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# Thermal degradation kinetics of poly(methylvinylsilylene-co-styrene)

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## Abstract

Thermal degradation kinetics of poly(methylvinylsilylene-co-styrene) copolymers, viz., PMVSS-I to PMVSS-V obtained by reacting methylvinyldichlorosilane (MVDCS) and styrene in 1:0.25, 1:0.5, 1:1, 1:3 and 1:7 mole ratios under dechlorination conditions, using sodium, was studied by thermogravimetry. The homopolymer, poly(methylvinylsilane) (PMVS), synthesized from MVDCS using sodium was also subjected to the above study for comparative evaluation. The kinetic parameters for thermal degradation, viz., activation energy (*E*) and pre-exponential factor (*A*) for the above polymers were estimated by non-isothermal kinetic methods such as Mac Callum–Tanner (M–T), Horowitz–Metzger (H–M), Madhusudhanan–Krishnan–Ninan (MKN) and Coats–Redfern (C–R). The order for thermal degradation of PMVS was found to be almost 0. In the case of the copolymers, the order was 1 for PMVSS-I and 2 for PMVSS-II to PMVSS-V. The observed difference in the order for thermal degradation of PMVSS-I when compared to the other copolymers is attributed to the presence of polysilyl linkages in PMVSS-I. It was found that the activation energy and pre-exponential factor showed an increase in trend with increase in concentration of styrene in the copolymer system.

*Keywords:* Polysilahydrocarbon; Poly(methylvinylsilylene-co-styrene); Thermal degradation kinetics

## 1. Introduction

Polysilahydrocarbons, containing Si–$C_x$–Si repeating units (where $x \geq 2$) in the polymer backbone have been synthesized in our laboratory [1–6]. These polymers were synthesized through the dechlorination of diorganodichlorosilanes such as dimethyldichlorosilane (DMDCS), methylphenyldichlorosilane and 1,2-bis(chlorodimethylsilyl) ethane (BCDMSE) with styrene under dechlorination conditions using sodium in toluene. The copolymers are linear in nature and undergo thermal degradation at temperatures above 350 °C leaving very low ceramic residue at 900 °C [1]. Our recent studies revealed that the polysilahydrocarbons can be converted to thermally stable polycarbosilanes by heat treatment in inert atmosphere [7]. These polycarbosilanes give ceramic residue in the range 20–85% when subjected to pyrolysis in inert atmosphere [7].

Of late, we have been looking into the possibility of synthesizing thermally stable polysilahydrocarbons in a single step synthesis [8]. Schilling et al. [9–12] reported that methylvinyldichlorosilane (MVDCS) on dechlorination gave a highly crosslinked polymer. Under dechlorination conditions MVDCS behaves as a tetrafunctional monomer as the vinyl group also takes part in the polymerization. Thus, it is expected that crosslinked polysilahydrocarbons could be obtained when MVDCS is used in place of DMDCS, methylphenyldichlorosilane (MPDCS) or BCDMSE for copolymerization with styrene. Recently, we have reported the synthesis and pyrolysis gas chromatographic studies of poly(methylvinylsilylene-co-styrene), a crosslinked polysilahydrocarbon, obtained by the copolymerization of MVDCS and styrene under dechlorination conditions using varying monomer feed ratios [8]. Pyrolysis gas chromatographic studies suggest the presence of polysilyl and

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polystyrene blocks in addition to silahydrocarbon repeating units. It was also observed that the overall thermal stability and ceramic residue depend on the monomer feed ratio. Thus, it is of interest to study the thermal behavior and degradation kinetics of poly(methylvinylsilylene-co-styrene) to understand the role played by the copolymer composition on the kinetic parameters. In the present paper, we report the reaction order, activation energy and pre-exponential factor obtained by four different methods for the thermal degradation of the homopolymer, poly(methylvinylsilane) (PMVS) and the copolymer, poly(methylvinylsilylene-co-styrene). A comparison of phenomenological data, viz., thermal properties such as initial decomposition temperature ($T_{\mathrm{i}}$), maximum decomposition temperature ($T_{\max}$) and final decomposition temperature ($T_{\mathrm{f}}$) along with the ceramic residue left at 900 °C is made. The Arrhenius activation parameters, viz., activation energy ($E$), pre-exponential factor ($A$) and order of the reaction ($n$) were also computed using four different kinetic equations. Attempts were made to correlate the results with the structure and composition of the copolymers.

