

Thermal Characteristics and Pyrolysis of Methyl-di(phenylethynyl)silane Resin

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Received 1 March 2006; accepted 12 June 2006

DOI 10.1002/app.24911

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Thermal stability of a recently synthesized polymeric methyl-di(phenylethynyl)silane (MDPES) resin was studied using a number of thermal and spectrometric analytical techniques. The polymer exhibits extremely high thermal stability. Thermogravimetric analysis (TGA) shows that the temperature of 5% weight loss (T_{d5}) was 615°C and total weight loss at 800°C was 8.9%, in nitrogen atmosphere, while in air, T_{d5} was found to be 562°C, and total weight loss at 800°C was found to be 55.8% of the initial weight. Differential thermal degradation (DTG) studies show that the thermal degradation of MDPES resin was single-stage in air and two-stage in nitrogen. The thermal degradation kinetics was stud-

ied using dynamic TGA, and the apparent activation energies were estimated to be 120.5 and 114.8 kJ/mol in air, respectively, by Kissinger and Coats-Redfern method. The white flaky pyrolysis residue was identified to be silicon dioxide by FTIR and EDS, indicating that the thermal stability of polymer may be enhanced by the formation of a thin silicon dioxide film on the material surface. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 605–610, 2007

Key words: pyrolysis; thermal properties; polymer kinetics; high temperature materials; methyl-di(phenylethynyl)silane (MDPES)

INTRODUCTION

There is a growing interest for developing special lightweight, high-temperature polymeric materials to replace traditional metals, glass, and ceramics in many advanced applications. One class of polymer that appears promising is acetylene-terminated resins. Acetylene-based materials can be prepared thermally or photochemically, and crosslinked networks can be formed through an addition reaction. The main advantage of these materials is their high processability, and can be cured without evolution of volatiles and high char yields.^{1,2} One disadvantage of the current commercial acetylene-based organic polymers is its low thermal stability, generally being limited to be used with temperature below 300°C. One practical approach to improve the thermal stability of the material is to incorporate inorganic elements such as silicon into the acetylene resins.

Corriu et al.^{3–5} reported that poly[(silylene) diethynylene]s exhibit remarkable heat-resistant properties and their thermogravimetric analyses in an argon atmosphere reveal no weight loss up to 450°C. The total weight loss at 1400°C varies from 13 to

37%, depending on the substituting group at the silicon atom. Ijadi-Maghsoodi et al.⁶ also found a similar high thermal stability for poly[(silylene) ethynylene] resin. Itoh et al.^{7,8} have reported the thermal property of poly(phenylsilylene)ethynylene-1,3-phenyleneethynylene (MSP) resins, which were prepared by the dehydrogenative coupling polymerization reaction between phenylsilane and *m*-diethynylbenzene in the of magnesium oxide. Thermogravimetric analysis (TGA) of the polymers in an argon atmosphere reveals 3–12% weight loss at 1000°C, and it has been proposed that the high heat-resistant properties of these polymers be attributed to the cross-linking reactions concerning the Si–H and C≡C bonds.

Recently, polymeric methyl-di(phenylethynyl)silane (MDPES) resin was synthesized in our laboratory. Its synthesis, characterization, and network polymer were discussed in an earlier publication.^{9,10} However, no thermal behavior research about MDPES has been reported. To assess its utility as thermally stable materials for related applications, it is necessary to study its relative thermal stability and degradation behavior. In this paper, we focus on the relative thermal behavior, kinetics of thermal degradation, and the pyrolysis under selected temperatures, which may be exploited to design new molecular structure and improve the property of the material.

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EXPERIMENTAL

Materials

MDPES was synthesized by the reaction of methdichlorosilane with phenylacetylene, using Grignard reagent.^{9,10}

Characterization

Infrared spectra (FTIR) were recorded on a Nicolet Magna 750 spectrometer. TGA was performed on a PerkinElmer Pyris Diamond. Energy dispersive spectrometer (EDS) was recorded on a NewQuiz 14 Elements.

