JOURNAL OF Materials CHEMISTRY

# A novel tube-structure entrapped curing accelerator for prolonging the shelf-life of epoxy resin-based microelectronic packaging material

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***Received 14th January 2002, Accepted 9th April 2002***
***First published as an Advance Article on the web 22nd May 2002***

A new curing system used for prolonging the shelf-life of epoxy resin-based microelectronic packaging material (E-MPM) was first prepared by an *in situ* tubing/entrapping method. Based on supramolecular interactions a curing accelerator (**C**) for epoxy resin, boron trifluoride–pyridine ($BF_3 \cdot Py$), has been trapped into the pores of polyorganosiloxane (**POS**) containing a nanoscale tubular structure, which is prepared by hydrosilylation of two reactive, *cis*-isotactic ladderlike polyallylsilsesquioxane (Allyl-T) molecules with two reactive, α,ω-coupling agents (1,1,3,3-tetramethyldisiloxane, H-MM) in two plus two (2 + 2) mode using $Cp_2PtCl_2$ as catalyst. Various characterizations including optical polarized microscopy (OPM) observations, differential scanning calorimetry (DSC) measurements, storage and curing tests and molecular mechanical simulation are combined to confirm that the accelerator $BF_3 \cdot Py$ is simultaneously trapped during the formation of **POS** and moreover, to indicate that entrapment of the accelerator **C** with **POS** is a promising alternative way to prolong the shelf-life of the E-MPM at ambient temperature.

## Introduction

Exhibiting many desirable properties, epoxy resin has been one of the most commonly used resins in sealants, print circuit boards, electrical mouldings and coatings in the past century.[1,2] However, from a practical viewpoint, achieving a long shelf-life has still been a thorny problem. So far, the commercially available epoxy resin-based microelectronic packaging material (E-MPM) must be stored or transported at low temperature (−20 to −10 °C).

To improve an epoxy curing system with a long shelf-life, the metals and coordination compounds used in the production and formulation of epoxy resins have been widely studied. For example, Kurnoskin found that the gel and cure times were dependent on the nature of the chelate[3,4] by introducing polyamine-based metal complexes into an epoxy resin structure. Dowbenko *et al.* first reported the use of coordination compounds containing imidazoles as latent curing agents for epoxy resins, which display longer shelf-lives at room temperature, typically in the order of 4–6 months.[5–7] Hamerton *et al.* have examined in great detail this series of latent catalysts and revealed that an imidazole complexed with Cu(II) displayed excellent storage stability at ambient temperature.[8–10] Reddy and Smith *et al.* found that the incorporation of coordination compounds containing acetylacetonate (acac) ligands significantly affected the storage times of the unmodified epoxy monomer.[11–13] However, as Hamerton pointed out recently,[14] although it is of major commercial interest that the use of coordination compounds in this fashion can significantly improve selected physical, thermal and chemical properties of epoxy resins, the presence of metal salts can inflate the density of the resins (if used in sufficient quantity) or adversely affect the conductivity of the cured resin and therefore render them of limited use in E-MPM applications.

On the other hand, it is also an effective strategy for prolonging the shelf-life of E-MPM to separate the curing accelerator (**C**) from the epoxy resin by encapsulating it in an inorganic or polymeric shell. When the temperature rises to a certain point, either the shell breaks by melting or the **C** molecules included are decomposed and/or move vigorously. Consequently, the **C** molecules would be released to cure the epoxy resin immediately. Now, the materials used to package the accelerator **C** include hollow inorganic materials such as zeolite,[15] and organic polymers.[16,17] This micro-encapsulation strategy is also significant and widely applied in other diverse fields such as medicine, materials science and the paint industry.[18–20] However, hardly any organic polymers have been reported for specifically entrapping **C** of E-MPM.

