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Change in Physico-chemical Properties of PMMA and PS by Copolymerization with an Anionic Amphiphilic Comonomer: Sodium 11-(methacryloyloxy) undecanylsulfate (MET)

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Summary: Sodium 11-(methacryloyloxy) undecanylsulfate (MET) monomer units were incorporated in polystyrene (PS) and poly(methyl methacrylate) (PMMA) by free radical copolymerization in solution with styrene and methyl methacrylate, respectively. Experimental compositions, thermal degradations, average molecular weights, glass transitions and affinities for moisture were experimentally determined for copolymers of various compositions. Both styrene and methyl methacrylate copolymerized well with MET. An increase in the moisture affinity and a change in the glass transition were observed with increasing MET content in the respective copolymers.

Keywords: amphiphilic copolymers; DMA; moisture affinity; polymerizable surfactant; TGA

Introduction

Polymerizable surfactants (''Surfmers'') are amphiphilic molecules containing a polymerizable chemical group. Many different surfmers, with different reactive groups localized in various positions (head or tail), have been synthesized and characterized.[1] Among the different types of surfmers, almost all of them have been used for their self-assembly properties in water. They have been mainly used either in templated polymerization or in emulsion polymerizations.[2–9] When surfmers are copolymerized with conventional monomers, the obtained polymers are generally used for their amphiphilic properties in different media. Very little has been published on the bulk properties of surfmer-containing copolymers.[10,11]

In a previous paper, we reported on the changes in the organization and on the thermal properties of copolymers of PS and of PMMA arising from the presence of MET comonomers.[12] The undecylsulfate groups of the MET monomer units self organize in the amorphous polymer matrices, giving rise to the formation of clusters between the macromolecular chains. The present article deals with PMMA-MET and PS-MET copolymers containing different ratios of MET. The changes in their water-affinity and mechanical properties with changing MET content are discussed.

Experimental

Styrene and methyl methacrylate (Acros) were distilled prior to use. The synthesis of MET is described elsewhere.[13] Azo(bis)-isobutyronitrile (AIBN) was recrystallized from methanol.

Size exclusion chromatography (SEC) was performed with a Waters 600E system controller equipped with a Waters 610 Fluid Unit pump, a Waters 410 Differential Refractometer as detector, and a column set of PLgel 5 μm guard 50*7.5 mm and

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PLgel 5 μm mixed-C 300*7.5 mm (Polymer Laboratories). Measurements were done at 30 °C using THF as eluent, with a flow rate of 1 mL/min. Molar masses were determined relative to narrow polystyrene standards calibration (EasiVial PS from Polymer Laboratories).

^{1}H NMR was performed at 298 K, using a Varian VXR-Unity 400 MHz, with a 90° pulse sequence. Copolymers were dissolved in $CDCl_3$ containing 0.05 v/v % of tetrametylsilane (TMS) as reference.

Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer Pyris 1 DSC Differential Scanning Calorimeter, at a temperature rate of 10 °C/min.

Thermogravimetric analysis (TGA) was performed using a Perkin-Elmer TGA 7 Thermo-Gravimetric Analyser, at a temperature rate of 20 °C/min.

Dynamic mechanical analysis was performed using a Dynamic Mechanical Analyser Perkin Elmer DMA 7e, using a temperature rate of 5 °C/min. A 3-mm diameter probe was used with a 1 Hz frequency.

Copolymerizations (cf. Table 1). Varying quantities of the monomer (styrene or MMA), MET, AIBN, and 90 g of dimethylformamide (DMF) were placed in a 250 mL Schlenk tube equipped with a stirrer bar and a glass cap. The mixture was degassed by three consecutive freeze-thaw cycles, using a liquid nitrogen bath. The Schlenk tube was then placed in a silicon oil bath and the content was stirred at 70 °C for 12 h. The DMF was distilled off under reduced pressure. Copolymers P(MMA-co-MET) were purified three times by precipitation into petroleum ether (400 mL) from a concentrated solution in chloroform. Copolymers P(S-co-MET) were purified by washing with 400 mL of methanol (three times).

