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Thermogravimetric study of ultrathin PMMA films on silica: effect of tacticity

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Abstract

The degradation of isotactic and syndiotactic poly(methyl methacrylate) (PMMA) was studied by thermogravimetric analysis (TGA) with an emphasis on their behavior in ultrathin films on silica. Both PMMA tacticity and adsorbed amounts were found to affect the degradation. In bulk, syndiotactic PMMA (*syn*-PMMA) has higher thermal stability than isotactic PMMA (*iso*-PMMA) due to its lower chain mobility. The T_{max} (maximum rate decomposition temperature) is lower than that of bulk samples at higher adsorbed amounts for both *iso*- and *syn*-PMMA. T_{max} increases when the adsorbed amount on the silica surface decreases for *syn*-PMMA. The degradation behavior of adsorbed *iso*-PMMA became very complex at low adsorbed amounts.

Keywords: Thermogravimetric analysis; Poly(methyl methacrylate); Tacticity; Adsorption

1. Introduction

The thermal degradation of poly(methyl methacrylate) (PMMA) has been extensively studied in both bulk and composite materials. The groups of Kashiwagi et al. [1–7] and Manring [8–12] focused their attention on the degradation mechanism of this polymer. Kashiwagi et al. have implicated “weak links” in radical polymerized PMMA as the principal initiating sites of degradation. Three steps in the degradation process of PMMA were observed and attributed to the presence of head-to-head linkages end group unsaturation (resulting from the combination and disproportionation termination of two radicals) [13], and random scission [3]. It was suggested that side chain cleavage of the carbomethoxy group occurs after random scission of the backbone. Manring proposed that random scission in PMMA is initiated by homolytic scission of the methoxycarbonyl side group rather than by main-chain scission.

The effects of tacticity on the degradation of PMMA were investigated by Kitayama and coworkers [6] Jellinek and Luh [14] and Chiantore and Guaita [15]. The results from Jellinek’s group indicated that both isotactic-PMMA (*iso*-PMMA) and syndiotactic-PMMA (*syn*-PMMA) have similar decomposition pathways and activation energies. Kitayama et al. found that the *iso*-PMMA will decompose at a lower temperature with a broader range, compared to the *syn*-PMMA with the same chain ends and similar molecular mass. It was also reported that *iso*-PMMA is more sensitive to electron-beam radiation than *syn*-PMMA [16] namely, the former degrades more easily than the latter.

The PMMA–SiO_2 system was investigated by several groups [17–25]. The results from Aruchamy et al. [18] indicated that the more acidic the particle

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surface was, the higher the decomposition temperature of PMMA. They suggested that the interaction of the carbonyl group with the Si–OH groups on the surface was responsible for the increased stability due to the electron donating capacity of the carbonyl group [18,19]. Morgan et al. [17] also observed a higher decomposition temperature in a PMMA–SiO_2 nanocomposite. They attributed it to the barrier function of silica particles that prevents the release of evolved degradation products that recombine to form thermally stable residue/char. On the other hand, contradictory results were obtained by Chang et al. [23]. Their explanation for the reduced thermal stability of PMMA in the PMMA–SiO_2 was the higher thermal conductivity of SiO_2 compared to bulk PMMA. So, even though some useful information has been obtained, the decomposition mechanism is still not fully understood. In the present work, the effects of interfacial interaction, configuration and tacticity on the degradation of ultrathin PMMA films, adsorbed on silica, are addressed. We studied films of very low adsorbed amounts with thermogravimetric analysis (TGA), so that the interfacial effects can be observed without major interference from bulk-like material.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA) was dried over calcium hydrate for several days and purified by vacuum distillation under argon. Tetrahydrofuran (THF, HPLC grade) and toluene (HPLC grade) were refluxed over sodium and benzophenone and distilled under argon before use. 1,1-Diphenylethylene (97%, Aldrich Chemical, Milwaukee, WI) was dried over calcium hydrate. *sec*-Butyllithium solution (2.0 M in cyclohexane, Aldrich) was diluted to about 0.5 M with dry toluene. Untreated amorphous fumed silica (Cab-O-Sil M-5P, surface area 200 m^2/g, Cabot Corp., Tuscola, IL) was dried at 500 °C for ca. 6 h before use.

