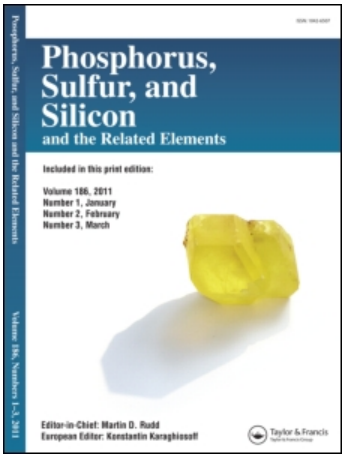

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ORGANIC-INORGANIC HYBRID MATERIALS 8: STABILITY OF POLY(METHYL METHACRYLATE) IN PMMA-SiO_2 HYBRIDS

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Poly(methyl methacrylate) modified silica hybrid materials (PMMA-SiO_2 hybrids) were prepared by in situ polycondensation of alkoxysilane in the presence of trialkoxysilane-functional poly(methyl methacrylate). The thermal stabilities and apparent activation energies E_a for the thermal and thermo-oxidative degradations of these samples were studied by thermogravimetric analysis (TGA). The effects of alkoxysilane content and atmosphere on the stability of the PMMA moiety were investigated in this study. The values of E_a were evaluated by van Krevelen method.

Keywords: Poly(methyl methacrylate); silica; hybrid; degradation

INTRODUCTION

At present, popular ceramic substrates used in industry are made of alumina or its composites, owing to excellent thermal and mechanical properties. However, the dielectric permittivity of alumina is relatively high. For use in multilayer ceramic substrates, it is therefore necessary to explore other low dielectric permittivity materials. Silica gel and thin films prepared from colloidal silica could be promising for meeting the needs of high-speed, high-performance substrates with very low dielectric permittivity, but their gels had to be pressed to form a desirable shape that could

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be handled. Within the past decade, crack-free monolithic pieces are prepared from sol-gel techniques, and the control porous network have opened up many different applications including solid-state dye laser[1], laser-densified waveguides[2], wavelength shifters, and matrices for non-linear optical materials[3].

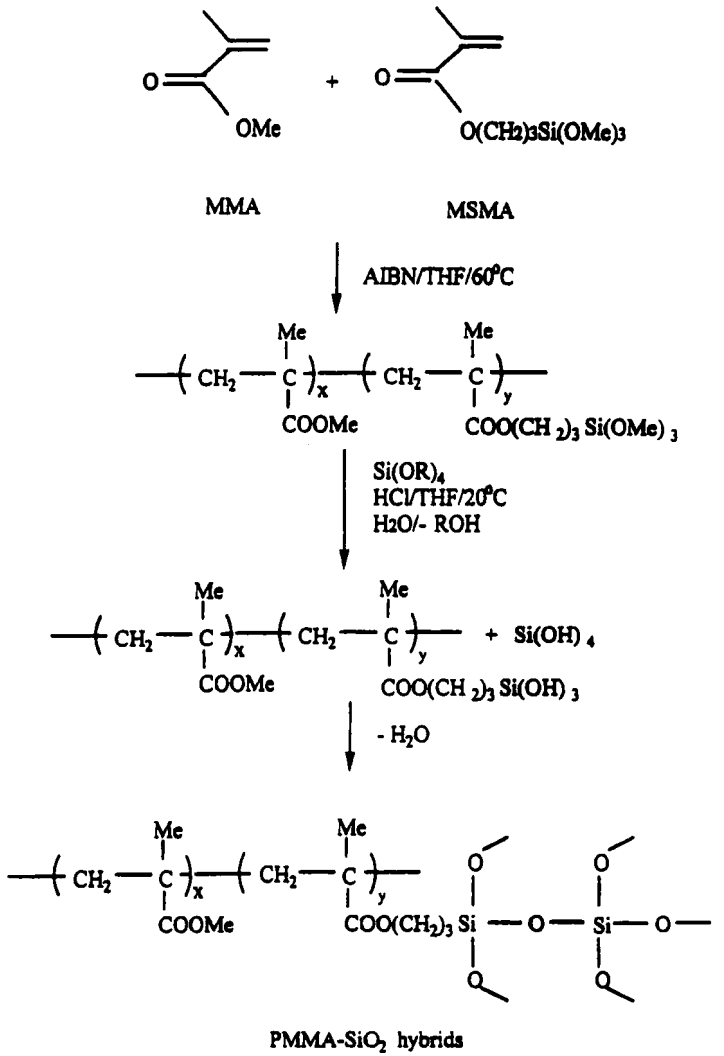
In the search for substrate materials, silica gels and polymers with dielectric constant close to 3 have been considered, but they have the problem of moisture absorption and interfacial stress, respectivity. The combination of silica gel and the hydrophobic poly(methyl methacrylate), PMMA, has shown better resistance to erosion, solvent crazing, weathering, thermal expansion, thermal conductivity, and thermal shock resistance than bulk PMMA[4,5]. The organic polymers combining with inorganic oxides using variations of the sol-gel method have become prevalent as a means of preparing organic-inorganic hybrid materials. Two main procedures are used to prepare poly(methyl methacrylate)-silica (PMMA-SiO_2) hybrid materials. The first uses a mixture of a tetrafunctional silicon alkoxide and the PMMA to produce composite materials[6–13]. The extensive hydrogen bonding between the PMMA and the silicate network can inhibit macroscopic phase separation. The second creates bonding sites between the PMMA with trialkoxysilyl functional group and the silica, resulting in homogeneous, transparent hybrid materials[14–19].