## 2. Experimental

### 2.1. Synthesis of poly(methylvinylsilylene-co-styrene)

The copolymers were synthesized by reacting MVDCS with styrene in mole ratios of 1:0.25, 1:0.5, 1:1, 1:3 and 1:7 under dechlorination conditions using sodium in toluene at 110 °C. The polymers were obtained in 80–95% yield. The copolymers were fractionated into soluble and insoluble fractions using toluene. The insoluble fractions of the copolymers obtained by reacting with MVDCS:styrene mole ratios of 1:0.25, 1:0.5, 1:1, 1:3 and 1:7 are designated as PMVSS-I to PMVSS-V, respectively. The insoluble and soluble fractions of the copolymers were characterized by IR, elemental analysis and pyrolysis gas chromatography and the details were discussed in our earlier paper [8]. $^{1}$H-NMR and pyrolysis gas chromatographic studies indicate that the soluble fractions are mostly polystyrene and contain negligible amount of methylvinylsilylene (MVS) units. The insoluble fractions of the copolymers were used for the thermal degradation studies.

### 2.2. Synthesis of PMVS

A homopolymer, PMVS, was synthesized for comparing the thermal properties and thermal degradation kinetics with those of the copolymers synthesized. PMVS was synthesized by dechlorinating MVDCS using sodium in toluene at 110 °C following the procedure similar to that of the copolymer.

### 2.3. Thermal studies

Thermogravimetric analysis of the copolymers and the homopolymer was performed on a TA-2000 thermal analyzer in conjunction with 951 thermogravimetric analyzer. TG experiments were conducted at a heating rate of 10 °C/min under nitrogen atmosphere purged at a rate of 50 ml/min over a temperature range 30–900 °C. The computation of fractional conversion ($\alpha$) at different temperatures and the curve fittings using different equations were carried out by the General Analysis software version V4.0D.

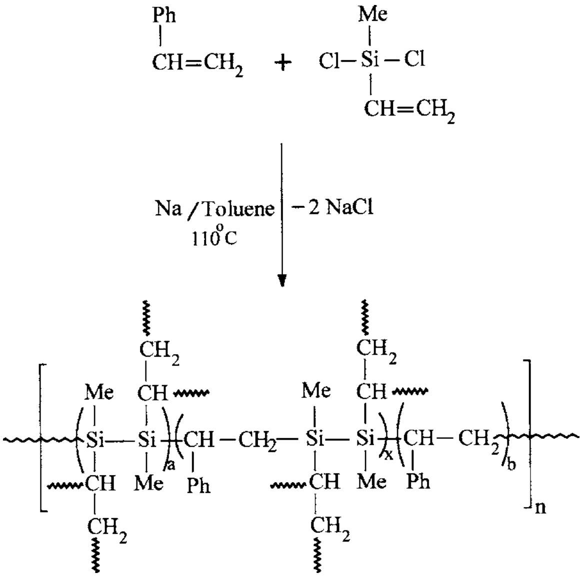
## 3. Results and discussion

### 3.1. Composition of the copolymers

The composition of the copolymers (Table 1) was calculated based on the pyrolysis gas chromatography data and ratio of absorbance ($A$) of Si–Me (of MVS units) and phenyl group (styryl units) and the details are given elsewhere [8]. As the copolymers are insoluble in organic solvents, microstructural analysis of the copolymers could not be carried out. Detailed microstructural analysis of the polysilahydrocarbons [1–6] obtained by the dechlorination of DMDCS, MPDCS or a mixture of DMDCS and MPDCS in presence of styrene suggests that the polymer backbone contains alternating units of disilyl and styryl. The copolymers synthesized with diorganodichlorosilanes to styrene feed ratio of 2 contain alternating units of disilyl and styryl while the copolymers synthesized with the monomer feed ratios greater than 2 and less than 2 contain polysilyl and polystyryl blocks, respectively, in addition to the alternating units of disilyl and styryl. Thus, it is expected that the microstructure of the copolymers synthesized from styrene and MVDCS, a diorganodichlorosilane monomer whose reactivity is expected to fall between DMDCS and MPDCS will be similar to the ones synthesized from DMDCS and MPDCS. However, the polysilahydrocarbons synthesized from styrene and MVDCS would have a highly crosslinked structure as the vinyl group takes part in the polymerization. The participation of the vinyl group in the polymerization with resultant crosslinking is evident from the highly insoluble nature of the copolymers obtained. Based on the above discussion, the reaction scheme for the synthesis of poly(methylvinylsilylene-co-styrene) can be depicted as shown in Scheme 1.