2.2. Polymerization

PMMA samples were prepared by anionic polymerization, with all vessels purged with argon. *syn*-PMMA was obtained by the polymerization of MMA in THF at −78 °C, initiated by the reaction product of *sec*-butyllithium and 1,1-diphenylethylene. After 1 h, the polymerization was terminated by methanol. The resulting *syn*-PMMA was precipitated from the mixture by distilled water and purified by re-precipitation from acetone with hexane. The PMMA was dried overnight in a vacuum oven at 70 °C. *iso*-PMMA was prepared in the same way except that the solvent was changed from THF to toluene and the reaction temperature was 0 °C.

Table 1
Characterization of bulk PMMA

Polymer	Molecular mass (M_n)	Polydispersity	Tacticity (%, triads)		
			mm	rm	rr
syn-PMMA	71,100	1.23	2.3	23.0	74.7
iso-PMMA	35,000	1.65	88.9	8.0	3.1

Molecular mass was measured by gel permeation chromatography (GPC) in THF, relative to standard polystyrene samples. The amounts of *iso*-(mm) *syndio*-(rr) and *hetero*-(mr) triads were calculated from the peak areas at 1.2, 0.8 and 1.0 ppm, respectively, in the ^1H NMR spectra [26]. The results are shown in Table 1.

2.3. Adsorption

THF was used to prepare PMMA solutions of different concentrations. Ten milliliters of polymer solution were transferred into centrifuge tubes containing ca. 0.3 g of silica. The tubes were put into a mechanical shaker for 24 h at 23 °C. The tubes were centrifuged after adsorption and the supernatant solutions were discarded. The residue was blow-dried with air while being stirred. The adsorbed samples were dried in a vacuum oven overnight at ca. 70 °C. The adsorbed amounts calculated from the TGA results are listed in Table 2.

Table 2
Adsorbed PMMA samples on silica (M-5P)

Designation	Polymer	Adsorbed amount (%)	T_{max} (°C)
Si-SYN-01	*syn*-PMMA	3.49	382.3
Si-SYN-02	*syn*-PMMA	11.6	369.0
Si-ISO-01	*iso*-PMMA	2.81	360–420
Si-ISO-02	*iso*-PMMA	10.1	367.5

2.4. Characterization

The degradation of bulk and adsorbed samples were followed with a TA Instruments model 2950 TGA (New Castle, DE) at a heating rate of 10 °C/min under nitrogen. The sample weight was about 10 mg for bulk samples, and about 20 mg for adsorbed samples. The purge gas flow rate was kept at 25 ml/min.

3. Results and discussion

3.1. Bulk samples

The derivative thermogravimetric analysis (DTG) results for the bulk samples are shown in Fig. 1. The T_{max} (maximum rate decomposition temperature, namely the peak temperature) for each sample is indicated on the curves. It is clear that there was negligible mass loss until about 325 °C for both the isotactic and syndiotactic samples. Single decomposition peaks were observed with a narrow width (ca. 50 K). The narrow range and high temperature suggests that anionically polymerized PMMA does not have weak linkages such as those found in free radical polymerized PMMA. A weak linkage might be an unsaturated bond or head-to-head linkage. The chains appear to start degradation via random scission [3]. *iso*-PMMA degraded at a slightly lower temperature than *syn*-PMMA, about 7 K lower in this case. Similar phenomena were noted by Kitayama and coworkers