Investigations of PMMA-SiO_2 hybrids recently have been carried out on the microstructure[6,10], morphology[9], optical properties[6,8,10,13], dielectric[6], mechanical[12–14], and thermal stability[11,14,17]. However, there are very few articles on the apparent activation energy (E_a) of degradation of PMMA-SiO_2 hybrids. The thermal stability of hybrids is then studied by TGA[20–22] in this work and the values of E_a are evaluated by the van Krevelen method[23].

EXPERIMENTAL

Materials

The monomer methyl methacrylate (MMA; Janssen) was purified by distillation before use. [3-(Methacryloxy)propyl]trimethoxysilane (MSMA; TCI), and tetramethoxysilane (TMOS, TCI) were used without purifica-



SCHEME I

tion. Azoisobutyronitrile (AIBN; BDH) was recrystallized from ethanol just before use. Tetrahydrofuran (THF; Aldrich) was fractionally distilled in the presence of metallic sodium and benzophenone under nitrogen atmosphere. Deionized water (18 MΩ) was used during the hydrolysis.

Preparation

PMMA-SiO_2 hybrids were prepared by sol-gel method, as described in scheme 1[19]. M5–70 donates that PMMA with 5 mol % trialkoxysilyl functional group condenses with 70 wt% TMOS based on weight of monomer (MMA and MSMA). Hybrids were confirmed by infared (IR) spectrum (Bomem DA 3.002) of sample prepared as KBr pellets technique. IR (KBr): 1710 cm^{-1} (C=O symmetric stretching), and 1013–1015 cm^{-1} (Si-O-Si stretching); ^{29}Si NMR (Bruker MSL-400): −57 ppm (T^2), −65 ppm (T^3), −101 ppm (Q^3), and −109 ppm (Q^4); ^{13}C NMR (Bruker MSL-400): 178 ppm (carboxyl), 56 ppm (methylene), 52 ppm (methoxy), 45 ppm (quaternary), and 17 ppm (methyl). The nomenclatures of T^i and Q^i is taken from Glaser *et al*[24], where i refers to the number of -O-Si groups bounded to the silicon atom of interest. T^i and Q^i denote species that have one and no organic side group, respectively.

Characterization

Differential scanning calorimetry (DSC) was conducted in a Perkin Elmer 7 unit. The characteristics and kinetics of degradation of hybrids were measured by a Perkin-Elmer TGA-2 at heating rate of 10°C/min under air and nitrogen. The sample weight was about 10 mg, and the gas flow rate was kept at 100 mL/min. The decomposed each thermogram into individual Gaussian peaks and assumed a linear background over the temperature range of the fit. Deconvolution was optimized for modeling the experimental spectrum.