Polysiloxanes are very important polymers used to modify epoxy resins[21–23] because of their many excellent properties, such as good thermal oxidative stability, low flammability, low surface energy and excellent dielectric properties. Especially, ladderlike polysilsesquioxanes (LPS) have been well known for a long time.[24] Compared with single-chained polysiloxanes, these double-chained ladderlike polymers have even better heat resistance and other physical properties.[25–27] Therefore they are expected to offer access to new materials with properties tailored for applications such as encapsulants for electronics, low dielectric materials, and so forth.[28–31] Encouragingly, during the last ten years or more, a series of novel ladderlike polysiloxanes (LPS) with different side groups[32–35] or organic bridges[36,37] have been synthesized by "Stepwise Coupling Polymerization" (SCP)[38,39] in our group. Recently, our further researches demonstrated that an encapsulated curing accelerator, micrometre (μm)-scale imidazole (Im) particles, with ladder-like copoly(phenyloctylsilsesquioxane) as the capsule-shell material indeed plays a significant role for improving the storage stability of E-MPM at ambient temperatures and moreover, it does not inhibit curing at the expected temperature because the capsules can be broken at the desired softening



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point of ~160 °C.[40] Our recent work proved that the steric configuration of the novel LPSs prepared by SCP is predominantly *cis*-isotactic.[41] Based on this analysis, some polyorganosiloxanes (**POS**) containing nanoscale tubular structures have been synthesized by a two plus two (2 + 2) method by linking two reactive, *cis*-isotactic ladderlike molecules (Vi-T or Allyl-T) with two reactive, α,ω-coupling agents[42,43] using $Cp_2PtCl_2$ as catalyst. Furthermore, *via* weak interactions (*e.g.* H-bonding and van der Waals force *etc.*) between the interior tube structure and the molecules required to be trapped, some corresponding supramolecular **POS**s clathrates have been prepared successfully by *in situ* tube-closure tubing/trapping. For example, a europium compound,[44] a fluorescent molecule[45] and a rodlike liquid crystal molecule (*p*-butoxybenzylidene-*p*′-dodecyloxyaniline BBDA),[46,47] were included within the pores of tubular structures with different pore sizes and different chemical affinities. Because the **POS**s possess high thermal stability and excellent electro-insulating properties, and especially, because their accommodation ability can be controlled by choosing suitable bridging groups and side groups for the monomer of **POS**,[48,49] one can expect that **POS/C** will be a very effective and promising candidate for prolonging the shelf-life and improving the storage stability of E-MPM at ambient temperatures.

In this context, we describe the preparation of a **POS**-trapped $BF_3\cdot Py$-based epoxy curative system and its effect to prolong the shelf life of E-MPM. The accelerator $BF_3\cdot Py$ is reported as a latent one[50] to cure epoxy resins over a long period of time even at high temperatures (140 °C).[51,52] The mechanism of the reaction has not been investigated clearly[53,54] so far. The reason here for choosing complex $BF_3\cdot Py$ as the model epoxy curing accelerator is that $BF_3$ and its derivatives as Lewis acids are almost non-poisonous to the hydrosilylation catalysts ($Cp_2PtCl_2$), while the common curing accelerator, such as imidazole (Im) or other electron donating amine derivatives,[55] can adversely poison the hydrosilylation catalyst.

## Experimental

### General

**Measurements.** IR measurements were obtained on a Perkin-Elmer 683 Infrared Spectrophotometer over the range 400–4000 $cm^{-1}$ with a maximum resolution of 4 $cm^{-1}$. Powder samples were finely ground with dried spectroscopic potassium bromide (KBr) pellet. $^1$H-NMR determinations were performed with a JNH-FX100 (JBOX), 200 MHz. The chemical shifts were measured with deuterated chloroform ($CDCl_3$) as solvent and tetramethylsilane (TMS) as standard respectively. Molecular weights were measured by a KNAUER vapor pressure osmometer (VPO) with the molecular weight range 40 to approximately 35 000 g $mol^{-1}$ in organic solvents. For calibration, a graduated concentration series of standard substance of known weight average molecular weight ($M_w$), polydimethylsiloxane (PDMS, $M_w$ = 2262 g $mol^{-1}$), were tested in advance to obtain the average calibration factors ($K_s$ = 10 048) at 40 °C in THF. Molecular simulations were performed on a PentiumIII-550 MHz PC, using Alchemy III V 3.0 for Windows 95 (Tripos Associates, Inc.), Molgen 4.0 Real (Single) for DOS. A differential scanning calorimetry (Perkin-Elmer DSC-7) investigation was used to measure the thermal properties of the curing samples. All the samples were sealed in aluminium DSC pans (and thereby piercing a hole in the pan) under a nitrogen flow (flow rate = 50 $cm^3$ $min^{-1}$). Thermal analysis data were collected in the range 50–300 °C with a heating rate of 10 °C $min^{-1}$. Thermal gravity analysis (TGA) was carried out on a Perkin-Elmer DSC-7 Analysis System equipped with platinum sample pans under a nitrogen flow (flow rate = 40 $cm^3$ $min^{-1}$).

