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The effect of stereoregularity on the thermal behavior of poly(methacrylic acid)s

I. Thermal analysis studies

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Summary

The thermal degradation of a series of poly(methacrylic acid)s (PMADs) with different tacticities has been investigated under inert atmosphere. All the samples showed two main degradation stages. The first decomposition process of isotactic PMAD consisted of the formation of anhydride groups, almost quantitatively, by dehydration. In the case of PMADs with lower isotactic content, the elimination of water between neighboring carboxylic groups is less favored and the anhydridization shifts at higher temperatures where other degradation reactions may take place at the same time. The temperatures of maximum volatilization rates at the second step of decomposition increased in the order isotactic > atactic > syndiotactic.

Introduction

The stereochemical structure of a polymer strongly affects its thermal properties. A correlation between the glass transition temperature and the tacticity has been emphasized in several studies regarding, for example, polystyrene [1], polypropylene [2], poly(methyl methacrylate) (PMMA) [3] and other polymethacrylates [4]; similar works have also been carried out on the dependence of the melting point [5]. However, little is reported on the thermal degradation and only a few polymers have been subjected to a systematic investigation [6]. In the case of PMMA, the syndiotactic polymers have shown higher degradation temperatures than isotactic ones when molecular weights are lower than 25,000 and *vice versa* in the higher molecular weight range [7]; this behavior has been explained on the basis of a higher chain mobility of isotactic PMMA.

The thermal degradation behavior of poly(methacrylic acid) (PMAD) has been reported in many papers, usually concerning polymers with unknown tacticity, which were commercially available [8-11] or prepared via radical polymerization [12-16]. The degradation in inert atmosphere essentially consists of the formation of anhydride groups by elimination of water at *ca.* 200°C, followed by a wide fragmentation of the polymeric network in the temperature range between 300 and 420°C. Few works have also dealt with kinetics of dehydration at constant temperatures [17,18] and DSC studies [19] of samples with different tacticities.

We have already reported preliminary results on the tacticity dependence of the degradation behavior of PMADs; isotactic (*it*-) PMAD (mm:mr:rr = 93:5:2) and syndiotactic (*st*-) PMAD (mm:mr:rr = 3:24:73) showed weight losses at 195 and 243°C and main-chain scission degradation at 433 and 402°C, respectively [7]. Recently we found that the polymerization of trimethylsilyl methacrylate (TMSMA) with *t*-C_4H_9Li/

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bis(2,6-di-*t*-butylphenoxy)methylaluminum gives *st*-PMAD with much higher syndiotacticity (rr ≥ 96%) after hydrolysis of the ester groups [20]. Based on the finding, this work is the continuation of a program that intends to clarify the effect of stereoregularity on the thermal behavior of PMAD, taking into accounts the results already reported on the thermal degradation of stereoregular polymethacrylic polymers [7,17,21-24]. The present paper deals with thermal analysis studies of highly stereoregular PMADs with the same end groups.

Experimental

Materials.

TMSMA was used as a protected monomer of methacrylic acid to prepare stereoregular PMADs, since trimethylsilyl ester is easily hydrolyzed to form carboxylic function [25-28]. The synthetic procedures have been described in detail elsewhere [20]. *It*- and *st*-PMADs were synthesized by the polymerization of TMSMA with *t*-C_4H_9Li in toluene at -78°C in the absence and in the presence of bis(2,6-di-*t*-butylphenoxy)methylaluminium, respectively; termination with HCl (aq)/methanol (1M) converted quantitatively poly(TMSMA) to PMAD. A less stereoregular polymer, *at*-PMAD, was prepared by the similar procedures with *t*-C_4H_9MgBr in toluene at -40°C.

PMADs were also converted to PMMA by the reaction with diazomethane in chloroform [29] and the resulting polymers were subjected to tacticity determination by ^{1}H-NMR and molecular weight determination by gel permeation chromatography.

Thermal characterization

A Thermal Instruments TGA-DTA 2960 thermal analyzer was employed for thermogravimetry (TG) analysis under nitrogen flow at 100 ml/min, and differential scanning calorimetry (DSC) experiments were run with a Du Pont DSC unit under nitrogen flow at 60 ml/min. TG analyses were also carried out with temperature programming at 2°C/min on a Rigaku TG 8110 apparatus under nitrogen flow at 50 ml/min.