The degree of conversion α is defined as the ratio of actual weight loss to total weight loss. Therefore, the rate of degradation $d\alpha/dt$, dependent on temperature and weight of sample, is given by eqn (1)

$$d\alpha/dt = k(T) \times f(\alpha) \tag{1}$$

where $k(T)$ is the rate constant and $f(\alpha)$ is the conversion functional relationship. If $k(T) = A \exp(-E_a/RT)$ and $f(\alpha) = (1-\alpha)^n$, then eqn (1) can be expressed as:

$$d\alpha/dt = A \exp(-E_a/RT)(1-\alpha)^n \tag{2}$$

where A, E_a, R, T, and n represent preexponential factor, activation energy, gas constant, temperature, and reaction order, respectively. The integrated

form of eqn (2) introducing the initial condition of $\alpha = 0$ at $T = T_0$ expression is obtained:

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{q} \int_{T_0}^{T} \exp\left(\frac{-E_a}{RT}\right) dT \qquad (3)$$

where q is heating rate (dT/dt). For the special case $n = 1$,

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{(1-\alpha)^n} = -\ln(1-\alpha) \qquad (4)$$

For n not equal to zero or unit,

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{(1-\alpha)^n} = -\frac{1-(1-\alpha)^{1-n}}{1-n} \qquad (5)$$

Reactions of polymer decomposition may take place by one of a number of elementary mechanisms, as well as combinations of these mechanisms. Thus, it is difficult to find a meaning of the reaction order of a polymer thermal degradation. The reaction order n of thermal degradation in this paper is determined by the Kissinger's equation[25]. In this work, Van Krevelen method solving the integral of eqn (3) gave the following expression[23]:

$$\ln g(\alpha) = \ln\left[\frac{A(0.368/T_{max})^x}{q(x+1)}\right] + (x+1)\ln T \qquad (6)$$

where $x = E_a/RT_{max}$. T_{max} is the temperature corresponding to the maximum of the derivative weight loss curve. The activation energies were evaluated from the slopes in the plot of $\ln g(\alpha)$ versus $\ln T$.

RESULTS AND DISCUSSION

Thermal Degradation

The TGA curves of PMMA-SiO_2 hybrids under nitrogen indicate two main reaction stages, as shown in Figure 1. The initial weight loss below 120 °C is mainly due to the vaporization of residual water remaining on the acidic Si-OH surface[26]. Generally, a polymer with a side chain easily tends to depolymerize because of radical depolymerization. The weight loss at the interval of 200–300 °C is thus attributed to the ester bond decomposition. The maximum rate temperature of weight loss (T_{max}) of