Thermal curing

The MDPES resin was cured in an oven by heating under nitrogen as the following cure schedule: 200°C/2 h → 250°C/2 h → 300°C/4 h → 350°C/2 h → 400°C/2 h.

Thermal degradation kinetics

The thermal degradation kinetics of cured MDPES was investigated using TGA. The system was operated in the dynamic mode over the temperature range 30–800°C, under a nitrogen or air purge of 50 cm³/min at various heating rates: 5, 10, 15, 20°C/min.

RESULTS AND DISCUSSION

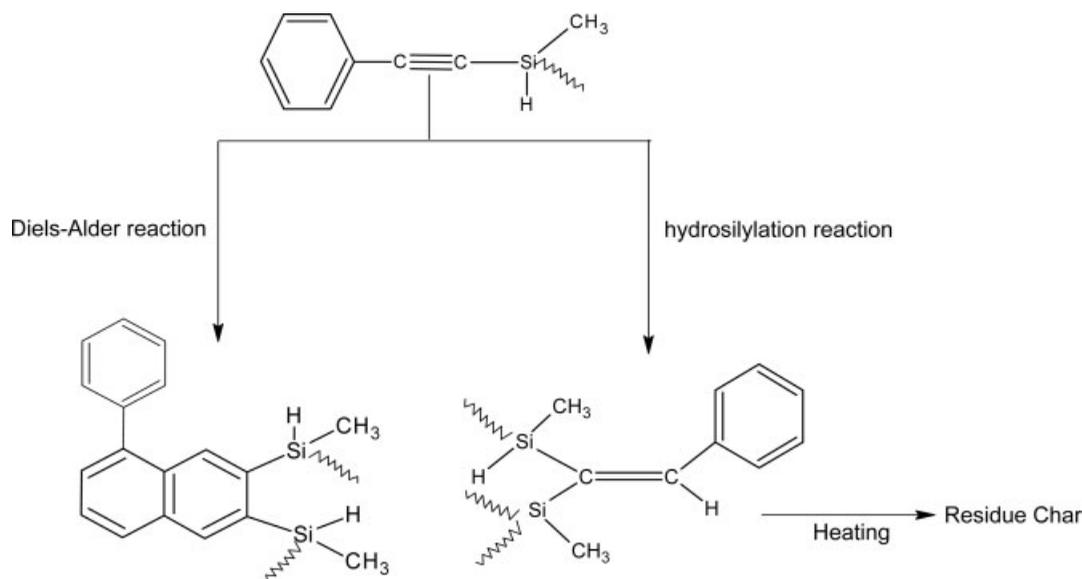
Thermal curing and residual char

MDPES is a low molecular weight compound characterized with low viscosity and high solubility in

many commonly used organic solvents, such as acetone, THF, and so on. Cured MDPES resin was synthesized from monomer MDPES by bulk thermal polymerization without using catalysts or initiators under nitrogen atmosphere. Polymerization takes place through both hydrosilylation reaction between Si—H and C≡C bond and Diels–Alder intermolecular cyclization involving two C≡C bonds, which results in insoluble, void free, hard solid (Scheme 1).⁹ Residue char is obtained by heating either cured MDPES or monomer up to 1000°C.

Thermal and oxidative stability

The TGA curves of cured MDPES (Fig. 1) provided valuable information regarding to its thermal and oxidative properties. Temperature resulting in a 5% weight loss based on the initial weight (T_{d5}) and residual char yield at 800°C were obtained and shown in Table I. As shown in Table I, cured MDPES exhibits excellent heat-resistant properties in nitrogen. With increase in the heating rate, T_{d5} increased from 594 to 679°C and char yield is slightly increased from 90.2% to 92.1%. When heating rate is 10°C/min, T_{d5} and char yield are 615°C and 91.1%, respectively. In air, however, cured MDPES shows a significant decrease both in T_{d5} and in char yield. With increase in the heating rate, T_{d5} increased from 550 to 623°C and residual char yield at 800°C obviously increased from 31.1% to 71.1%. The effect of the atmosphere on the degradation is shown in Figure 2. When the heating rate is 10°C/min, T_{d5} and char yield in air are only 562°C and 44.2%, respectively, which elucidates that the existence of oxygen accelerates thermal decomposition of cured MDPES. Different thermal behaviors between air and nitrogen



Scheme 1 Polymerization of MDPES to cured MDPES and residual char.