**Reagents.** All the reagents and solvents were commercially available and of analytical grade. Some reagents were dealt with as follows prior to use. Tetrahydrofuran (THF) was distilled from blue sodium–benzophenone. Toluene was washed with concentrated $H_2SO_4$ to remove thiophene or methylthiophene, which could poison the $Cp_2PtCl_2$ catalyst for the hydrosilylation reaction, and was distilled from sodium sand. Allyl-T was synthesized by precoupling allyltrichlorosilane with phenylene-1,4-diamine (PDA) and subsequent hydrolysis and polycondensation.[32] Allyl-T was obtained as a white solid with a number average molecular weight ($M_n$) of 3580 (by VPO). Meanwhile 1,1,3,3-tetramethyldisiloxane (H-MM) was purchased from ACROS Corp. and was used as a THF solution of 0.1 g $mL^{-1}$. $Cp_2PtCl_2$ catalyst was prepared according to reference 56 and used as a THF solution of $1.0 \times 10^{-3}$ g $mL^{-1}$. Trimethylchlorosilane was used as a THF solution of $1.0 \times 10^{-4}$ g $mL^{-1}$.

### Synthesis

**Preparation of POS.** 0.93 g ($5.0 \times 10^{-3}$ mol of one unit) of Allyl-T was placed in a 100 mL round-bottomed flask equipped with a reflux condenser, a magnetic stirrer and a three-way tap. The equipment was evacuated and purged with dry argon three times in succession. Then the flask was charged with 2.0 mL ($1.0 \times 10^{-4}$ g $mL^{-1}$) of $Cp_2PtCl_2$ solution and 35 mL of THF and stirred at rt for 30 min and subsequently warmed up to 40 °C. After that, 7.5 mL ($5.6 \times 10^{-3}$ mol, 0.1 g $mL^{-1}$) of H-MM solution was carefully added. The resulting mixture was kept stirring for 40 h, and followed by adding 0.4 mL ($3 \times 10^{-3}$ mol) of trimethylchlorosilane solution. After heating was stopped, the resulting mixture was kept stirring for an additional 10 h and allowed to cool down to rt. The product was dried under vacuum under the protection of dry argon at rt for 12 h to obtain 1.57 g white soluble solid **POS** ($M_n$ 13 400 by VPO) with a yield of nearly 98%.

**Preparation of the titled POS/C.** The entrapment of $BF_3\cdot Py$ within the pores of **POS** by *in situ* tubing/trapping was carried out as follows: similarly to the above-mentioned procedure, 0.93 g ($5.0 \times 10^{-3}$ mol of one unit) of Allyl-T, 0.40 g ($2.9 \times 10^{-3}$ mol) $BF_3\cdot Py$ was added to a flask charged with 2.0 mL ($1.0 \times 10^{-4}$ g $mL^{-1}$) of $Cp_2PtCl_2$ solution and 35 mL of THF and stirred at rt for 30 min and subsequently warmed up to 40 °C. Then 7.5 mL of H-MM solution (0.1 g $mL^{-1}$) was carefully added. The resulting mixture was kept stirring for 60 h. After heating was stopped, the resulting mixture was kept stirring for an additional 10 h and allowed to cool down to rt. The product was dried under vacuum under the protection of dry argon at rt for 12 h. Finally, 1.84 g yellow soluble solid **POS/C** ($M_n$ 17 800 by VPO) was obtained in a yield of nearly 92%. Based on the recipe the content of $BF_3\cdot Py$ in **POS/C** is 20 wt%.

### Sampling for curing and storage tests

A homogeneous mixture (termed as Epoxy/Phenolic resin) of epoxy resin (Sumitomo ESCN-195XL) and phenolic resin (Bakelite, Sumitomo H-1, Japan) was blended with a weight ratio of 100 : 60. As shown in Table 1, there were three samples. The title sample was prepared by dispersing 9.1 wt% (based on the total weight of Epoxy/Phenolic resin, $BF_3\cdot Py$ and **POS**) of entrapped **POS/C** particles into the Epoxy/Phenolic resin. The other two were comparative samples, one containing the same content of non-encapsulated $BF_3\cdot Py$ and another containing the same content of non-encapsulated $BF_3\cdot Py$ blended with the pure **POS** in the same stoichiometric ratio. All the three samples were finely ground in an agate mortar under ambient atmosphere at rt.

