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THERMOGRAVIMETRIC STUDIES OF PMMA ON SILICA

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Introduction

The thermal degradation of poly(methyl methacrylate) (PMMA) has been studied extensively. It is well accepted that the degradation process is a radical chain reaction involving initiation, depropagation, transfer, and termination reactions. In the degradation process, the factors having observable effects on the decomposition behavior include molecular mass, polydispersity,¹ tacticity,² and sample dimensions.³ The effects of tacticity on the degradation behavior of PMMA were investigated by Kashiwagi et al.,² Jellinek et al.⁴ and Chiamtore et al.⁵ The results indicated that both isotactic and syndiotactic PMMA have similar decomposition pathways and activation energies. Isotactic PMMA will decompose at a slightly lower temperature and over a broader range, compared to syndiotactic PMMA with the similar chain ends and molecular masses. It has also been reported that isotactic PMMA is more sensitive to electron-beam radiation, namely, it degrades more easily, than syndiotactic PMMA.⁶

The PMMA-SiO₂ system has been investigated by a few groups.^{7,8} The results indicated that the interaction between the carbonyl groups and silica surfaces can increase the decomposition temperature of PMMA. However, how different variables affect the decomposition behavior of PMMA is still far from clear. In the present work, we report studies of the degradation of ultrathin adsorbed PMMA on silica with a specific focus on the effects of adsorbed amount and tacticity on decomposition.

Experimental

Both isotactic and syndiotactic PMMA samples were prepared by anionic polymerization, initiated by the reaction product of *sec*-butyllithium and 1,1-diphenylethylene. For syndiotactic PMMA, polymerization was conducted in THF at -78 °C. The isotactic PMMA was made in toluene at 0 °C. The resulting PMMA samples were reprecipitated from acetone by hexane several times and then dried overnight in a vacuum oven at 70 °C. Molecular mass was measured by gel permeation chromatography (GPC) in THF, relative to standard polystyrene samples. The relative amounts of iso-(mm) syndio-(rr) and hetero-(mr) triads were calculated from the ¹H-NMR spectra⁹ resonance intensities at 1.2, 0.8 and 1.0 ppm respectively. The results are shown in Table 1.

Table 1. Characterization of Bulk PMMA

Polymer	Molecular Mass (M_n)	Polydispersity	Tacticity (% triads)		
			mm	rm	rr
SynPMMA	71,100	1.23	2.3	23.0	74.7
IsoPMMA	35,000	1.65	88.9	8.0	3.1

THF was used to prepare PMMA solutions of different concentrations. Polymer solutions (10 ml) were transferred into centrifuge tubes containing ~0.3 g fumed silica (CAB-O-SIL M-P5, surface area 200 m²/g, Cabot Corp., Tuscola, IL). The mixtures were shaken for 24 hours at 23 °C. The tubes were centrifuged after adsorption and the supernatant solutions were discarded. The residue was initially blow-dried in air. The adsorbed samples were dried completely in a vacuum oven at ~70 °C overnight. The degradation of bulk and adsorbed samples was measured with a TA Instruments model 2950 TGA (New Castle, DE) with a heating rate of 10 K/min from 25 to 600 °C under nitrogen. The sample weight was about 10 mg for the bulk samples, and about 20 mg for adsorbed samples. The purge gas flow rate was 25 ml/min. The adsorbed amounts were calculated from TGA results and are listed in Table 2.

Results and Discussion

The thermal degradation of bulk PMMA was studied in order to compare its results with those of the surface adsorbed samples. The derivative TGA scans of the bulk samples are shown in Figure 1. The T_{max} (maximum rate decomposition temperature, namely the peak temperature) values are indicated on the scans. Single decomposition peaks were observed within a narrow temperature range. Isotactic PMMA degraded at a slightly lower

temperature than syndiotactic PMMA did (about 7 K lower in this case) and with a similar transition range (syndiotactic 48 K, isotactic 47 K). The same phenomena were noted by Kitayama et al. in the degradation measurements by DSC.²