Results and Discussion

Synthesis and Characterization of Copolymers

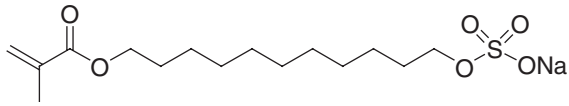
The chemical structure of MET is depicted in Scheme 1.

Copolymers were synthesized by free-radical polymerization in solution (DMF), initiated by AIBN. The same molar ratio of AIBN to monomers (i.e. 0.6 mol%) and the same weight ratio monomers to DMF (i.e. 10 wt%) were used for all copolymeriza-

Table 1.
Copolymerization conditions of MET with styrene and methyl methacrylate.

	wt% of MET		MMA (g)	Styrene (g)	MET (g)	AIBN (mg)	DMF (g)	$\overline{M_n}$ (g/mol)	$\overline{M_w}$ (g/mol	$\overline{M_w}/\overline{M_n}$
	Feed	exp.[1]								
P(MMA-co-MET)	0	0	10.0	—	0	100.3	90	33,590	51,890	1.54
	0.10	—[2]	9.99	—	0.01	100.3	90	53,730	97,230	1.81
	0.50	—[2]	9.95	—	0.05	100.0	90	43,930	100,340	2.28
	1.00	0.8	9.90	—	0.10	99.6	90	29,700	66,930	2.25
	2.50	2.02	9.75	—	0.25	98.5	90	10,030	37,190	3.71
	5.00	3.94	9.50	—	0.50	96.7	90	7,380	30,932	4.19
	7.50	4.13	9.25	—	0.75	94.9	90	4,680	17,780	3.80
	10.00	5.04	9.00	—	1.00	93.0	90	3,240	12,640	3.91
	20.00	12.00	8.00	—	2.00	85.7	90	1,450	4,300	2.98
P(S-co-MET)	0	0	—	10.00	0	93.9	90	10,110	16,060	1.59
	0.10	—[2]	—	9.99	0.01	93.9	90	8,800	16,190	1.84
	0.50	—[2]	—	9.95	0.05	93.6	90	8,280	17,270	2.09
	1.00	0.97	—	9.90	0.1.00	93.2	90	7,470	16,180	2.17
	2.50	2.56	—	9.75	0.25	92.2	90	6,400	14,510	2.27
	5.00	5.36	—	9.50	0.50	90.6	90	5,830	13,530	2.32
	7.50	7.84	—	9.25	0.75	88.9	90	4,630	10,620	2.29
	10.00	12.40	—	9.00	1.00	87.2	90	3,160	8,060	2.55
	20.00	29.94	—-	8.00	2.00	80.6	90	2,030	5,740	2.82

[1] Determined by ^{1}H NMR.
[2] Signal too small to be integrated accurately to determine a value.



Scheme 1.
Structure of the monomer sodium 11-(methacryloyloxy) undecanylsulfate (MET).

tions. Two series were synthesized with different ratios of MET i.e. copolymers of MET with methyl methacrylate, noted P(MMA-co-MET), and copolymers of MET with styrene, noted P(S-co-MET). In each series the MET ratio was varied from 0 to 20 wt% (cf. Table 1). The polymerization mixture was magnetically stirred for 12 h at 70 °C. The purification of the obtained copolymer was not possible by precipitation in methanol, as a stable fine suspension formed. This could be explained by an increase of the polarity of the polymers due to the presence of MET monomer units. Copolymers of P(MMA-co-MET) were precipitated into petroleum ether from a solution in chloroform (after the DMF was firstly distilled off). No solvent miscible with petroleum ether was found able to dissolve the copolymers P(S-co-MET); hence they were purified by direct washing of the crude polymer with methanol after the reaction solvent (DMF) was removed under reduced pressure. The copolymer obtained with 20 wt% of MET was washed with petroleum ether, as it was found soluble in methanol. This is in accordance with an increase in the polarity of the macromolecular chain of PS by incorporating MET monomer units.