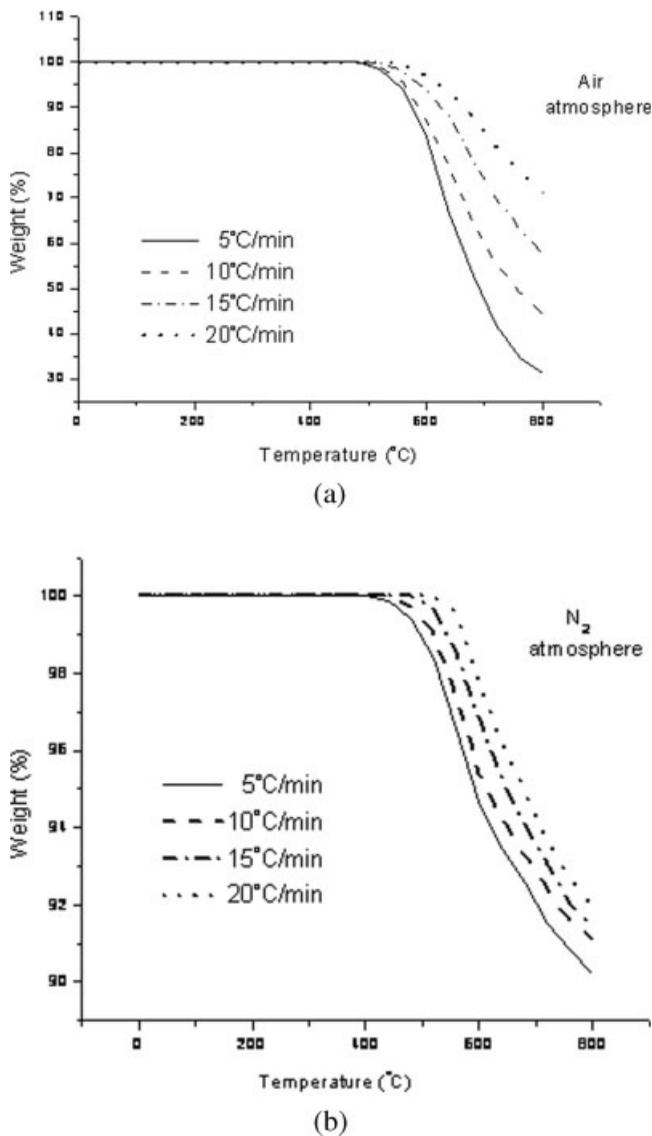


Figure 1 TGA curves of cured MDPES in (a) air and (b) nitrogen atmosphere at different heating rates.

indicate that the degradation of cured MDPES in nitrogen is a thermal decomposition process and in air is a thermal oxidation reaction.

TABLE I
Dynamic TGA of Cured MDPES

Atmosphere	Heating rate (°C/min)	T _{d5} ^a (°C)	Residual char yield at 800°C (%)
Air	5	550	31.1
	10	562	44.2
	15	589	57.8
	20	623	71.1
N ₂	5	594	90.2
	10	615	91.1
	15	650	91.5
	20	679	92.1

^a Temperature of 5% weight loss, based on the initial weight.