Table 2. Adsorbed PMMA Samples on Silica

Designation	polymer	Adsorbed Amount (%)	T_{max} (°C)
Si-SYN-01	SynPMMA	3.49	382
Si-SYN-02	SynPMMA	3.42	383
Si-SYN-03	SynPMMA	5.41	373
Si-SYN-04	SynPMMA	11.6	369
Si-ISO-01	IsoPMMA	2.81	360-420
Si-ISO-02	IsoPMMA	4.09	360-410
Si-ISO-03	IsoPMMA	4.68	360-410
Si-ISO-04	IsoPMMA	10.1	368

The work of Jellinek⁴ suggests that the random initiation rate constant, k_{ir} , of isotactic PMMA is 5 times higher than the k_{ir} of syndiotactic PMMA. Also the kinetic chain length for depropagation of isotactic PMMA is shorter than that of syndiotactic PMMA.⁴ This means the degradation of isotactic PMMA chains is easier to start, but easier to interrupt. Molecular mass has an opposite effect under these conditions.¹⁰ Low molecular mass PMMA should have a higher T_{max} than high molecular mass PMMA under similar conditions. In our experiments, the isotactic PMMA had a lower molecular mass and lower T_{max} than syndiotactic PMMA. Therefore, molecular mass differences can not account for the lower T_{max} of isotactic PMMA.

We believe that the "cage recombination effect" discussed by Manring¹¹ could be why decomposition of isotactic PMMA was initiated at lower temperatures. The higher chain mobility of isotactic PMMA, as evidenced by a lower T_g ,¹² 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 the radicals easier, resulting in a higher depropagation rate and lower degradation temperature.

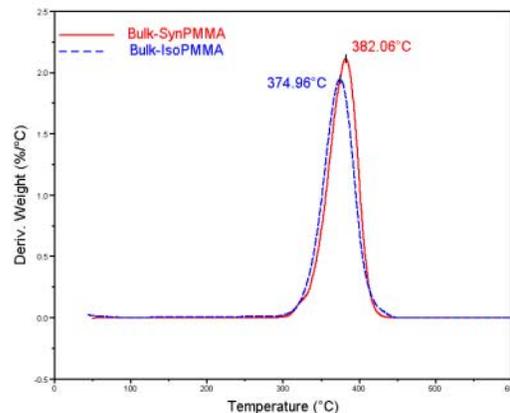


Figure 1. Derivative TGA results for bulk isotactic and syndiotactic PMMA.

The derivative TGA results of four syndiotactic PMMA samples adsorbed on silica are shown in Figure 2. From the TGA curves of those four samples, several features can be noted. Single peaks at temperatures of about 370 to 390 °C were observed, except for sample Si-SYN-03. The peak at about 260 °C for sample Si-SYN-03 was similar to that observed for the isotactic samples; this will be discussed later with those samples. The sample with the highest adsorbed amount (Si-SYN-04) has a lower T_{max} (369 °C) than the bulk sample (382 °C). We believe that this may also be explained by the cage recombination and monomer diffusion effects. If we assume that the density of PMMA is 1.2 g/cm³ (same as bulk) on the silica surface, the thickness of the adsorbed layer would correspond to about 6 Å for sample Si-SYN-04. The chains are unlikely to form a uniform thin film at this adsorbed amount, but the polymer regions must be very small indeed. The cage recombination effect would be expected to be insignificant in such a thin layer

because there are few segments close enough to make a true “cage”. In addition, the monomer diffusion effect will be minimized as well, since any monomer molecules formed from depolymerization can escape rapidly. These effects would be expected to result in a greatly depressed first-order termination reaction between polymer radicals and monomers.¹³ Both of the effects above would be expected to accelerate the degradation process, and decrease the T_{max} .

The value of T_{max} also increased when the adsorbed amount decreased, and ultimately became higher than the T_{max} of the bulk sample when the adsorbed amount was very low. It has been shown by IR spectroscopy that the H-bonding affects the structure and electron distribution of the related groups.¹⁴ The results of Aruchamy and Morgan^{7,8} suggested that the interaction might interrupt the chain depropagation. A higher fraction 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 plus lower mobility. This resulted in an increase of T_{max} when the adsorbed amount decreased.