Table 1
Composition of the PMVSS copolymers obtained from pyrolysis GC

| Copolymer | Mole ratio of styrene to MVDCS in the monomer feed | Mole ratio of styryl to MVS units in the copolymer |
|---|---|---|
| PMVSS-I | 0.25 | 0.25 |
| PMVSS-II | 0.50 | 0.50 |
| PMVSS-III | 1.00 | 1.10 |
| PMVSS-IV | 3.00 | 1.80 |
| PMVSS-V | 7.00 | 2.80 |



Scheme 1. Synthesis of poly(methylvinylsilylene-co-styrene).

### 3.2. Thermal properties

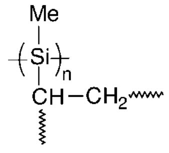
TG curves of PMVS (homopolymer) and copolymers PMVSS-I to PMVSS-V are compared in Fig. 1 and the DTG curves of PMVS, PMVSS-I and PMVSS-II are compared in Fig. 2. Initial decomposition temperature ($T_i$), maximum decomposition temperature ($T_{max}$) and final decomposition temperature ($T_f$) and the ceramic residue at 900 °C of the copolymers and PMVS are summarized in Table 2. PMVS has the highest thermal stability which is clearly understood from $T_i$ (435 °C) and $T_f$ (595 °C).

Table 2
Comparison of the thermal properties of PMVSS (insoluble fraction) and PMVS and the ceramic residue obtained at 900 °C

| Copolymer | Decomposition temperature (°C) | | | Ceramic residue at 900 °C (%) |
|---|---|---|---|---|
| | $T_i$[a] | $T_{max}$[b] | $T_f$[c] | |
| PMVS | 435 | 559 | 595 | 54 |
| PMVSS-I | 420 | 460 | 590 | 40 |
| PMVSS-II | 400 | 457 | 560 | 43 |
| PMVSS-III | 395 | 445 | 540 | 17 |
| PMVSS-IV | 390 | 438 | 520 | 19 |
| PMVSS-V | 380 | 429 | 480 | 20 |

[a] Initial decomposition temperature.
[b] Maximum decomposition temperature.
[c] Final decomposition temperature.

In the case of copolymers from PMVSS-I to PMVSS-V, it is found that all the reaction temperatures are decreasing with the increase in the concentration of styrene. The DTG curve of PMVS shows a single peak at 559 °C. As PMVS contains only polysilyl linkages, the decomposition at 559 °C is attributed to the degradation of these linkages. Linear polysilanes normally degrade at a relatively lower temperature. The higher $T_{max}$ for PMVS is due to the presence of extensive crosslinks resulting from the participation of the vinyl group in the polymerization.