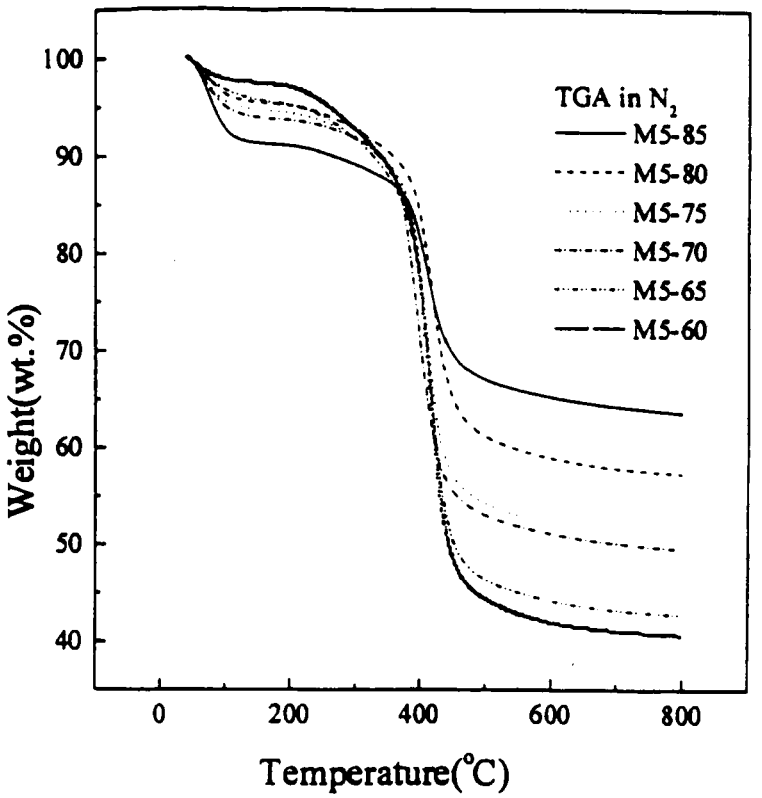


FIGURE 1 TGA thermograms of PMMA-SiO_2 hybrids under nitrogen at the heating rate 10°C/min

PMMA-SiO_2 hybrids is around 410 °C, while their rate (dW_t/dt) increases with increasing PMMA content (Table I). On the other hand, the values of T_{max} are quite comparable with those obtained from DSC (~405 °C). Therefore, the weight loss at the interval of 300–580 °C (second step) is attributed to scissions of the PMMA chain and that above 580°C is attributed to silanol condensation[27]. The char yield (Y_c) at 800°C decreases with increasing PMMA content (Table I).

The differential weight loss (DTG) curve of PMMA-SiO_2 hybrids under nitrogen displays one main reaction stage at the interval of 300–580°C. However, its standard line shape analysis with Gaussian fitting functions

reveals three steps. A typical result of M5–70 hybrid is shown in Figure 2. The peak temperature of each degradation in PMMA-moieties is about 315, 397, and 412°C, respectively. The least stable step (2.3 wt%) can be attributed to scissions of head-to-head linkages[28,29], the second step (25 wt%) to scissions at chain-end initiation from vinylidene ends[30], and the most stable step (11 wt%) to random scission within the polymer chain[31].

TABLE I The characteristic parameters[a] of degradation for hybrids at a heating rate of 10°C/min under N_2

Hybrids	*DSC (°C)*	T_{max} *(°C)*	dw_t/dt *(%/min)*	Y_c *(wt%)*	*n*	E_a *(kJ/mol)*
M5–85	407	418(360)[b]	0.33(0.47)	64.9(64.6)	1.29(1.07)	98(96)
M5–80	409	418(359)	0.50(0.50)	58.7(55.9)	1.33(1.18)	120(86)
M5–75	407	394(350)	0.63(0.80)	53.0(50.3)	1.28(0.91)	128(115)
M5–70	388	396(361)	0.59(0.75)	51.6(49.3)	1.33(0.91)	125(106)
M5–65	404	416(350)	0.68(0.68)	44.6(41.6)	1.33(1.10)	143(93)
M5–60	411	418(369)	0.79(0.73)	41.7(38.4)	1.30(0.93)	145(88)

[a] T_{max} is the maximum rate temperature of weight loss, dw_t/dt is the maximum rate of the weight loss, Y_c is the char yield at 800°C; *n* is the reaction order.

[b] Numbers in parentheses indicate that the values of parameters degrade under air.

Thermo-oxidative Degradation

Figure 3 shows the TGA results of the M5-SiO_2hybrid in air. The values of T_{max} of the PMMA-SiO_2 hybrids in air is around 360°C (Table I) which is less than that in nitrogen (~410 °C). On the other hand, the values of dW_t/dt and Y_c in air is less than that in nitrogen. This result reveals that oxygen has a catalytic influence on the degradation of the PMMA. The deconvoluted DTG curve of the PMMA segments in the M5–70 hybrid is fitting two main reactions (Fig. 4). It demonstrates that the degradation of MMA segments in the hybrid shows basically the same as in PMMA. The first term is due to degradation of partially oxidized groups. These polymer chains are formed by oxygen trapping of the radicals that are generated from the weak linkages. The other is an oxygen attack to the radicals that are generated by random scission within the polymer chain[31]. This characteristic degradation is also observed in other PMMA-SiO_2 hybrids