**Table 1** Formulation of curative epoxy resin system with different kind of curing accelerators

| | Comparative sample 1 (no **POS**) | Comparative sample 2 (blend of **POS** & cat.) | Title sample (trapped **POS/C**) |
|---|---|---|---|
| | Amount/g | | |
| **POS/C** | 0 | 0 | 0.30[a] |
| Pure **POS** | 0 | 0.25 | 0 |
| Pure $BF_3 \cdot Py$ | 0.05 | 0.05 | 0 |
| Epoxy/ Phenolic resin | 0.25 | 0.25 | 0.25 |
| Total weight | 0.30 | 0.55 | 0.55 |

[a]Calculated from the synthesis route, 0.30 g **POS/C** contains 0.25 g **POS** and 0.05 g $BF_3 \cdot Py$.

## Results and discussion

### *In situ* tubing/trapping of $BF_3 \cdot Py$ with POS

As confirmed in our previous work,[42–47] that some compounds (liquid crystal or fluorescent molecules *etc.*) were entrapped within the tubular structure by weak supramolecular interactions, the polar crystal of $BF_3 \cdot Py$ was also entrapped within **POS**. The accelerator $BF_3 \cdot Py$ was gradually dissolved to form a homogeneous solution while the hydrosilylation reaction occurred. It indicates that a new polar local environment (*i.e.* a tube structure) is generated during the hydrosilylation tubing process. Namely, it can be imagined that $BF_3 \cdot Py$ molecules are simultaneously trapped into the pores of **POS** when the latter gradually form through supramolecular interactions between the polar $BF_3 \cdot Py$ molecule and the polar interior of the tube.

**Table 2** Comparison of $BF_3 \cdot Py$ appearance

| | Title system (1) | | Comparative system (2) |
|---|---|---|---|
| | Amount/g | | |
| Allyl-T | 0.93 | | 0.93 |
| H-MM | 0.75 | | 0.75 |
| THF/ml | 35 | | 35 |
| $Cp_2PtCl_2$ | 0.002 | | 0 |
| $BF_3 \cdot Py$ | 0.40 | | 0.40 |
| Reaction temp./°C | 40 | | 40 |
| Reaction time /h | 24 | 60 | 60 |
| $BF_3 \cdot Py$ appearance | Mainly dissolved | Completely dissolved | Mainly un-dissolved |

To prove the above-mentioned point, two comparative experiments shown in Table 2 were designed. The $BF_3 \cdot Py$ crystal for the title system (1) was gradually dissolved and finally disappeared completely. In contrast, in the absence of a hydrosilylation catalyst the comparative system (2) was stirred for 60 h at the same temperature and the crystals of $BF_3 \cdot Py$ still remained predominantly insoluble.

All the characterization data for Allyl-T, pure **POS** and **POS/C** are listed in Table 3. Concerning the IR spectra of pure **POS** and **POS/C**, the peak (2250 $cm^{-1}$) assigned to the Si–H group has disappeared and the peak (1635 $cm^{-1}$) assigned to $Si–CH_2CH=CH_2$ group is extremely weak after the hydrosilylation reaction compared with that of Allyl-T. These results indicate that the hydrosilylation tubing reaction is complete. Similarly, the same conclusion can be drawn from the $^1$H-NMR spectrum of **POS**: the peaks which are assigned to Si–H ($\delta$ 4.72), $-CH=CH_2$ (5.0, 5.8) and $Si–CH_2$ adjacent to $-CH=CH_2$ (1.62) respectively, almost disappeared. Meanwhile, it is noticed that the hydrosilylation in the presence of $BF_3 \cdot Py$ was slightly retarded in comparison with the counterparts: $BF_3 \cdot$ether or $BF_3 \cdot$THF. That is mainly attributed to the weak poisoning effect of pyridine on the catalyst Pt complex.