*Structure of PMVS*

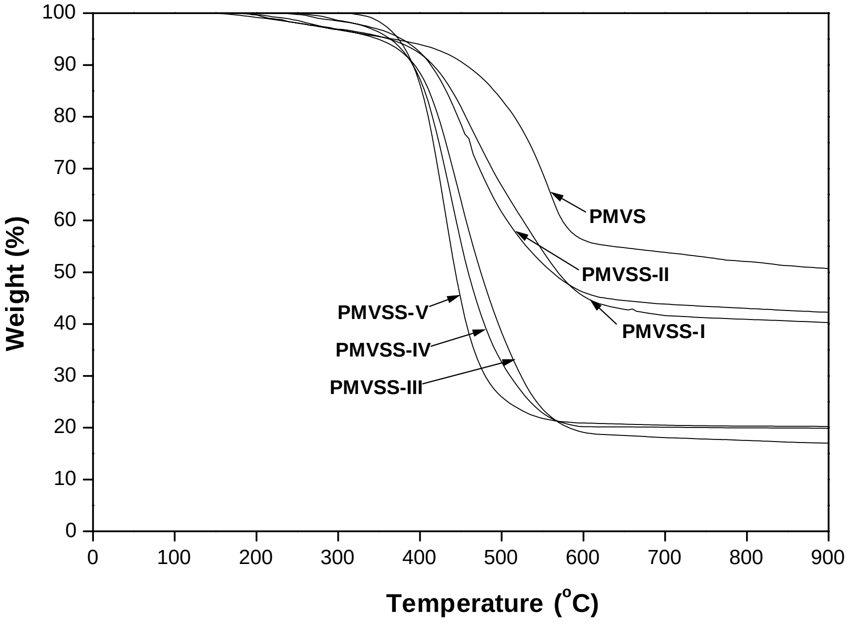


Fig. 1. TG curves of PMVS and PMVSS-I to PMVSS-V.

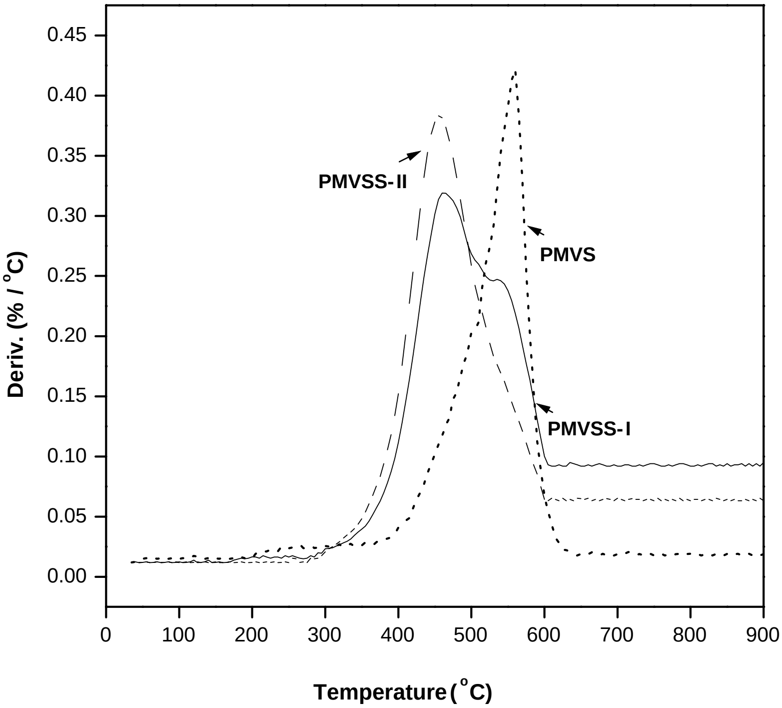


Fig. 2. DTG curves of PMVS, PMVSS-I and PMVSS-II.

The DTG curve of PMVSS-I shows two peaks at 460 and 545 °C whereas in the case of PMVSS-II the second peak is not well resolved. The peak at 460 °C for PMVSS-I and the peak at 457 °C for PMVSS-II are attributed to the degradation of –Si–Si–$CH_2CH(Ph)$– repeating units (alternating units of disilyl and styryl) present in the copolymers. In the case of PMVSS-I in addition to the above repeating units, polysilyl blocks are also present. By comparing the DTG curve of PMVSS-I with that of PMVS, it can be concluded that the second peak at 545 °C for PMVSS-I is due to the degradation of polysilyl linkages. The higher decomposition temperature for polysilyl linkages when compared to that of Si–Si–$CH_2$–CH(Ph) linkages is understood in view of the higher extent of crosslinking present in the case of the former. It is observed that the second peak is practically absent in the DTG curves of the copolymers, PMVSS-III, PMVSS-IV and PMVSS-V. It is also noticed that $T_{max}$ gradually decreases with the increase in styrene concentration in the monomer feed suggesting that the incorporation of styryl blocks in the polymer backbone decreases the overall thermal stability.