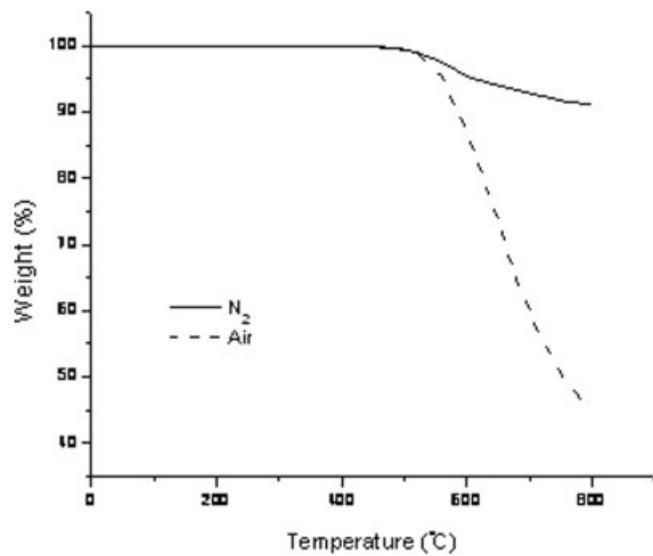


Figure 2 TGA curves of cured MDPES in air and nitrogen atmosphere at heating rate 10°C/min.

Since the residual char had been formed under nitrogen at 1000°C, the thermooxidative stability of the chars was determined by heat treatment to 800°C in air (Fig. 3). We found that the char from MDPES posses excellent oxidative stability. When heated in air to 800°C at a rate of 10°C/min, no additional weight loss and final weight retention of 101% was observed. The reason for this slight weight increase is surface oxidation and the formation of a protective layer. The outstanding thermal oxidative property is attributed to the synergistic effects obtained via the incorporation of silicon into the molecular structure. When the residual char was exposed to an oxidative environment at elevated temperatures, the silicon elements presumably form protective oxides on the

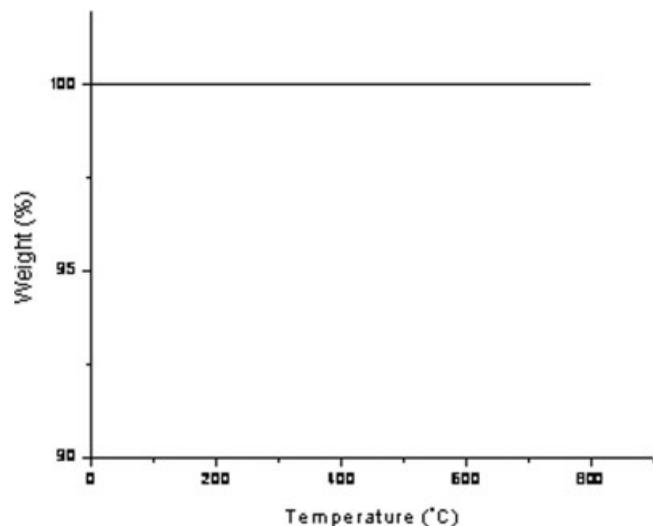


Figure 3 Thermal oxidative stability in air of residual char obtained from MDPES.

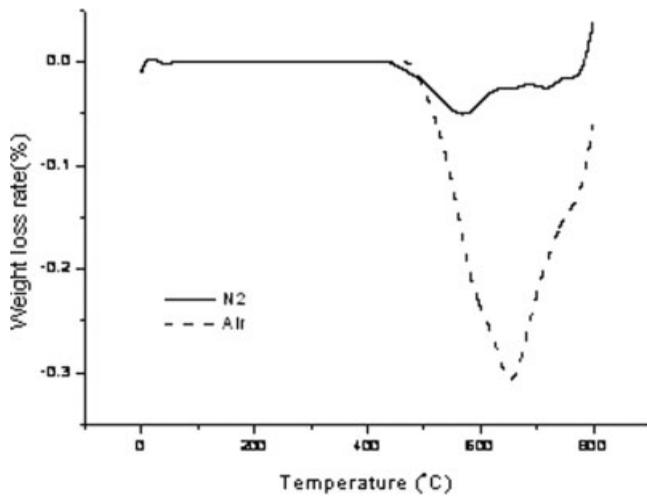


Figure 4 DTG curves of cured MDPEs in nitrogen and air at the heating rate of 10°C/min.