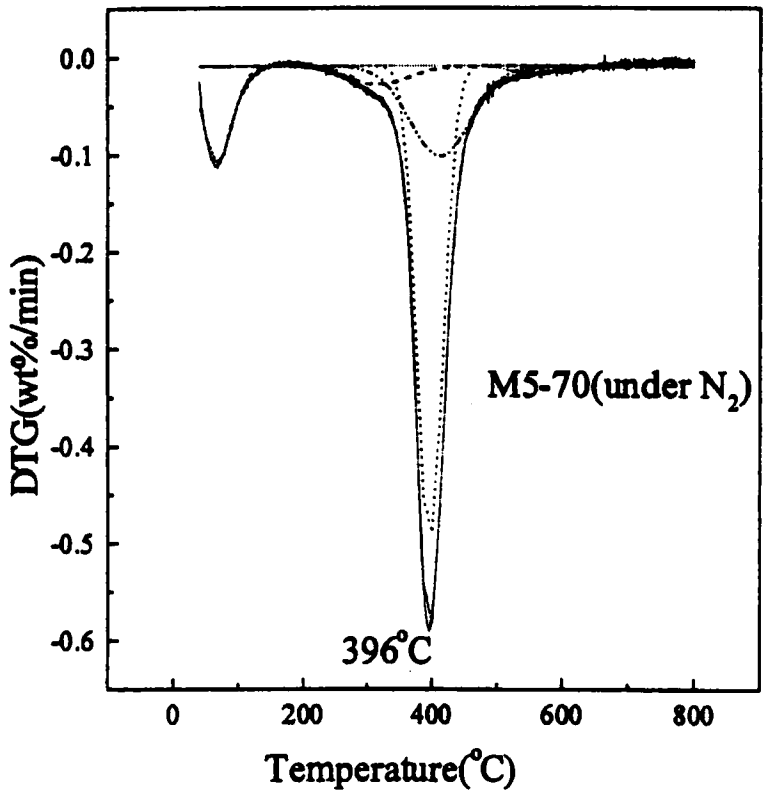


FIGURE 2 DTG thermogram of M5–70 hybrid under nitrogen at the heating rate 10°C /min

in this work. Therefore, the formation of peroxide and hydroperoxides accelerate oxidative degradation.

Kinetic Analysis

The reaction order n of PMMA segments in degradation, determined by the Kissinger's equation, is respectively about 1.3 and 1.0 under nitrogen and air (Table I). Figures 5 and 6 show the logarithmic plot for degradation rate $g(\alpha)$ of PMMA-SiO_2 hybrids versus temperature under nitrogen and air, respectively. The apparent activation energy E_a of random scission for

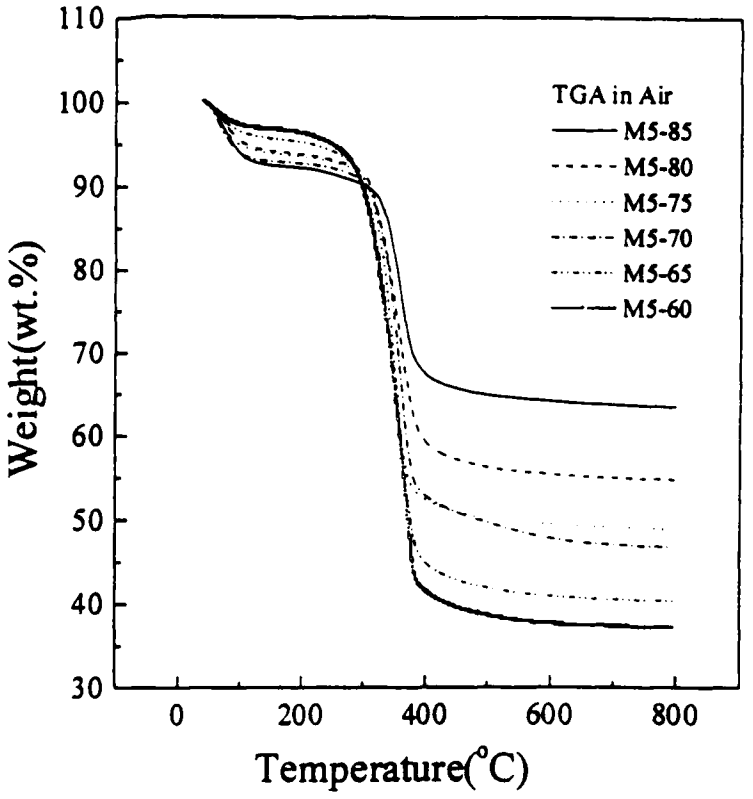


FIGURE 3 TGA thermograms of PMMA-SiO_2 hybrids under air at the heating rate 10 °C /min