Comparison of TG curves (Fig. 1) suggests that PMVS has the highest overall thermal stability and the incorporation of styryl moieties by way of copolymerization decreases the thermal stability. This is understood in view of the fact that the incorporation of styryl units results in reduction of concentration of methylvinylsilyl units which in turn results in reduction of crosslinking. Though it is expected that the overall thermal stability and ceramic residue should gradually decrease while going from PMVSS-I to PMVSS-V, the thermograms of PMVSS-I and PMVSS-II are significantly different from those of PMVSS-III to PMVSS-V. The marked difference in the ceramic yield at 900 °C and the lower thermal stability of PMVSS-III to PMVSS-V compared to those of PMVSS-I and PMVSS-II are consistent with the gross difference in their structure with respect to the concentration of styrene blocks present in them, the former set of polymers having high concentration of styrene blocks and the latter having very little styrene blocks as reported elsewhere [8].

### 3.3. Thermal degradation kinetics

The compositional analysis by pyrolysis gas chromatography reveals that the copolymers differ in their composition [8]. PMVSS-I contains appreciable amount of polysilyl block while PMVSS-III, PMVSS-IV and PMVSS-V contain polystyryl blocks and the concentration of such blocks increases with the increase in concentration of styrene in the monomer feed. TG studies indicate that the overall thermal stability and the ceramic residue at 900 °C are influenced by the composition and structure of the copolymers. Thus, it is expected that the thermal degradation kinetics would also be influenced by the above such factors. Using the TG curves, the kinetics of thermal degradation of the copolymers were carried out by the following four methods: Mac Callum–Tanner (M–T) method [13], Horowitz–Metzger (H–M) method [14], Madhusudhanan–Krishnan–Ninan (MKN) method [15] and Coats–Redfern (C–R) method [16]. The order of thermal degradation reaction ($n$) was

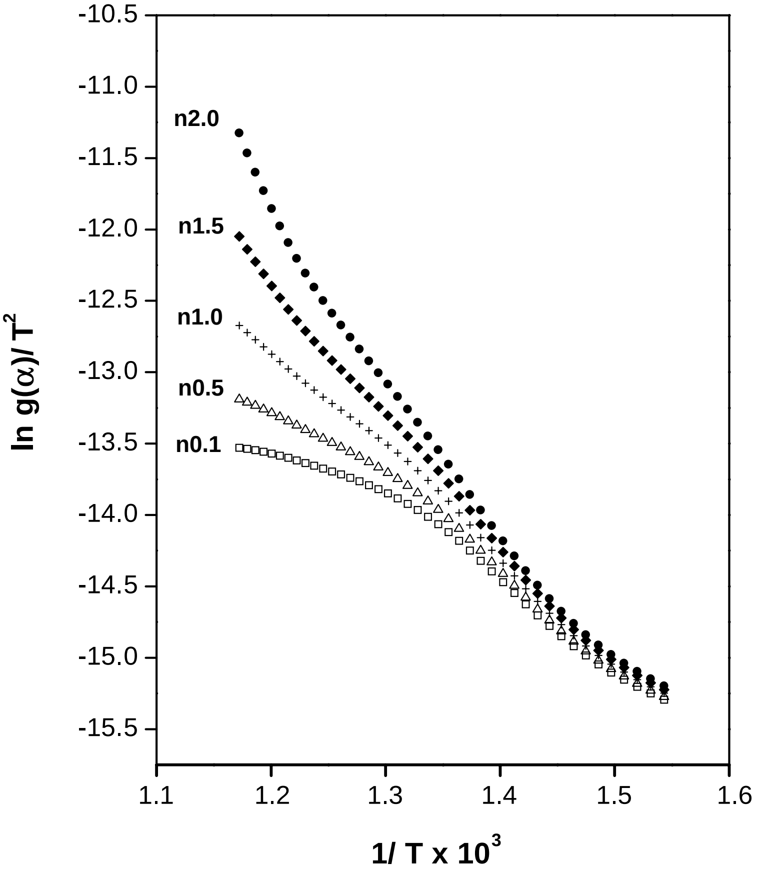


Fig. 3. C–R kinetic plot for different values of *n* for PMVSS-I.