Polymer decompositions were also performed using a coil-type flash pyrolysis apparatus, with direct analysis of volatiles in a combined gas-chromatography/mass spectrometry (GC/MS) system. A CDS Pyroprobe 1000 was used and the volatile decomposition products were analyzed by a Hewlett-Packard HP5890A gas-chromatograph interfaced with a Hewlett-Packard 5970 quadrupole mass spectrometer. Separations were obtained with a HP5, methyl silicone coated column (0.25 μm thickness, 0.25 mm *i.d.*, 30 m length).

Results and Discussion

It is well known that differences in the molecular weight may affect the thermal degradation behavior of polymers. In order to overcome this trouble PMADs with almost the same number-average molecular weight, $\overline{M}_n$, have been prepared and used for this investigation. Their molecular characteristics are summarized in Table I.

Thermogravimetric curves obtained under nitrogen at a heating rate of 10°C/min for highly isotactic, atactic and highly syndiotactic PMADs are shown in Figure 1, together with the corresponding derivative curves. All the samples show the same pattern with two

Table I. *Molecular characteristics of poly(methacrylic acid) samples.*

			Tacticity (%)		
Sample	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	mm	mr	rr
it-PMAD	10400	1.48	95	4	1
at-PMAD	9900	1.26	24	27	49
st-PMAD	10320	1.36	0	3	97

main degradation stages but temperatures of beginning of volatilization, temperatures of maximum volatilization rates ($T_{I\,max}$ and $T_{II\,max}$) and weight losses at the first and second decomposition processes (%W_I and %W_{II}) are sensitive to the tacticity (Table II). The values of $T_{I\,max}$ and $T_{II\,max}$ for *it* and *st*-PMADs are in good agreement with those found in a previous investigation, where polymers with higher molecular weight and lower content of isotactic and syndiotactic units respectively, were used [7].

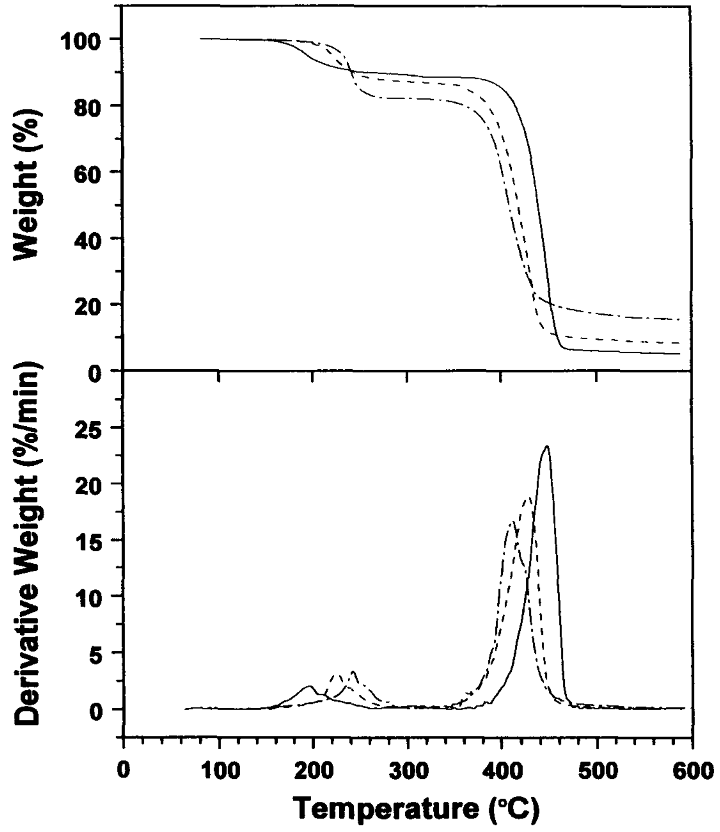

Figure 1. *Thermogravimetric and corresponding derivative curves for it-*PMAD *(solid lines), at-*PMAD *(dashed lines) and st-*PMAD *(dash-dotted lines) under nitrogen flow, at a heating rate of 10°C/min.*

Table II. *Thermogravimetric analysis parameters of poly(methacrylic acid) samples.*

Sample	$T_{I\,max}$	%W_I	$T_{II\,max}$	%W_{II}	*Res* (%)
it-PMAD	194	10.7	446	83.4	5.9
at-PMAD	224	12.7	427	77.8	9.5
st-PMAD	244	17.8	410	65.0	17.3

$T_{I\,max}$ and $T_{II\,max}$ are the temperatures of maximum volatilization rates of the first and second decomposition processes. %W_I and %W_{II} are the weight losses at the first and second decomposition processes. *Res* is the amount of the residue at 500°C.