From OPM observations, the physical blend of $BF_3 \cdot Py$ and **POS** showed an obvious birefringence resulting from crystalline $BF_3 \cdot Py$, while the clathrate **POS/C** does not. Reasonably, it suggests that $BF_3 \cdot Py$ molecules are dispersed into **POS** pores at the molecular level so that they are incapable of forming crystalline aggregates. It is noteworthy that the amount of $BF_3 \cdot Py$ to be included should not exceed 25 wt% of **POS/C**, otherwise birefringence would emerge again because the amount of $BF_3 \cdot Py$ included is more than what the **POS** hollows can hold.

In choosing the curing accelerators, a neutral triphenylphosphine ($PPh_3$) is not only non-poisonous but also can promote the hydrosilylation reaction catalyzed with $[Cp_2PtCl_2]$.[57] Unfortunately, it failed to entrap the crystal $PPh_3$ into **POS**, based on OPM observations. By molecular mechanical simulation as shown in Fig. 1, the **POS**'s tubular structure has an approximately rectangular pore-size of 0.50 nm in width × 1.17 nm in height. Meanwhile, the wheel-like molecule $PPh_3$ has a diameter of 1.1 nm which is too large to be entrapped. In contrast, the rod-like molecule $BF_3 \cdot Py$ with diameter of 0.43 nm can be trapped into the pores of POS to form the supramolecular clathrate of **POS/C**. Therefore, the rod-like molecule $BF_3 \cdot Py$ was chosen as the curing accelerator instead of the wheel-like molecule $PPh_3$.

As shown in Table 2 and 3, the positive results of the above-mentioned solubility tests and various characterization data such as IR, H-NMR, OPM and molecular simulation, can

**Table 3** Characterization data of Allyl-T, pure **POS** and **POS/C**

| Item | Allyl-T | Pure **POS** | **POS/C** |
|---|---|---|---|
| Solubility | Transparent solid film, soluble in both polar THF and non-polar toluene | Transparent solid film, only soluble in polar THF, but insoluble in non-polar toluene | Same as pure **POS** |
| IR ($v$ /$cm^{-1}$) | A peak at 1635 assigned to $Si–CH_2CH=CH_2$ group, and sharp peaks at 1100 assigned to Si–O–Si | Peaks assigned to $Si–CH_2CH=CH_2$ and Si–H group disappeared, and the peak at 1100 assigned to Si–O–Si was broadened | Very weak peaks assigned to $Si–CH_2CH=CH_2$ |
| $^1$H-NMR ($\delta$) | Strong peaks at 5.0, 5.8 assigned to $-CH=CH_2$ | No peaks assigned to $-CH=CH_2$ and Si–H | Very weak peak assigned to $-CH=CH_2$ |
| Molecular weight ($M_n$, by VPO) | 3580 ($n \approx 19$) | 13 400 ($n \approx 21$) | 17 800 |
| Molecular simulation (nm) | A *cis*-isotactic ladderlike structure has the width of the chain of 0.8–1.0 | The pore size is 0.5 in width × 1.17 in height. The **POS** tube is *ca.* 6 in length | The rod-like $BF_3 \cdot Py$ with diameter of 0.43 is trapped into the pore of **POS** |

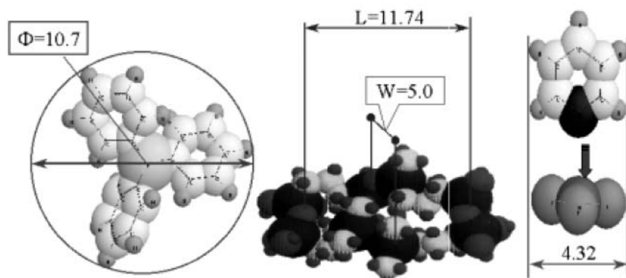



**Fig. 1** Molecular simulation for POS and epoxy curing acceptor–$PPh_3$ and $BF_3$·Py: A) the diameter of the wheel-like $PPh_3$ molecule is 1.07 nm; B) the cross-sections of POS with pore size of 0.5 nm in width × 1.17 nm in height; C) the diameter of the rod-like $BF_3$·Py molecule is 0.43 nm.

confirm that the crystal $BF_3$·Py is successfully trapped into the pores of **POS**. It is noteworthy that we had tried to obtain a direct image of this **POS/C** system by transmission electronic microscopy, but unfortunately, it failed because of its low contrast and too small size. Considering that ladderlike polysilsesquioxanes prepared by stepwise coupling polymerization are of *cis*-isotactic stereoconfiguration,[41] and they have a strong tendency to be cyclized in dilute solution to form tubular structures, we put forward a proposed mechanism depicted in Scheme 1 for the *in situ* tubing/trapping process.