No trace of residual monomer was observed by ^{1}H NMR from the precipitated copolymers. Experimental compositions reported in Table 1 (second column) were determined by calculation using the integration values found for typical peaks of MET and PS (or MMA) monomer units. As shown in Figure 1, MET monomers seemed to copolymerize more easily with styrene than with MMA, as the determined experimental compositions were higher than the values expected (% feed) for copolymers of styrene and lower for copolymers of MMA. Moreover, the polymerization yields were

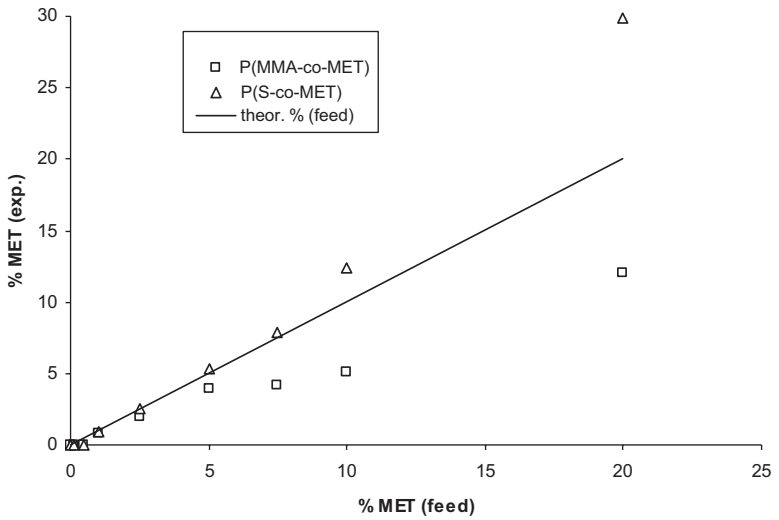


Figure 1.
Theoretical (feed) and experimental compositions in the copolymers P(MMA-co-MET) and P(S-co-MET) (wt% of MET).

found to be higher for copolymers of styrene than for copolymers of MMA. The bulkiness of MET appears therefore to hinder its copolymerization with MMA, while in case of copolymerization with styrene its bulkiness seems to be largely compensated by favourable reactivity ratios, as described elsewhere.[14,15] Reactivity ratios between styrene and MET, and between MMA and MET, were not determined in the present work.

No direct analysis was performed to determine whether a true copolymerization occurred between MET and styrene (or MMA). Nevertheless, obvious changes in the copolymers' solubility were observed as the MET ratio increased. Copolymers were found to be increasingly soluble in polar solvents as the MET ratio increased. The copolymers that were obtained were probably random copolymers, because of the method of polymerization (in solution) and the changes in the polymer solubility observed.

Molecular weights were determined by SEC using THF as eluent. $\overline{M_w}$ and $\overline{M_n}$ were calculated from elution times using a PS standards scale. Taking this into account, the values obtained for the two series of copolymers could not be compared. Molecular weights decreased and polydispersities increased as the MET content increased in both the P(MMA-co-MET) and P(S-co-MET) series. This could be due to an increase in the rate of the termination reaction by disproportionation with increasing the ratio of methacrylic monomers MET. The amphiphilic feature of MET probably favours association processes and therefore increases the probability of two MET radicals encountering each other. Nevertheless, regarding to the relatively high molecular mass polydispersities obtained for high MET-containing copolymers, one can not exclude that the results were influenced by both PS calibration and/or adsorption of the polymer on the columns.