PMMA segments in hybrids, evaluated from van Krevelen method, is listed in Table I. It indicates that E_a value increases with increasing PMMA content in hybrids under nitrogen, while that are around 95 kJ/mol under air. However, the E_a values of random scission in homopolymer are around 192 kJ/mol under nitrogen and 115 kJ/mol under air[22]. This difference reveals that chain scission of the PMMA segments in hybrids may be easier than in homopolymer. The reduction in E_a may be rationalized on the basis of the higher thermal conductivity of the silica (5 mcal/cm · s · °C) than that of PMMA (0.5 mcal/cm · s · °C)[32].

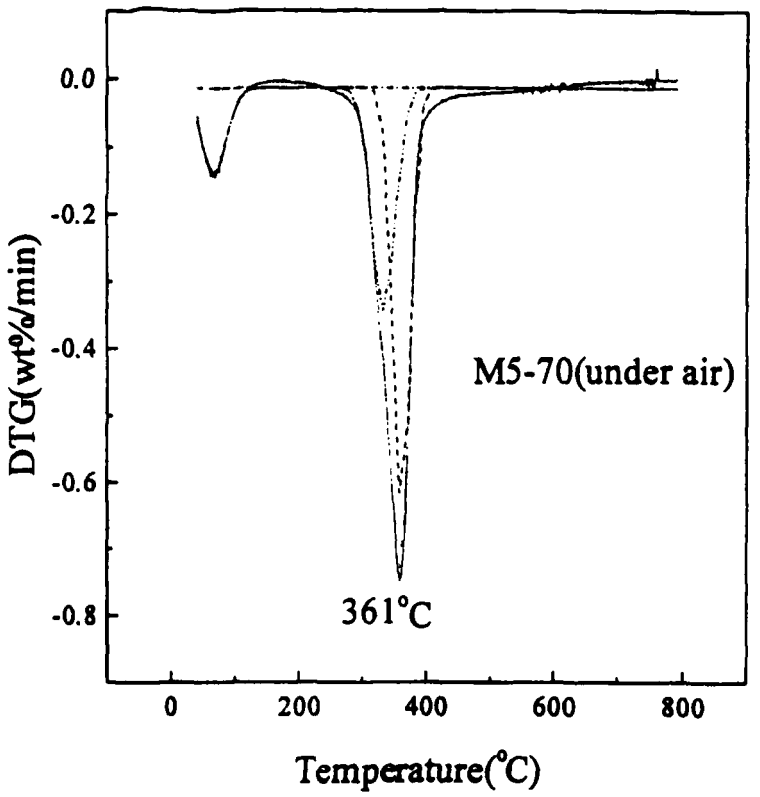


FIGURE 4 DTG thermogram of M5–70 hybrid under air at the heating rate 10°C/min

CONCLUSIONS

In this study we have tried to see the effect of reaction atmosphere and hybrid composition on the stability of the PMMA moietis. PMMA moieties in hybrids, in comparison with the homopolymer, acquire lower thermal stability both under nitrogen and air. The apparent activation energies E_a for random scission of PMMA moieties under nitrogen decreased with increasing silica content, while that was around 95 kJ/mol under air. The reduction in thermal stability may be rationalized on the basis of the higher thermal conductivity of the silica in comparison to that of PMMA.