determined by iterating the data using one of the methods (C–R method). Different *n* values were substituted in the equation and $\ln(g(\alpha)/T^2)$ was plotted against $(1/T) \times 10^3$ for different *n* values ranging from 0.1 to 3 with an increment of 0.1; where $g(\alpha) = -\ln(1-\alpha)$ for $n = 1$; $g(\alpha) = [1-(1-\alpha)^{1-n}/(1-n)]$ for $n \neq 1$. The *n* value that gave the best-fit (having the maximum correlation coefficient) was taken as the order of the reaction. A typical kinetic plot is shown in Fig. 3. The order of the reaction (for the best-fit) along with the correlation coefficient values for PMVSS-I to PMVSS-V and PMVS are given in Table 3. The correlation coefficient values for all the kinetic plots are greater than 0.99 indicating the accuracy of the fits. It is found that the best-fit value for PMVS is 0.1, for PMVSS-I it is 1 and for all the others it is 2. Thus, it is seen that PMVS, which contains only polysilyl linkages with extensive crosslinks resulting from the participation of vinyl groups, shows close to zero order for thermal degradation. In the case of copolymers of PMVSS-II to PMVSS-V which contain alternating disilyl and styryl units in the backbone and practically no polysilyl blocks, the order is found to be 2. The presence of linear polystyrene blocks in PMVSS-III to PMVSS-V does not alter the order, whereas for PMVSS-I, where polysilyl blocks are present in addition to the basic copolymer structure, the order is 1 which is in between that of homopolymer and the copolymers. Using these *n* values, the activation energy (*E*) and pre-exponential factor (*A*) for the thermal degradation of all the polymers were calculated by the four different methods and the results are given in Table 4. From the table it can be seen that except for H–M method [14], *E* and *A* values are very close. *E* and *A* values calculated by the H–M method are slightly higher than those obtained by the other three methods for all the polymeric systems. This difference may be due to the fact that the H–M method is an approximation method whereas the other three methods are integral methods [17]. It is observed that the *E* and *A* values increase with the increase in concentration of styryl units in the copolymer or in other words with the decrease in crosslinking density.

Table 3
Order parameter and correlation coefficients of the curve fits of PMVSS system

| System | Reaction order (*n*) | Correlation coefficient (*r*) |
|---|---|---|
| PMVS | 0.1 | 0.9908 |
| PMVSS-I | 1.0 | 0.9978 |
| PMVSS-II | 2.0 | 0.9989 |
| PMVSS-III | 2.0 | 0.9996 |
| PMVSS-IV | 2.0 | 0.9982 |
| PMVSS-V | 2.0 | 0.9984 |

Table 4
Kinetic parameters for the thermal degradation of PMVS and copolymers

| Polymer | Activation energy/pre-exponential factor | Kinetic equations | | | |
|---|---|---|---|---|---|
| | | M–T | H–M | MKN | C–R |
| PMVS | *E* (kJ/mol) | 50.82 | 72.31 | 46.98 | 46.54 |
| | *A* (s$^{-1}$) | 2.69 | 53.70 | 1.02 | 0.81 |
| PMVSS-I | *E* (kJ/mol) | 64.93 | 70.54 | 61.11 | 60.68 |
| | *A* (s$^{-1}$) | 57.54 | 112.20 | 25.12 | 20.41 |
| PMVSS-II | *E* (kJ/mol) | 106.1 | 108.50 | 101.92 | 101.53 |
| | *A* (s$^{-1}$) | $1.09 \times 10^5$ | $1.41 \times 10^5$ | $5.0 \times 10^4$ | $4.4 \times 10^4$ |
| PMVSS-III | *E* (kJ/mol) | 119.3 | 121.8 | 115.2 | 114.8 |
| | *A* (s$^{-1}$) | $1.41 \times 10^6$ | $1.95 \times 10^6$ | $7.0 \times 10^5$ | 6.0 x10$^5$ |
| PMVSS-IV | *E* (kJ/mol) | 131.1 | 133.8 | 127.1 | 126.7 |
| | *A* (s$^{-1}$) | $1.58 \times 10^7$ | $2.23 \times 10^7$ | $7.8 \times 10^6$ | $6.8 \times 10^6$ |
| PMVSS-V | *E* (kJ/mol) | 169.9 | 174.5 | 165.8 | 165.5 |
| | *A* (s$^{-1}$) | $2.57 \times 10^{10}$ | $5.12 \times 10^{10}$ | $1.23 \times 10^{10}$ | $1.09 \times 10^{10}$ |