Thermal Stability

Degradation temperatures of P(MMA-co-MET) and P(S-co-MET) are tabulated in Table 2. The degradation of copolymers of PMMA occurred in several steps, while in

Table 2.
Thermal data of copolymers P(MMA-co-MET) and P(S-co-MET)

	MET exp. (wt%)	T_g (°C)[b]	Storage modulus[c] $\times 10^{-7}$ Pa	Degradation Temp. (°C)	
				T_{onset}	T_{end}
P(MMA-co-MET)	0	105*	—	280	428
	0.1[a]	—	—	280	435
	0.5[a]	—	—	278	420
	0.8	119	34	281	421
	2.0	133	6.7	247	418
	3.9	132	1.1	252	419
	4.1	—	—	244	421
	5.0	129	2.2	272	426
	12.0	129	3.5	298	487
P(S-co-MET)	0	100*	—	372	481
	0.1*	112	38	387	495
	0.5*	—	—	380	485
	1.0	119	34	370	461
	2.6	—	—	380	479
	5.4	—	—	397	493
	7.8	104	32	386	471
	12.4	—	—	388	474
	29.9	94	11	388	492

[a] theoretical composition.
[b] determined from tanδ curve by DMA.
[c] maximum storage modulus on the plateau determined by DMA before the T_g.
* *Polymer Handbook, 2nd Ed.*[17].

only one step for copolymers of PS. The thermal degradation of PMMA prepared by free radical polymerization generally takes place in four weight losses, corresponding to four degradation stages. The first stage corresponds to the degradation initiated by radical transfer to the unsaturated chain end, while the other stages result from scissions of the macromolecular chain as well as degradation initiated by radical transfer to the unsaturated chain end.[16] As the MET unit content increased, degradation of P(MMA-co-MET) changed progressively from a multi-step process to a one-step process.

It is noteworthy that T_{onset} of P(MMA-co-MET) copolymers decreased for ratios of MET up to 4 wt%, and then increased again to reach a higher value than for PMMA (for 12 wt% of MET) with $T_{onset} = 298\,^{\circ}C$. Furthermore, for this same composition T_{end} was much higher ($>50\,^{\circ}C$) than for PMMA or for copolymers P(MMA-co-MET) with lower MET content. The multi-step degradation of PMMA tended to turn into a one-step process as the MET ratio increases in the copolymers P(MMA-co-MET). In consequence, when copolymerized with 12 wt% MET, the thermal stability of PMMA was found to greatly improve. Increase in temperature degradation with formation of lamellar structures has been reported elsewhere.[18] The enhancement of the thermal degradability could be due to the ability of MET monomer units to form clusters or lamellar structures. The existence of such structures in copolymers containing MET has been previously observed by TEM.[12]

The onset degradation temperature of P(S-co-MET) copolymers was found to be around 380 °C. The higher temperature of thermal degradation of PS vs. PMMA polymers has been reported elsewhere.[19] No noticeable improvement in the thermal degradation temperatures with increasing the MET ratio was observed for copolymers of P(S-co-MET) (Fig. 2–4).

Phase Transitions and Storage Modulus

Glass transition temperatures (T_g) were determined by DMA from *tan* δ curves. Polymer samples were pressed at 150 °C. Samples were then slowly cooled to room temperature. This was done to minimize the occurrence of stress relaxation peaks observed on the storage modulus plateau before the T_g. Despite using this preparation method, an important stress relaxation peak was observed with all the samples.

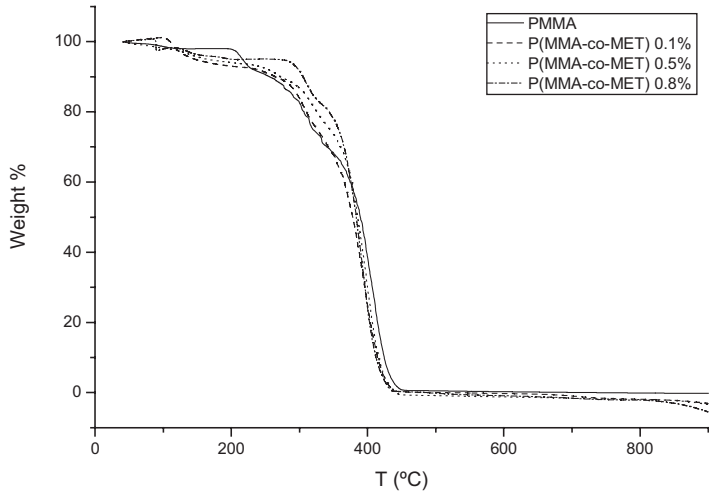


Figure 2.
TGA plots of copolymers P(MMA-co-MET) with low MET contents.