surface of the material, which protects the interior from further oxidation.¹¹

Derivative thermogravimetry (DTG) curves of cured MDPEs are shown in Figure 4. It can be seen from Figure 4 that the thermal degradation process of cured MDPEs in nitrogen and in air is different. These curves show that the degradation is a two-stage process in nitrogen and single-stage in air, which indicates that the influence of the atmosphere on the degradation is different for various stages. In air, the weight loss between 475 and 800°C is about 55.8%, while in nitrogen, the weight loss in first stage between 430 and 686°C is about 6.7% and in second stage between 686 and 800°C is about 2.2%. Total weight loss at 800°C is about 8.9%, which manifested that the thermal degradation in nitrogen is a complicated reaction process. Considering the structure changes shown in Figure 7, the weight loss in air may be corresponding to the loss of the small

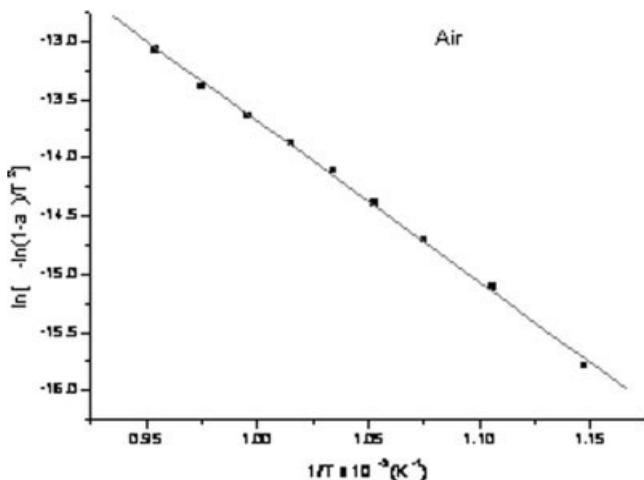


Figure 5 Plots of $\ln[-\ln(1-\alpha)/T^2]$ versus $1/T$ by Coats-Redfern method.

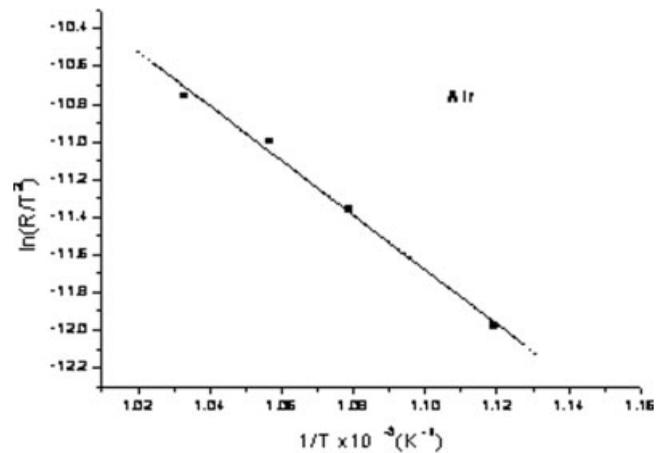


Figure 6 Plots of $\ln(\beta/T_{\max}^2)$ versus $1/T_{\max}$ by Kissinger method.

groups and weaker bonds in the chains of cured MDPEs, such as benzene ring and methyl group.

Thermal degradation kinetics

In thermal degradation, the weight change of the sample is registered as a function of temperature (nonisothermal experiments) or time (isothermal experiments). The fractional extent of reaction is expressed as

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty} \quad (1)$$

where m is an actual mass at time t (or at temperature T), m_0 is the initial sample mass, and m_∞ is the mass at the end of isothermal or nonisothermal experiment.

The differential kinetic equation for thermal degradation process can be expressed as

$$\left(\frac{d\alpha}{dt}\right) = Ae^{-E_a/RT}(1-\alpha)^n \quad (2)$$

where A is preexponential factor, E_a is apparent activation energy, R is gas constant.