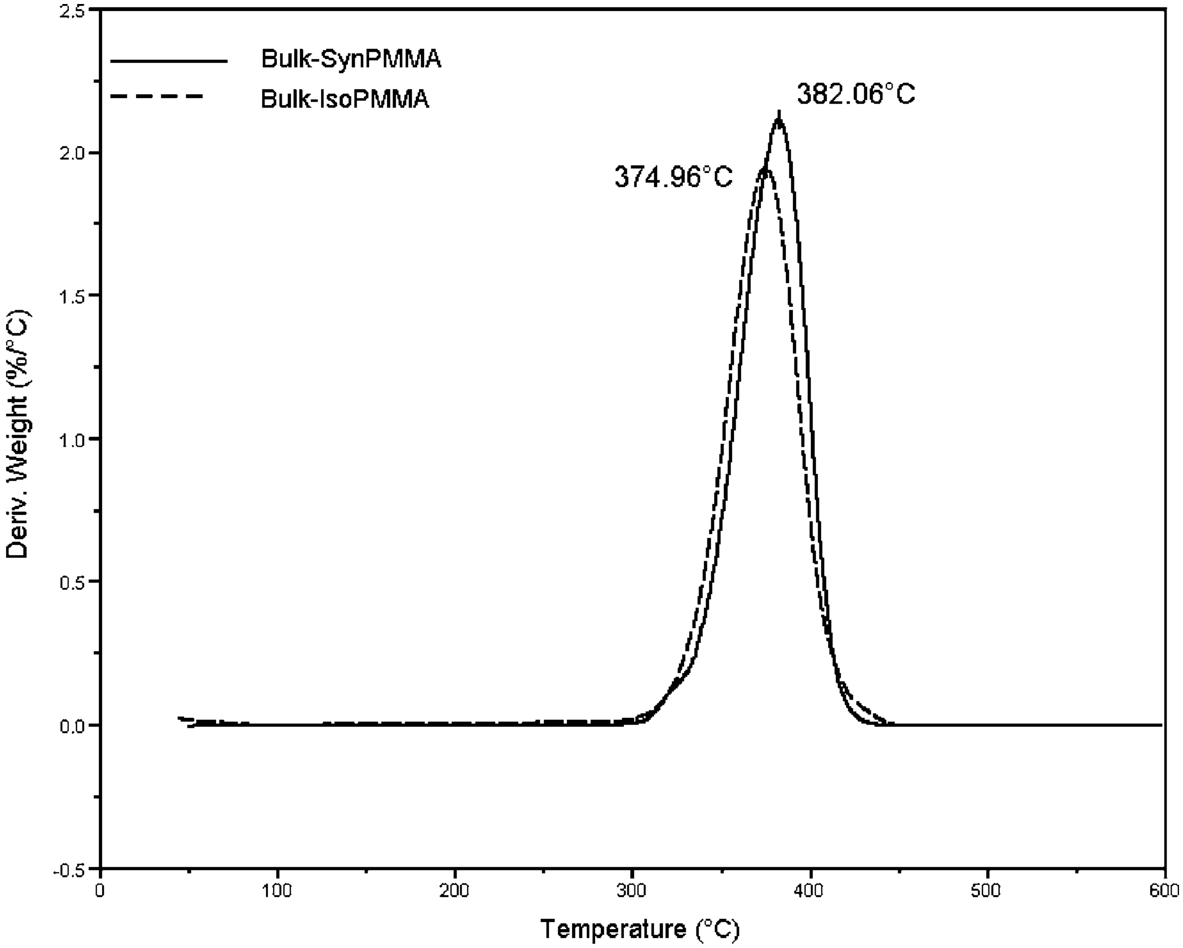

Fig. 1. DTG results for bulk *iso*-PMMA and *syn*-PMMA under N_2. Heating rate: 10 °C/min.

[6] from DSC measurements. They attributed the difference in degradation temperature to the higher segmental mobility of *iso*-PMMA. Sharma et al. [16] suggested that the self-association of *syn*-PMMA chains could also influence its degradation behavior. Neither group gave a detailed explanation for these effects.

The work of Jellinek and Luh [14] suggests that *iso*-PMMA has a much faster initiation rate than the *syn*-PMMA. The random initiation rate constant, k_{ir}, of *iso*-PMMA is five times higher than that of *syn*-PMMA. We believe that the “cage recombination effect” discussed by Manring [10] could be why the decomposition of isotactic PMMA was initiated at lower temperatures. Manring proposed that the high viscosity of the polymer allows the newly formed radicals to recombine. The higher chain mobility of isotactic PMMA [27,28], as evidenced by a lower T_g [29] may result in radical pairs, formed by random scission, which separate rapidly. Consequently, the cage recombination effect would be weaker, leading to a higher k_{ir}. In addition, the newly formed monomer molecules can escape from the radicals easier, resulting in a higher depropagation rate and lower degradation temperature. Molecular mass has an opposite effect under these conditions [5]. Experimentally, low molecular mass PMMA has a *higher* T_{max} than high molecular mass PMMA under similar conditions. This is probably because the depolymerization of higher molecular mass chains yields more mass loss per chain. In our experiments, isotactic PMMA had