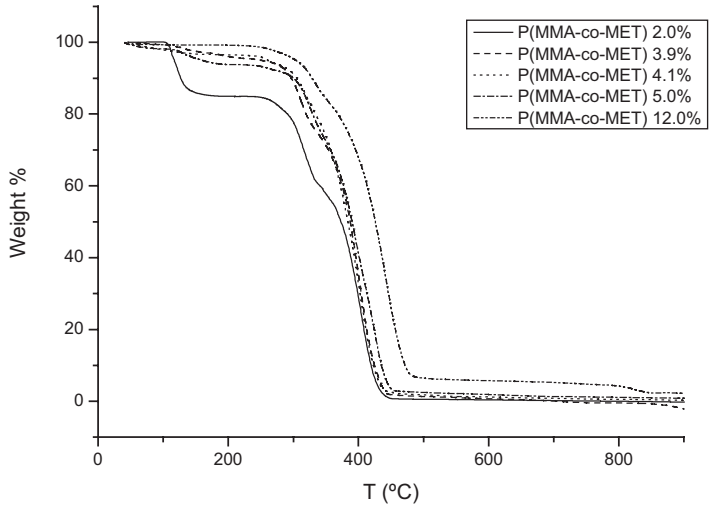


Figure 3.
TGA plots of copolymers P(MMA-co-MET) with medium MET contents.

Therefore, the absence of a plateau on the storage modulus curve reduced the accuracy the of T_g and storage modulus values determined.

Storage modulus, *tan* δ and loss modulus curves for the copolymer P(S-co-MET) 1% are plotted in Figure 5 as a typical example. Storage modulus values below the glass transition temperatures are reported in Table 2. For each copolymer, the highest value of the storage modulus was retained because the curves did not exhibit any satisfactory plateau before the T_g (see Figure 5). Copolymers of PMMA displayed higher T_g than copolymers of PS. Change of the MET content had a different effect on T_g values for both series. P(MMA-co-MET) copolymers exhibited a T_g around 130 °C from 2.5 to 12 wt% MET. The measured T_g was 119 °C for 1 wt% MET in both series P(MMA-co-MET) and P(S-co-MET). A very low amount of MET (0.1 wt%) monomer units was sufficient to raise the T_g of PS from 100 °C[17] to 112 °C. Then the

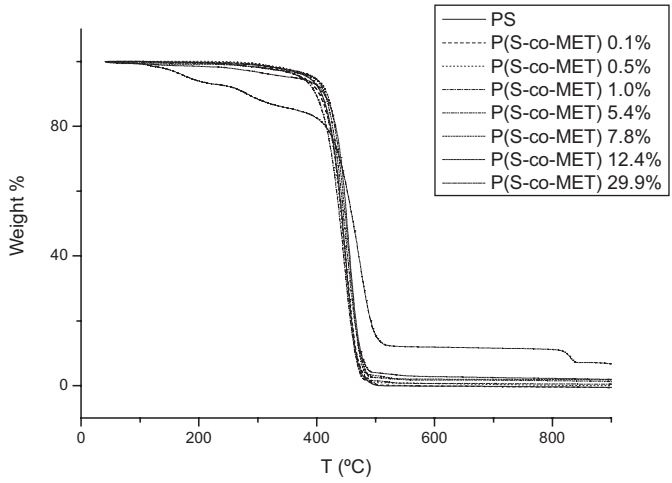


Figure 4.
TGA plots of copolymers P(S-co-MET) with various MET contents.

