyl stearate.

## The Homopolymerization of AANa

Figure 13 shows that the molecular weight of the polymer which has the carrier $SiO_2$ is greater than the one which has the carrier $Al_2O_3$.

## The Homopolymerization of AM

Figure 14 shows that the molecular weight of the polymer which has the carrier $Al_2O_3$ is greater than the one which has the carrier $SiO_2$.

## The Homopolymerization of IA

Figure 15, shows the inherent viscosity of the polymer which has the carrier $Al_2O_3$ is greater than the one of which has carrier $SiO_2$.

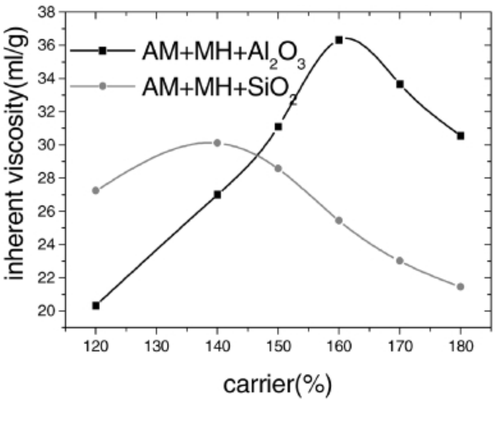

***Figure 12.*** Relation between quantity of carrier and polymer inherent viscosity.

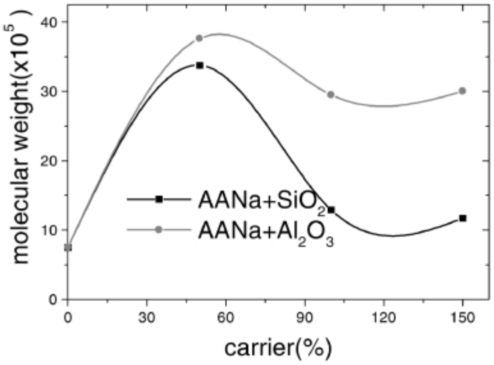

***Figure 13.*** Relation between polymer molecular weight.

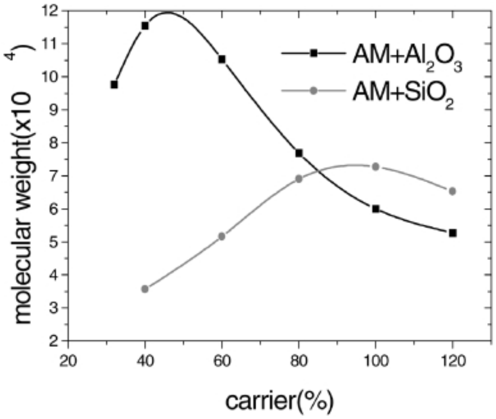

***Figure 14.*** Relation between carrier and polymer molecular weight.

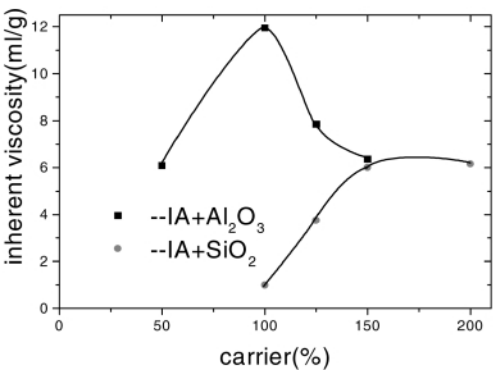

***Figure 15.*** Relation between polymer inherent viscosity and carrier species.

*Table 2.* Influence of Carrier $Al_2O_3$ and $SiO_2$ to the Inherent Viscosity of Different System's Polymer

| System | DBTM + AT | DBTM + SAVE | SAVE + MH | SAVE + AM | AM + MH | SAVE + 1A | AANa | AM | 1A | 1A + AM |
|---|---|---|---|---|---|---|---|---|---|---|
| pH Value | Neutral | Neutral | Neutral | Neutral | Neutral | Acid | Basic | Neutral | Acid | Acid |
| Inherent viscosity under different carrier | $Al_2O_3 > SiO_2$ | $Al_2O_3 > SiO_2$ | $Al_2O_3 > SiO_2$ | $SiO_2 > Al_2O_3$ | $Al_2O_3 > SiO_2$ | $Al_2O_3 > SiO_2$ | $SiO_2 > Al_2O_3$ | $Al_2O_3 > SiO_2$ | $Al_2O_3 > SiO_2$ | $Al_2O_3 > SiO_2$ |

## CONCLUSION

Summarizing the above ten systems, the influence of carriers $Al_2O_3$ and $SiO_2$ to different copolymerization was obtained, as seen in Table 2.

The $SiO_2$ is an acidic carrier and the $Al_2O_3$ is the basic carrier. Irradiated under microwave, the $SiO_2$ will be better to the basic system, and $Al_2O_3$ will be better to the acidic or neutral system. The different influence of the carrier to the different systems might be caused by microwave efficiency that is influenced by the shape and size of what was irradiated under microwave, and by the change of the dielectric property [10–12] which resulted from the interaction between the carrier and the reactant (acid-base effect).

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## REFERENCES

1. Rongshun, Z.; Pinjie, H.; Shushan, D. Synth. Commun. **1994**, *24*, 2471.
2. Csiba, M.; Clephax, J.; Loupy, A.; Malthete, J.; Gero, S.D. Tetrahedron Lett. **1993**, *34*, 1787.
3. Villemin, D.; Alloum, A.B.; Thibault-Starzyk, F. Synth. Commun. **1992**, *22*, 1359.
4. Varma, R.S.; Varma, M.; Chatterjee, A.K. J. Chem. Soc. Perkin Trans. **1993**, *1*, 999.
5. Varma, R.S.; Chatterjee, A.K.; Varma, M. Tetrahedron Lett. **1993**, *34*, 3207.

6. Varma, R.S.; Chatterjee, A.K.; Varma, M. Tetrahedron Lett. **1993**, *34*, 4603
7. Varma, R.S.; Lamture, J.B.; Varma, M. Tetrahedron Lett. **1993**, *34*, 3209.
8. Ley, S.V.; Mynett, D.M. Synlett. **1993**, 793; Loupy, A.; Pigeon, P.; Ramdani, M.; Jaequault, P. Synth. Commun. **1994**, *24*, 159.
9. Lu, J.; Zhu, X.; Ji, S.-J.; Zhu, J.; Chen, Z. J. Appl. Polym. Sci. **1998**, *68*, 1563–1566.
10. Langhoff, P.W.; Epstein, S.T.; Karplus, M. Rev. Mod. Phys. **1990**, *11*, 82.
11. Sekino, H.; Bartlett, R.J. J. Chem. Phys. **1986**, *85*, 976.
12. Karma, S.P.; Dupuis, M. J. Comp. Chem. **1991**, *12*, 487.

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