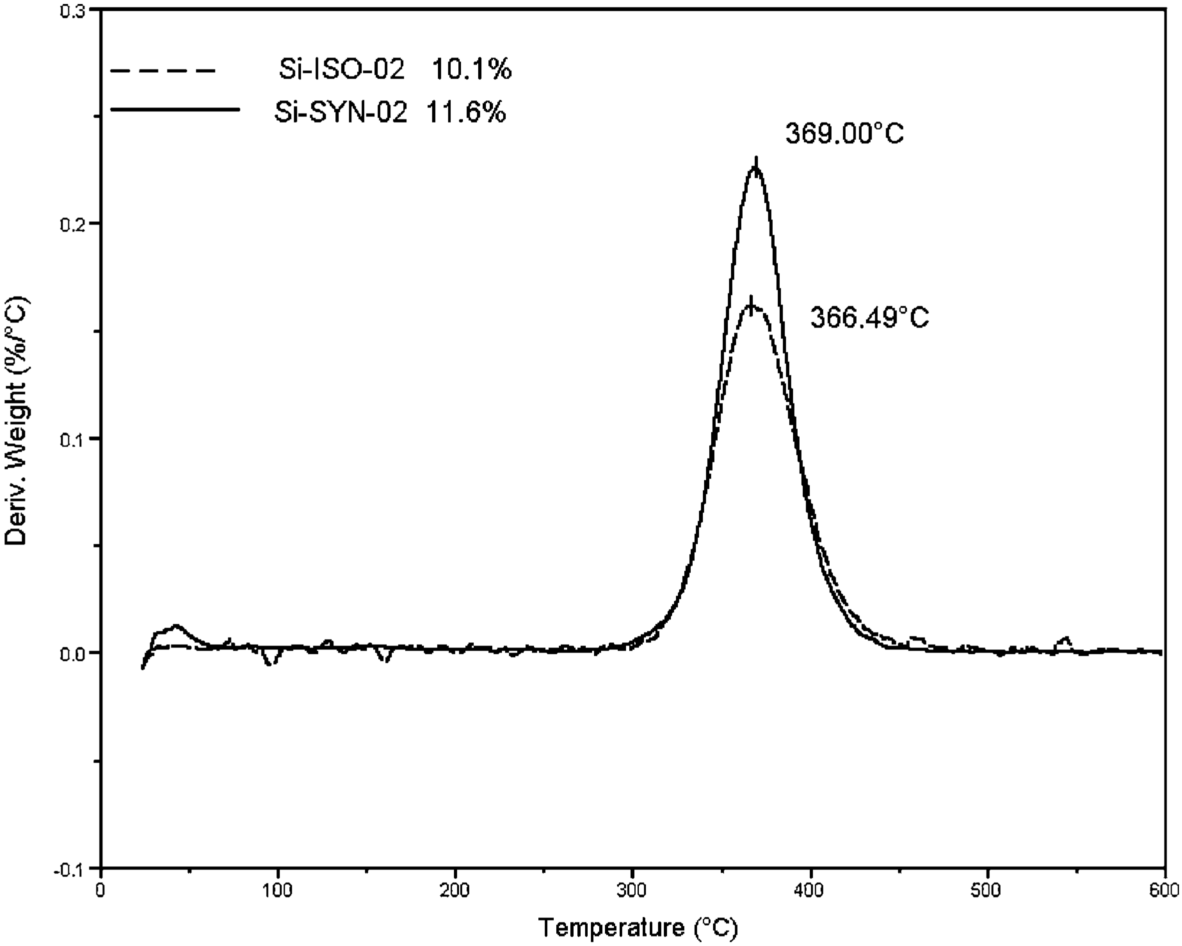

Fig. 2. DTG results of *syn*-PMMA and *iso*-PMMA adsorbed on silica M-5P with larger adsorbed amounts.

a lower molecular mass and *lower* T_{max} than syndiotactic PMMA. Therefore, molecular mass differences cannot account for the lower T_{max} of *iso*-PMMA.

3.2. PMMA adsorbed on M-5P silica

The DTG results of *syn*-PMMA and *iso*-PMMA samples adsorbed on M-5P silica, with adsorbed amounts of about 11% (by mass), are shown in Fig. 2. From the DTG curves of those samples, two features can be noted. First, the degradation peaks have a single feature in the range 300–450 °C. Second, the T_{max}'s (369 °C for *syn*-PMMA, 366 °C for *iso*-PMMA) are lower than those of the bulk sample (382 °C for *syn*-PMMA, 375 °C for *iso*-PMMA).