TABLE II
Kinetics Parameters of Thermal Degradation of Cured MDPEs

	Method	
	Coats-Redfern	Kissinger
Atmosphere	Air	Air
R	0.999	0.996
E_a (kJ/mol)	114.8	120.5
$\ln A$ (S^{-1})	5.1	6.9
Linear regression	$y = 0.124 - 13.809x$	$y = 4.267 - 14.498x$

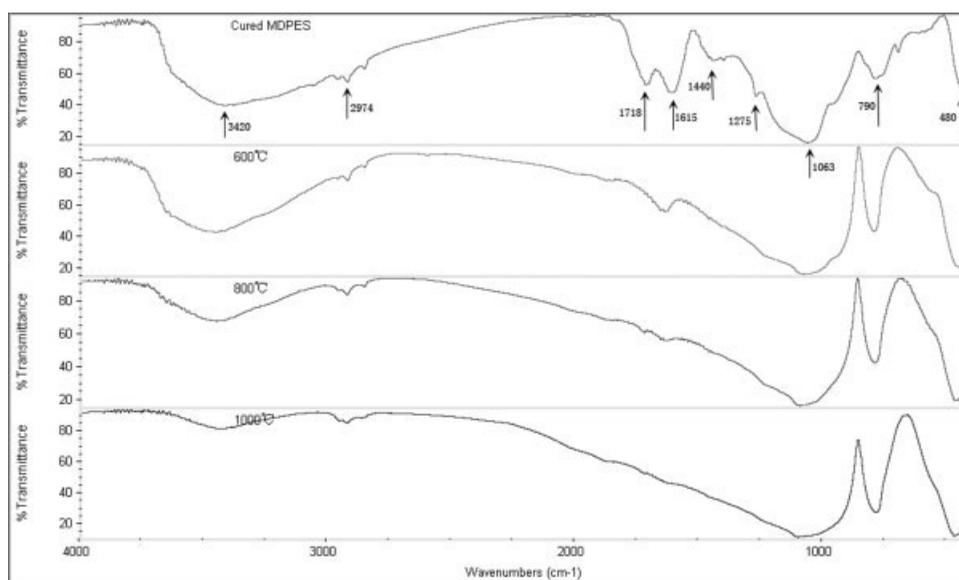


Figure 7 FTIR spectra of MDPEs: (a) Cured MDPEs; and afterwards heated to (b) 600°C; (c) 800°C; (d) 1000°C in air.

In case of crosslinked polymers as the present case, a first-order kinetics is usually assigned, since they undergo degradation by a random process.

The mutual correlation of Arrhenius kinetic parameters (apparent activation energy and preexponential factor) does not allow an accurate kinetic analysis to be performed by using only one experimental TG. This problem can be solved by calculating the apparent activation energy from several isothermal (or nonisothermal) experiments and by determining the most probable kinetic model.

Coats–Redfern method

One of the integrated forms of the above equation is Coats–Redfern equation given as¹²

$$\ln[-\ln(1 - \alpha)/T^2] = \ln[(AR/\beta E)(1 - 2RT/E_a)] - E_a/RT \quad (3)$$

where β is the heating rate and α is conversion. By plotting $\ln[-\ln(1 - \alpha)/T^2]$ against $1/T$, a straight line was obtained with the slope and intercept equal to $-E_a/R$ and preexponential factor A .

Both A and E_a values are useful for predicting the isothermal degradation of the polymers at a given temperature. The dynamic method proposed here gave appa-

rent activation energy of 114.8 kJ/mol for degradation in air at heating rate of 10°C/min (Fig. 5).