### Curing tests

**DSC heating run measurement for different samples.** The DSC heating run curves seem to give some dynamic information of the epoxy curing process. As shown in Table 1 and Fig. 2, there are obvious differences between curves (a), (b) and (c) in the range of 50–250 °C. From Fig. 3, the heat capacities ($\Delta C_p$) for both of **POS** and **POS/C** themselves are very small, about zero and less than 0.5 J $g^{-1}$ $K^{-1}$ respectively.[42,43] So, their performance does not have a profound effect on curing behavior of the epoxy resin even when the contents of **POS** and **POS/C** used approach 50 wt% of the formulation. Therefore, it is suggested that these curves mainly represent the heat evolution of cured epoxy itself in different conditions.

Curve (a) representing comparative sample 1 shows that the epoxy begins to cure below 75 °C, then the heat evolution is remarkably accelerated accompanying the increase in the temperature, and achieves the peak at ~125 °C, which is consistent with the reported result.[50] Curve (b) representing comparative sample 2 shows a similar trend of heat evolution to curve (a), but the heat evolution achieves a peak at ~190 °C, higher than 125 °C for curve (a). The difference may be attributed to the possibility that the macromolecular **POS** can also

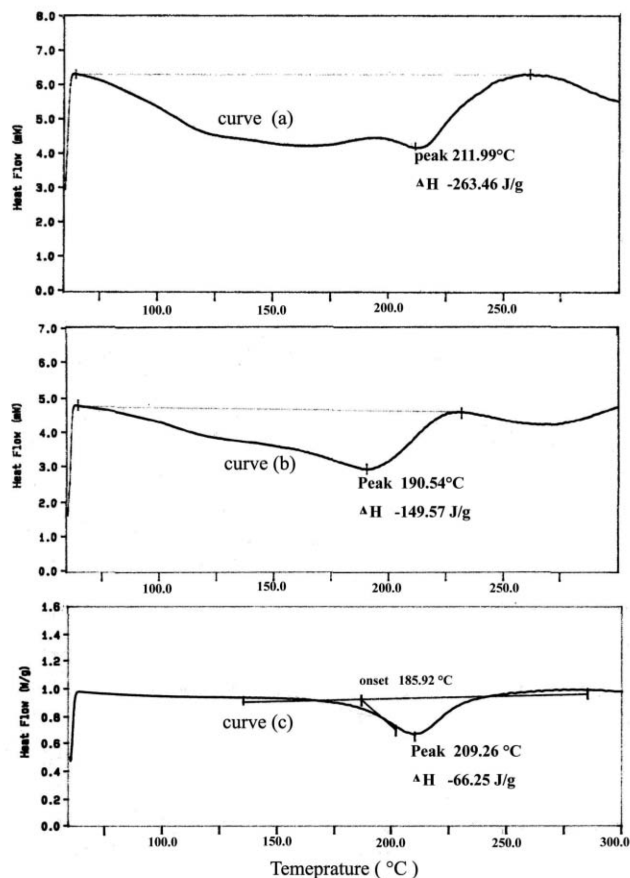
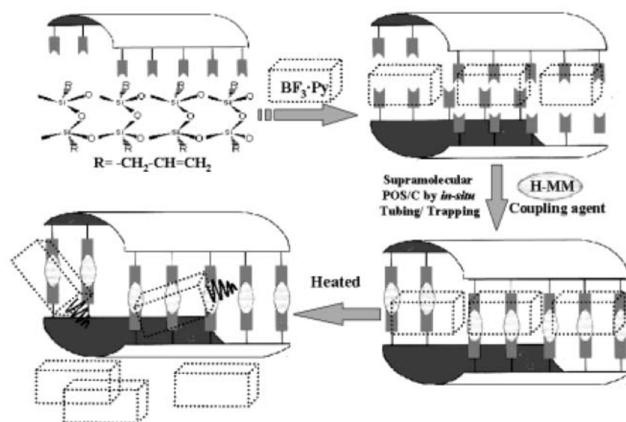



**Fig. 2** Comparison of the heating DSC curves: curve (a) represents comparative sample 1; curve (b) represents comparative sample 2; curve (c) represents title sample.

partly wrap $BF_3$·Py molecules, and moreover, the addition of POS can also dilute the concentration of the curing accelerator **C** in the epoxy resin, so as to slow down the curing process to some extent.