The single peaks at about 370–390 °C probably correspond to a random scission initiation mechanism for anionically polymerized PMMA that appears not to have weak linkages [3]. We believe the lower T_{max} for the sample with a high adsorbed amount may be explained by the cage-recombination and monomer-diffusion effects [30]. If we assume that the density of PMMA is 1.2 g/cm^3 (same as bulk) on the silica surface, the thickness of the adsorbed layer would correspond to about 6 Å for sample Si-SYN-02. The polymer chains are unlikely to form a uniform thin film at this adsorbed amount, since the polymer regions would be too thin. However, even with some segregation, the polymer must be very thin. The cage recombination effect would be expected to

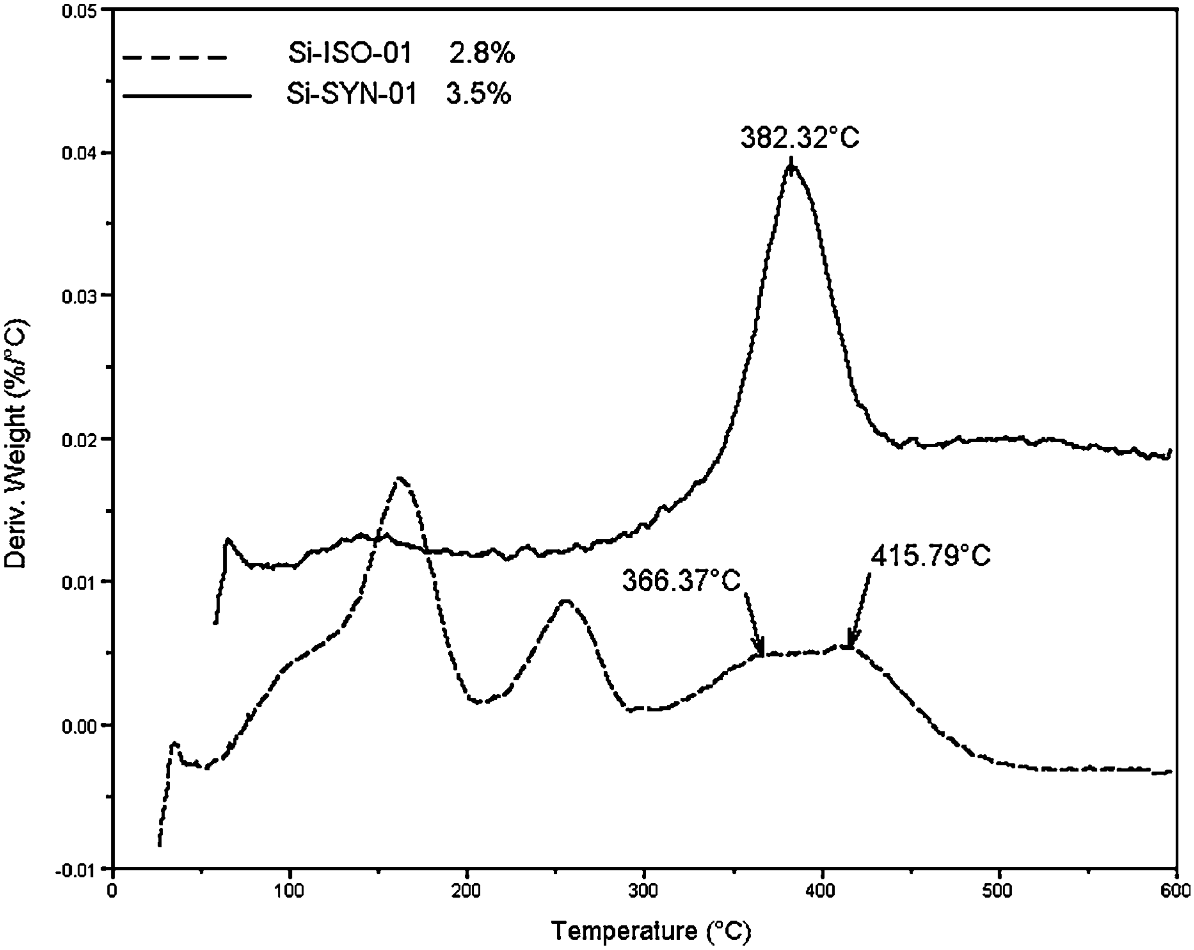

Fig. 3. DTG results of *syn*-PMMA and *iso*-PMMA adsorbed on silica M-5P with low adsorbed amounts.

be insignificant in such a thin layer because there are few segments close enough to make a true "cage". Meanwhile, the monomer diffusion effect will be minimized as well. Monomer molecules formed from depolymerization can get away easily in such a thin film; consequently, the rate of depropagation would be increased due to the loss of a reaction product. Both of the effects would accelerate the degradation process, and decrease the $T_{\max}$.