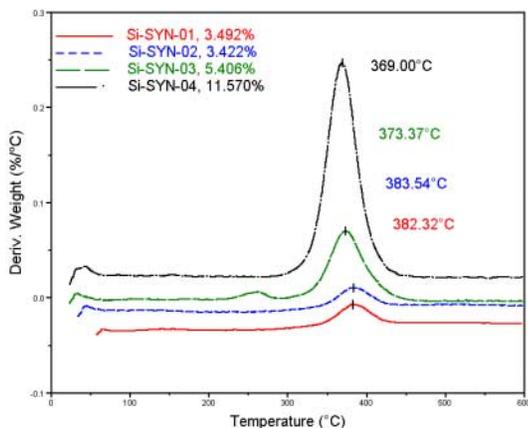


Figure 2. Derivative TGA results for syndiotactic PMMA films on silica with different adsorbed amounts.

The derivative TGA results for four isotactic PMMA samples adsorbed on silica are shown in Figure 4. The highest adsorbed amount sample (Si-ISO-04) also had a single decomposition peak, with a T_{max} (366 °C) lower than bulk. This is similar to the behavior of the syndiotactic polymer, probably for the same reasons. An interesting phenomenon is that all of the three low adsorbed amount samples have very complex, but similar degradation curves. Compared with the TGA curve of sample Si-ISO-04, the peak at about 370 °C split into two humps. The lower temperature humps are roughly in the same position as that for sample Si-ISO-04. The humps on the high temperature side are about 40-50 K higher. These humps moved even higher when the adsorbed amount decreased. Besides the two humps at high temperature, another two weight loss peaks appeared at about 260 °C and 170 °C. They were in the same positions as the small peaks observed for the adsorbed syndiotactic samples, but the intensities were much higher. At the present time, we do not have a satisfactory explanation for these low temperature degradations.

The complex humps at around 400 °C indicate a complicated degradation of segments in different situations. The degradation peaks at the temperatures lower than 300 °C may have resulted from some weak linkages resulting from stress on the polymer chains due to the interaction between PMMA chains and the silica surface. However, since there is no report in literature about the decomposition phenomena of such thin PMMA films, we do not have enough information to clarify the detailed degradation behavior of these surface species.

Because the more mobile isotactic PMMA chains have a stronger interaction with silica than syndiotactic PMMA, the fraction of surface bonded units can be as high as 0.7 (0.1 for syndiotactic PMMA).¹⁵ The effect of the silica surface would be expected to be more severe on the surface isotactic PMMA segments.

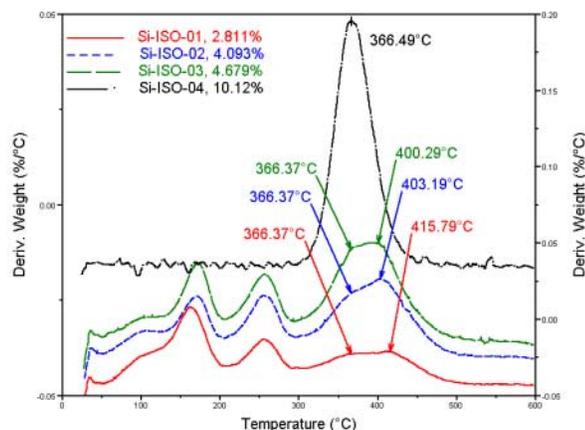


Figure 3. Derivative TGA results of isotactic PMMA films on silica with different adsorbed amounts.

Conclusions

In bulk, syndiotactic PMMA is more stable relative to degradation in nitrogen than isotactic PMMA due to the chain stiffness of the syndiotactic polymer backbone. The lower degradation temperatures for both adsorbed isotactic and syndiotactic PMMA, than for bulk, at higher adsorbed amounts are probably due to the absence of the “cage recombination effect” that blocks the initiation of chain depolymerization. The increasing T_{max} for adsorbed syndiotactic PMMA, with decreasing adsorbed amounts, is due to a larger fraction of polymer segments being much closer to the silica surface.

The adsorbed syndiotactic PMMA shows a much simpler degradation behavior than that of adsorbed isotactic PMMA. It generally has just a single degradation peak on a derivative TGA curve at around 380 °C, but the adsorbed isotactic PMMA has three strong degradation signals at about 150, 260, and 390 °C, unless the adsorbed amount is high (11%, by wt.). We are not sure why this is so at the present time.

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