Distinctly different from the curves (a) and (b), curve (c) representing the title sample containing the entrapped catalyst **POS/C**, shows an almost horizontal line prior to 150 °C and a smooth hump-like exothermic peak centered at about 209 °C. This means that the packaging polymer **POS** can protect the accelerator molecules from contacting directly with the outside epoxy resin over a certain temperature range. Here, it is noteworthy that the tubular **POS** has $M_n$ 13 400 by VPO measurement, which corresponds to 21 repeating units. We can estimate the average length of **POS** is approximately 6 nm by molecular simulation. Hence, $BF_3$ entrapped within the **POS** can easily




**Scheme 1** Illustrative representation of entrapping epoxy curing accelerator with POS.

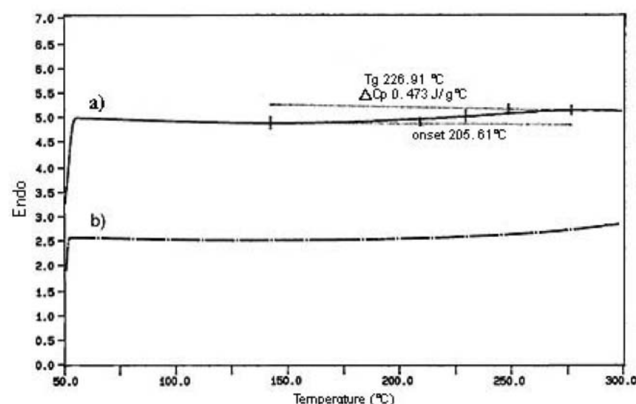



**Fig. 3** The DSC curve of **POS** and **POS/C**: curve a) represents **POS/C**; curve b) represents **POS**.

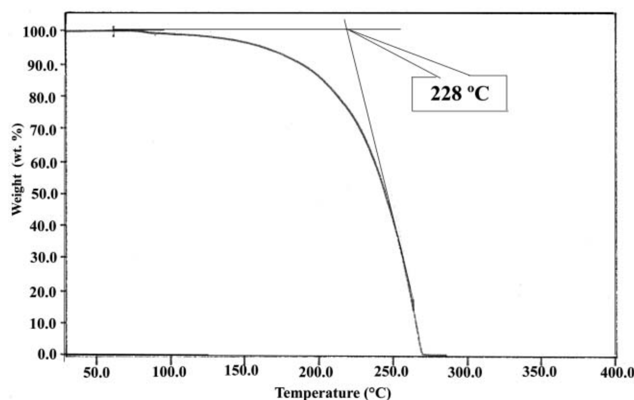



**Fig. 4** Thermal gravimetric analysis curve of $BF_3$·Py.

escaped from this short tube. When the temperature rises to a definite point (above 200 °C), the complex $BF_3$·Py is rapidly decomposed at 228 °C as shown by TGA investigation in Fig. 4 and by vigorous thermal movement the accelerator $BF_3$ molecules are thereby liberated from the pores of **POS** to cure the epoxy resin. As a result, the curing process can be effectively inhibited when the temperature is lower than 200 °C.

**Isothermal DSC (I-DSC) measurement at specific temperature for different samples.** The (I-DSC) curves (Fig. 5) describe the curing behavior of the title sample and two comparative samples 1, 2 respectively, at specific temperature (160 °C). Comparative sample 1 with $BF_3$·Py itself is cured rapidly at the peak time of 0.12 min. Meanwhile, the comparative sample 2 with non-entrapped $BF_3$·Py is cured somewhat more slowly shown by a later peak time of 0.24 min. On the contrary, the curve for the title sample is nearly a straight line, indicating no significant gelation occurred. These results clearly demonstrate that the polymeric tube structure-entrapped accelerator-based technology can effectively prolong the shelf-life at ambient temperature.