Kissinger method

In addition, Kissinger technique is another simple heating-rate treatment method for TG curves to find kinetic parameters of thermal decomposition, which is

$$\ln\left(\frac{\beta}{T_{\max}^2}\right) = \ln\left(\frac{AR}{E_a}\right) + \ln[n(1 - \alpha_{\max})^{n-1}] - \frac{E_a}{RT_{\max}} \quad (4)$$

where T_{\max} is the temperature of the inflection point of the thermograms that corresponds to the maximum

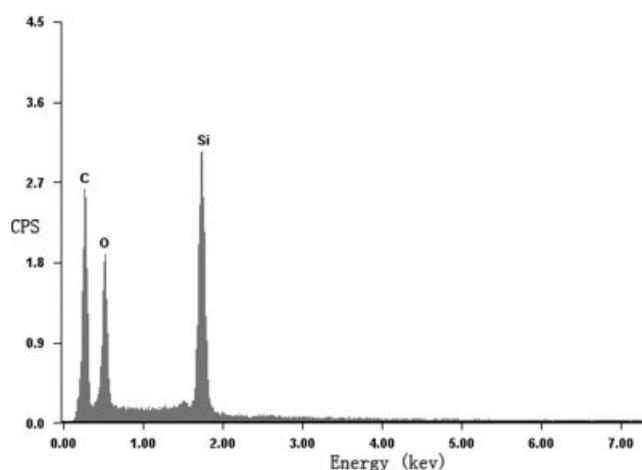


Figure 8 EDS pattern of the residue char at 1000°C in air.

Element	Weight (%)
C	59.7
O	29.8
Si	10.5

reaction rate, α_{\max} is the maximum conversion, n is the reaction order.¹³ From eq. (4), the straight lines were obtained by the least-squares method for air system (Fig. 6), and the activation energy was calculated from fitting the graph $\ln(\beta/T_{\max}^2)$ versus $1/T_{\max}$. The dynamic method proposed here gave apparent activation energy of 120.5 kJ/mol for degradation in air. The result is consistent with Coats–Redfern method (Table II). The data from dynamic TGA satisfied the assumption for reaction order $n = 1$.

Structure changes of MDPES during thermal degradation in air

FTIR analysis

To determine the structure change during the thermal degradation in air, cured MDPES was first scanned using FTIR, and then it was scanned at different temperatures during the dynamic degradation reaction at a heating rate of 10°C/min in air.

Figure 7 shows the IR absorption variation of MDPES during thermal degradation. FTIR of the pyrolysed samples showed that with increase in temperature, the absorption peak of benzene ring at 1615–1440 cm^{-1} decreases and disappears completely at 1000°C, and the absorption peak of silicon dioxide at 1063 cm^{-1} increases gradually. The disappearance of the absorption bands at 1275 cm^{-1} , as well as the increase in intensity of the bands at 480, 790, and 1063 cm^{-1} , are indications of the completion of decomposition of the organic constituents [see Fig. 7(a–d)]. This indicates that the residue is silicon dioxide. Very minor absorption corresponding to C–H groups was observed at 2900–2980 cm^{-1} and presence of –OH groups was evident from the peak at 3300–3600 and 1718 cm^{-1} , which was introduced by KBr pellet.

EDS analysis

The percentages of C, Si, and O in the residue (obtained after pyrolysis at 1000°C) obtained using energy dispersive spectrometry (EDS), which also confirms the existence of silicon dioxide by FTIR, are given in Table III. It can be inferred that the formation of thermally stable silicon dioxide creates a bar-

rier on the material surface and prevents further decomposition of in the inner polymer matrix, thus explaining this experimental findings (Fig. 8).

CONCLUSIONS

The present study suggests that introduction of silicon atom is quite effective to increase thermal stability of acetylene-based polymer. The high heat resistance of the polymer is ascribed to crosslinking reactions concerning ethynyl groups and Si–H. TGA results shows that the dynamic thermal degradation of cured MDPES appears single stage in air and two stages in nitrogen. The thermal degradation kinetics was studied using dynamic TGA, and the apparent activation energies were estimated to be 120.5 and 114.8 kJ/mol in air, respectively, by Kissinger and Coats–Redfern method. FTIR spectra and EDS of the pyrolysed sample confirm the existence of silicon dioxide, which prevents further decomposition of the inner polymer matrix.

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