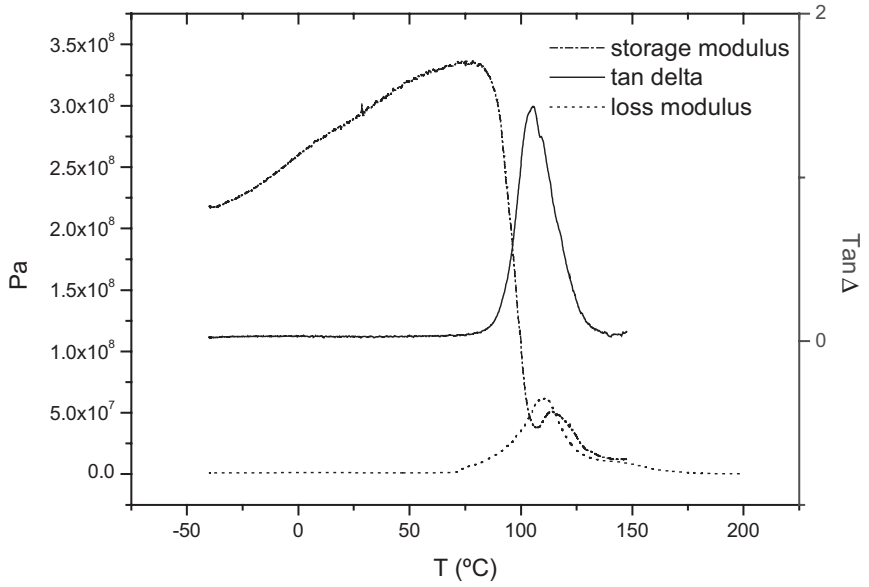


Figure 5.
DMA plot for P(S-co-MET) 1 wt%.

T_g decreased from 119 °C to 94 °C when the MET content increased from 1 to 29 wt% with copolymers of PS. The low T_g observed for the copolymer P(S-co-MET) 29.9% could be due to absorption of moisture by the sample before and during the measurement as the water affinity of the copolymers increased significantly with increasing MET content (see Figure 6). It is believed that a plasticization effect of MET in the presence of water lowered the T_g values.[20]

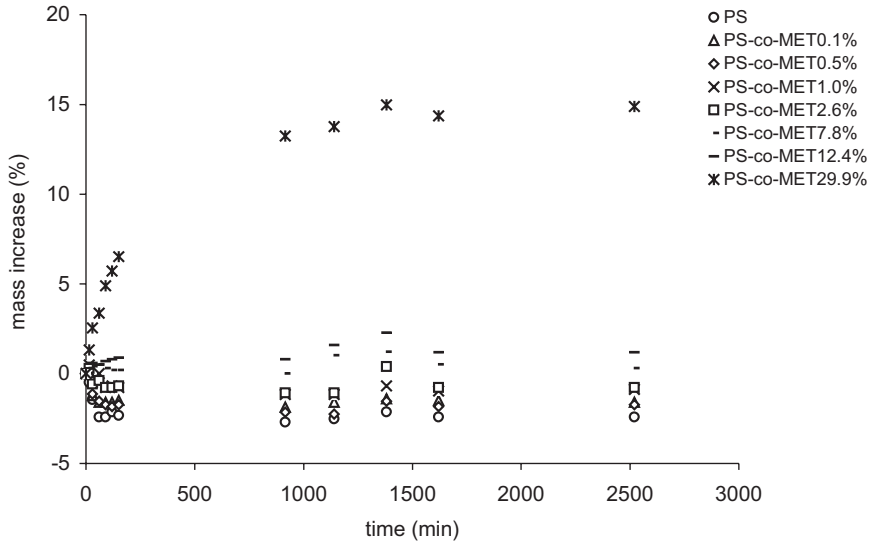


Figure 6.
Mass increase due to absorption of water by copolymers P(S-co-MET) versus time at 85% humidity and 32 °C.