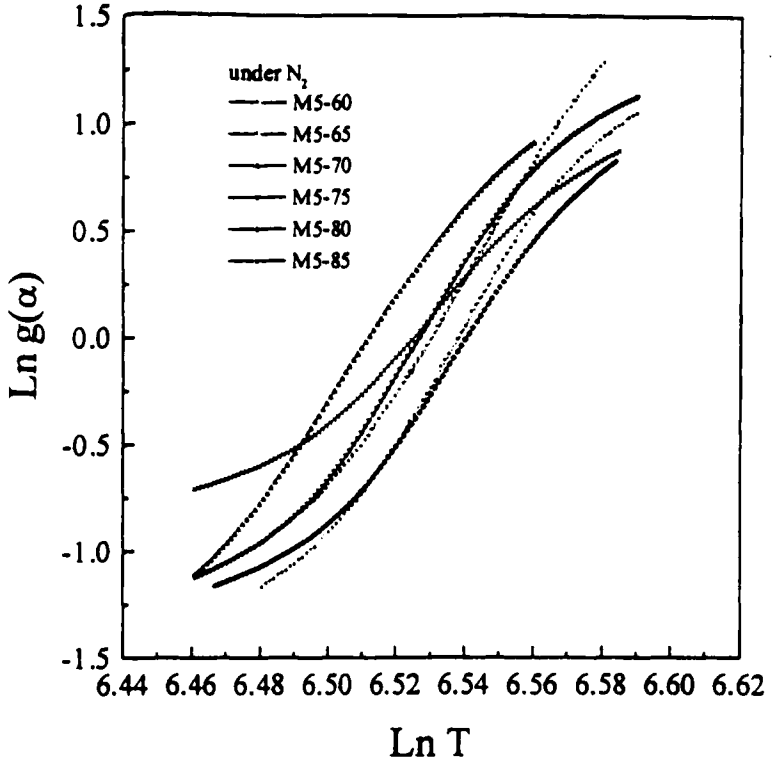


FIGURE 5 Plot of Ln g(α) versus Ln*T* for thermal degradation of PMMA segments in hybrids at the heating rate 10°C/min

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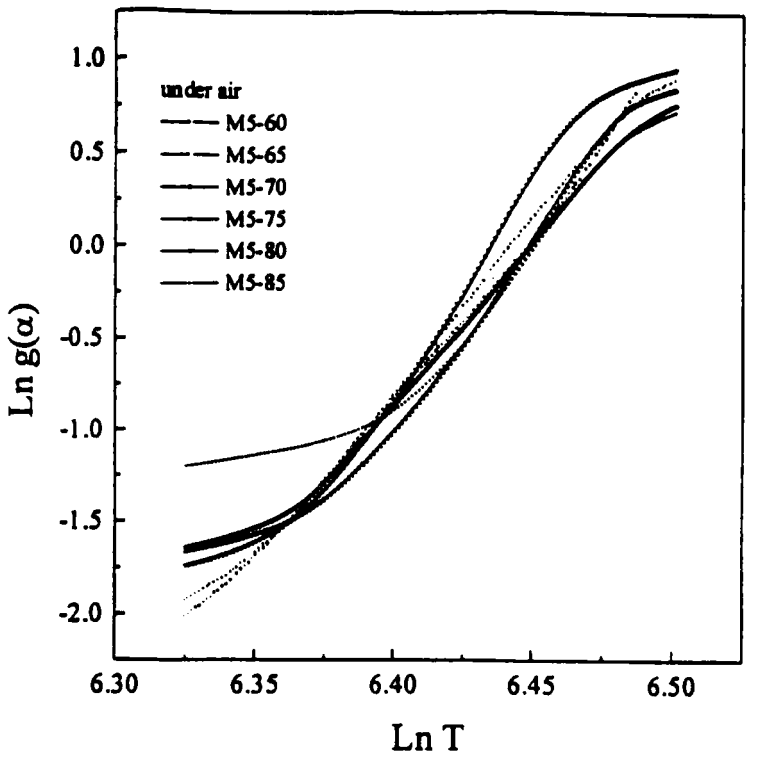

FIGURE 6 Plot of Ln g(α) versus Ln*T* for thermo-oxidative degradation of PMMA segments in hybrids at the heating rate 10°C/min

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