## 4. Conclusions

Copolymers containing MVS and styryl units in the mole ratios 1:0.25, 1:0.5, 1:1.10, 1:1.80, 1:2.80 were synthesized by reacting styrene and MVDCS in varying monomer feed ratios under dechlorination conditions and the thermal stability was compared with that of polymethylvinylsilane synthesized from MVDCS. Incorporation of styryl moieties by way of copolymerization results in the reduction of thermal stability. TG studies suggest that the overall thermal stability and ceramic residue of the copolymers containing MVS and styryl units in the ratio 1:0.25 and 1:0.5 are similar and differ considerably from the copolymers containing the units in the ratios 1:1.10, 1:1.80, 1:2.80, indicating that the copolymer structure undergoes a drastic change when styrene to MVDCS monomer feed ratio is increased from 0.5 to 1 or above.

The order for thermal degradation of the copolymers were calculated using C–R method and compared with that of the homopolymer, polymethylvinylsilane. The order of the reaction is close to zero (0.1) for PMVS, one for the copolymer synthesized with the monomer feed ratio (styrene: MVDCS) 0.25 and two for the ones synthesized using higher monomer feed ratios. This suggests that the order for thermal degradation is influenced by increase in styrene concentration or in other words decrease in crosslinking. The activation energy (*E*) and pre-exponential factor (*A*) calculated by four different methods, increase with increase in styrene concentration.

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## References

[1] M. Rama Rao, S. Packirisamy, P.V. Ravindran, P.K. Narendranath, Macromolecules 25 (1992) 565.
[2] S. Packirisamy, M. Rama Rao, P.K. Narendranath, P.V. Ravindran, in: S. Venkatachalam, V.C. Joseph, R. Ramaswamy, V.N. Krishnamurthy (Eds.), Macromolecules Current Trends, Proceedings of the International Symposium on Macromolecules, Thiruvananthapuram, Allied Publishers, New Delhi, January 1995, p. 92.
[3] S. Packirisamy, G. Ambadas, M. Rama Rao, K.N. Ninan, in: K.S.V. Srinivasan (Ed.), Macromolecules: New Frontiers, Proceedings of the IUPAC International Symposium on Advanced Polymer Science Technology, Chennai, Allied Publishers, New Delhi, January 1998, p. 1003.
[4] S. Packirisamy, G. Ambadas, M. Rama Rao, V.P. Balagangadharan, K.N. Ninan, Macromolecules, Communicated.
[5] S. Packirisamy, G. Ambadas, M. Rama Rao, K.N. Ninan, to be submitted for publication.
[6] G. Ambadas, Ph.D. Thesis, Kerala University, 2000.
[7] S. Packirisamy, G. Sundararajan, G. Ambadas, K.N. Ninan, to be submitted for publication.
[8] G. Ambadas, S. Packirisamy, T.S. Radhakrishnan, K.N. Ninan, J. Appl. Polym. Sci., Communicated.
[9] C.L. Schilling Jr., ONR Technical Report TR 83-3, 1983.
[10] C.L. Schilling Jr., T.C. Williams, J.P. Wesson, Am. Ceram. Soc. Bull. 62 (1983) 912.
[11] C.L. Schilling Jr., J.P. Wesson, T.C. Williams, J. Polym. Sci., Polym. Symp. 70 (1983) 121.
[12] C.L. Schilling Jr., J.P. Wesson, T.C. Williams, Org. Coat. Appl. Polym. Sci. Proc. 46 (1981) 137.
[13] J.R. MacCallum, J. Tanner, Eur. Polym. J. 6 (1970) 1033.
[14] H.H. Horowitz, G. Metzger, Anal. Chem. 35 (1963) 1464.
[15] P.M. Madhusudhanan, K. Krishnan, K.N. Ninan, Thermochim. Acta 97 (1986) 217.
[16] A.W. Coats, J.P. Redfern, Nature 201 (1964) 68.
[17] K.N. Ninan, C.G.R. Nair, Thermochim. Acta 15 (1976) 345.