Water Affinity

Due to their polar sodium sulfate groups, the presence of MET monomer units may increase the water affinity of the polymer matrix. Water vapour absorption of dried samples containing different ratios of MET was monitored. Samples were placed in an oven with a constant humidity rate of 85% at 32 °C. Absorption of water was monitored by weighing the samples periodically. Changes in wt. % with time are reported in Figure 6 and Figure 7 for copolymers P(S-co-MET) and P(MMA-co-MET), respectively. For both types of copolymers, the rate and extent of water absorption increased with MET content. For equivalent MET ratios the increase in the water affinity was relatively higher for copolymers of PMMA. Copolymer P(S-co-MET) 29.9% swelled up to 15 wt% after 23 h of exposure in an environment of 85% humidity and 32 °C. Copolymer P(MMA-co-MET) 12.0% swelled up to 6 wt% after 17 h of exposure in an environment of 85% humidity at 32 °C, while P(S-co-MET) 12.4% absorbed only about 2% of moisture after 20 h of exposure under the same conditions. This is not surprising since PMMA is more a more polar polymer than PS. The increase in water uptake as the MET content increased is likely due to a partial water affinity of the copolymer provoked by a hydration of the sodium sulfate of the MET units. Surprisingly, a slight decrease in the samples' weights (down to −2.7%) occurred for copolymers P(S-co-MET) with low MET contents. This unexpected decrease could be due to the evaporation of traces of methanol that was used to wash the polymer samples.

Conclusion

Copolymers P(S-co-MET) and P(MMA-co-MET) of different compositions were successfully synthesised by free radical polymerization in solution. MET copolymerized well with both styrene and MMA. However, it was observed that MET copolymerized more easily with PS than with MMA. By incorporating MET, an improvement in the thermal stability was observed with only copolymers of MMA, while no noticeable changes in the degradation temperatures T_{onset} and T_{end} were observed with copolymers of styrene. The presence of MET monomer units along the

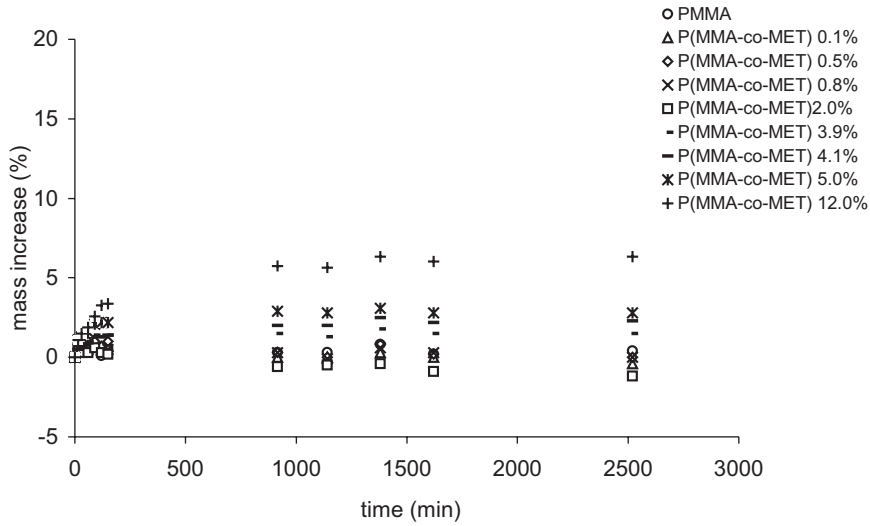


Figure 7.
Mass increase due to absorption of water by copolymers P(MMA-co-MET) versus time at 85% humidity and 32 °C.

macromolecular chain increases the water affinity of the material as shown by water vapour absorption. PMMA and PS containing about 12 wt% of MET absorbed up to 6 and 2 wt% of their mass, respectively, while P(S-co-MET) 30% could absorb up to 15 wt% of moisture. The presence of MET comonomer units along the macromolecular chain increased the T_g of PS and PMMA. Nevertheless, due to the increase of the water affinity with the MET content, absorption of water can lead to a decrease in the T_g for high MET containing copolymers. In this case, water probably plays the role of a plasticizer by hydration of the sodium sulfate groups of the MET side chains.

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