The DTG results for the *syn*-PMMA and *iso*-PMMA samples adsorbed on M-5P silica with lower adsorbed amounts (3.5 wt.% for *syn*-PMMA and 2.8 wt.% for *iso*-PMMA) are shown in Fig. 3. It is interesting that the *syn*-PMMA sample still has a single decomposition peak but the *iso*-PMMA sample has a very complex degradation curve. The $T_{\max}$ of the *syn*-PMMA sample (382 °C, Si-SYN-01) is higher than the $T_{\max}$ of that with the higher adsorbed amount (369 °C, Si-SYN-02). For the *iso*-PMMA sample Si-ISO-02, the high temperature peak split into two humps at around 370 °C with the highest peak greater than 400 °C. The lower temperature humps are much lower than in the other samples.

The increased $T_{\max}$ for the *syn*-PMMA sample with the lower adsorbed amount can be rationalized by the interaction between PMMA chains and the silica surface. Higher decomposition temperatures than those for bulk were observed by Aruchamy et al. [18] and Morgan et al. [17] in SiO_2–PMMA composites. Morgan et al. explained their results by the "trapping effect" on the degradation products from SiO_2 particles. This is unlikely to be the reason in our systems because that trapping effect is unlikely to exist in such a thin film. The H-bonding interaction between carbonyl groups in PMMA and Si–OH groups on silica surfaces was proposed by Aruchamy et al. [18] as another possible reason for enhanced stability. IR spectroscopy has shown that PMMA will hydrogen bond with silica [31–33] and that this H-bonding affects the electron density in parts of the polymer molecule. The results of Aruchamy et al. [18] and Morgan et al. [17] suggested that this interaction might interrupt the chain depropagation. A higher number of interaction sites would mean a higher decomposition temperature. In this study, when less syndiotactic PMMA was adsorbed onto a silica surface, the adsorbed polymer chains would be expected to have a flatter configuration, resulting in more contact sites [34,35], plus lower mobility. This probably resulted in an increase of $T_{\max}$ when the adsorbed amount decreased.

The complex humps at around 400 °C for the isotactic sample indicate a complicated degradation of segments in different situations. The degradation peaks at the temperatures lower than 300 °C may have resulted from chains under stress formed during the drying process. The nature of these chains and why the isotactic polymer is more sensitive to the effect are not currently known. We are continuing to study this effect.

4. Conclusions

The thermal degradation behavior of PMMA adsorbed on silica is dependent on factors that include tacticity and adsorbed amount. In bulk, the *syn*-PMMA is more stable than *iso*-PMMA due to the stiffness of backbone. When adsorbed on silica, the effects can become complicated. For both *iso*-PMMA and *syn*-PMMA, the $T_{\max}$'s were lower than the values for the bulk samples when adsorbed amounts were higher (ca. 11%). When the adsorbed amounts were lower, the adsorbed *syn*-PMMA showed much simpler degradation behavior than that of the adsorbed *iso*-PMMA. Low adsorbed amount *syn*-PMMA had a single degradation peak at 382 °C, which was higher than that of the *syn*-PMMA sample with a higher adsorbed amount. The lower degradation temperatures for adsorbed PMMA at high adsorbed amounts stem from the absence of a "cage recombination effect" that blocked the initiation of chain depolymerization and increased mobility of monomer molecules. The increased $T_{\max}$ with a decreased adsorbed amount is likely due to the flatter configurations on the surface. The adsorbed *iso*-PMMA with a low adsorbed amount (2.8 wt.%) has three strong degradation signals at about 150, 260, and 390 °C. The complex behavior of this polymer on silica may be due to a stronger interaction between the polymer and the silica surface, and possibly different conformations of the polymer, as compared to *syn*-PMMA.

Acknowledgements

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