**I-DSC measurement at different temperatures for the titled samples.** Fig. 6 shows the heat behaviors of the title sample at the different curing temperature. The isothermal curing curve (a) at 80 °C is nearly a straight line, indicating that the sample did not cure completely. Meanwhile, at constant curing temperature 160 °C, curve (b) is a smooth line with a weak hump-like peak centered at about 26.95 min. Compared with them, when the curing temperature is maintained at 210 °C, the curve (c) shows that the sample cured rapidly at the peak time of 2.16 min. Obviously, these tests indicate that the entrapment of curing accelerator $BF_3$·Py does play a role in improving storage stability of epoxy resin composition at room or moderate temperatures, and moreover, it does not inhibit the extent of reaction at the expected high temperature. Additionally, it is

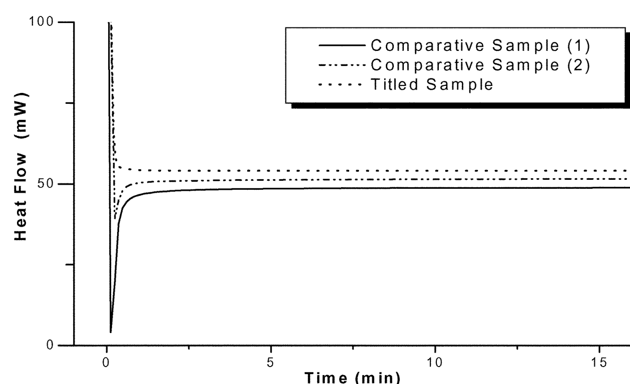



**Fig. 5** Comparison of the isothermal DSC curves at 160 °C.

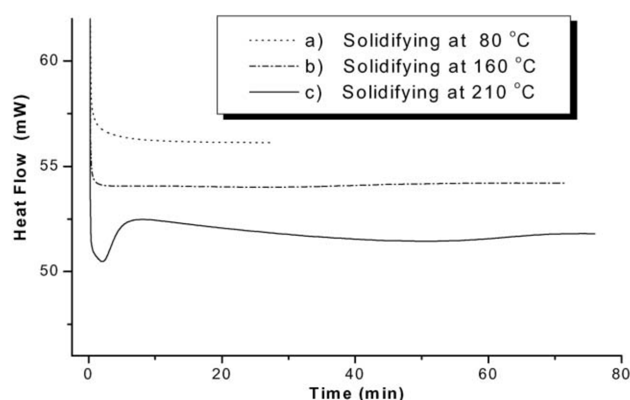



**Fig. 6** The isothermal DSC curves of the title sample **POS/C** at the different curing temperatures.

noticed that there is a subsequent smooth exothermic peak centered at about 51.00 min, which is attributed to the cross-linking of epoxy groups with some terminal silanol groups remaining in **POS**.

**Storage test for the titled samples.** After being in a desiccator at rt over 8 months, the title sample was still soluble in toluene. Further storage experiment of the sample heated at constant 80 °C even after 24 hours showed that no evident change had occurred. These results are in good agreement with those investigations mentioned above. So by *in situ* entrapping of the curing accelerator of the epoxy resin, the E-MPM could be stored or transported safely under ambient conditions.

From the point of practical applications, it is noteworthy that the $BF_3$·Py-based epoxy curative system is no better than that of the common imidazole-based system. In fact, the significant quantity of **POS** introduced here does not satisfy the comprehensive requirements for the advanced E-MPM. However, it is informative that this entrapment strategy paves a promising alternative way to prolong the shelf-life and to explore practical applications in other fields.

## Conclusions

The *in situ* tubing/entrapping of the curing accelerator $BF_3$·Py of epoxy resin using novel a polysilsesquioxane polymer (**POS**) containing a tubular structure has demonstrated that this method can play a remarkable role in prolonging shelf-life of the E-MPM. DSC measurements and curing tests indicated that the curing temperature for the title sample (containing entrapped $BF_3$·Py in **POS/C**) is effectively increased up to *ca.* 186 °C while that of the corresponding sample (containing non-entrapped $BF_3$·Py) is 75 °C. In addition, the entrapment technique of **POS/C** does not inhibit or retard the curing process of the epoxy resin at the desired high temperature.

## Acknowledgement

The authors would greatly like to thank the National Natural Science Foundation of China (NSFC, No. 20174047) and Dow Corning Corporation, U. S. A. for financial support.

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