From *it*-PMAD to *st*-PMAD through *at*-PMAD, the values of $T_{I\,max}$ and %W_I increased and those of $T_{II\,max}$ and %W_{II} decreased. The decomposition residue at 500°C (*Res*) increased in the same order. The residue left at 600°C remained constant in the amount at higher temperatures and was found to be a charred material. Thermogravimetries of *st*-PMAD performed at a heating rate of 2°C/min have shown a third degradation process, centered at 480°C, leading up to a complete volatilization (Figure 2). The third process did not occur in the cases of *it*- and *at*-PMADs.

The first decomposition step is generally attributed to the elimination of water between pairs of carboxyl groups [9,12] and the second one may be due to the extensive decomposition of the dehydrated polymer chain [10,14,15]. In the case of *it*-PMAD, a %W_I of 10.7% well agrees with the maximum yield of water which is equal to half of the moles of the repeating units, i.e. 10.5%. In the cases of *at*- and *st*-PMADs the higher values, 12.7 and 17.8% respectively, indicate that some other reactions took place. The composition of the volatile products evolved during the decomposition was determined

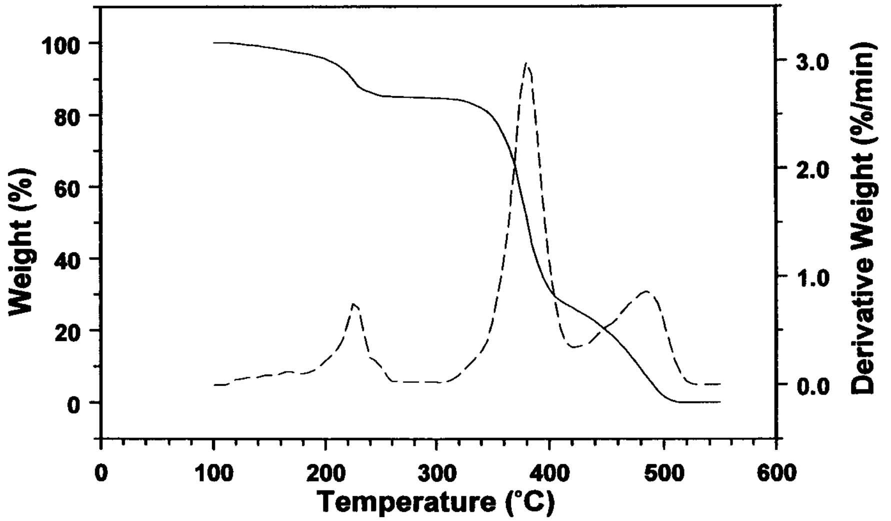

Figure 2. *Thermogravimetric curve (solid line) and corresponding derivative curve (dashed line) of st-*PMAD *under nitrogen flow, at a heating rate of 2°C/min.*

by pyrolysis/GC/MS. The samples, after previous elimination of sorbed water, were treated at 280°C for 30 sec. The results indicated for all the polymers that the degradation products mainly consisted of water with a very small amount of solvents used during the synthetic procedure. In the cases of *at*- and *st*-PMADs, CO_2 and a trace amount of 4-methyl-3-penten-2-one have also been found. The evolution of CO_2 is easily explained by decarboxylation reaction [10,11]. The formation of the α,β unsaturated ketone may be related to the decomposition of anhydride structures [30]. The remarkable difference in the weight losses of the first process between *it*-PMAD and *st*-PMAD (10.7% and 17.8%) is theoretically justified by decomposition of one carboxylic group every about seven monomeric units. The evolution of methacrylic acid was reported in previous works on the degradation at low temperatures of PMAD prepared by radical polymerization [11,13]. However, the present pyrolysis/GC/MS studies did not show any evidence of methacrylic acid evolution. Therefore, the previous observation may be due to the release of monomer trapped during the synthesis itself.

DSC experiments provide another means to emphasize the tacticity dependence of the behavior of PMADs. DSC measurements carried out under nitrogen flow with linear temperature programming of 10°C/min up to 300°C, showed endothermic signals at the same temperatures with that of the first degradation step in TG experiments (Figure 3). In *st*-PMAD a sharp exothermic peak at the end of the decomposition has also been noticed.

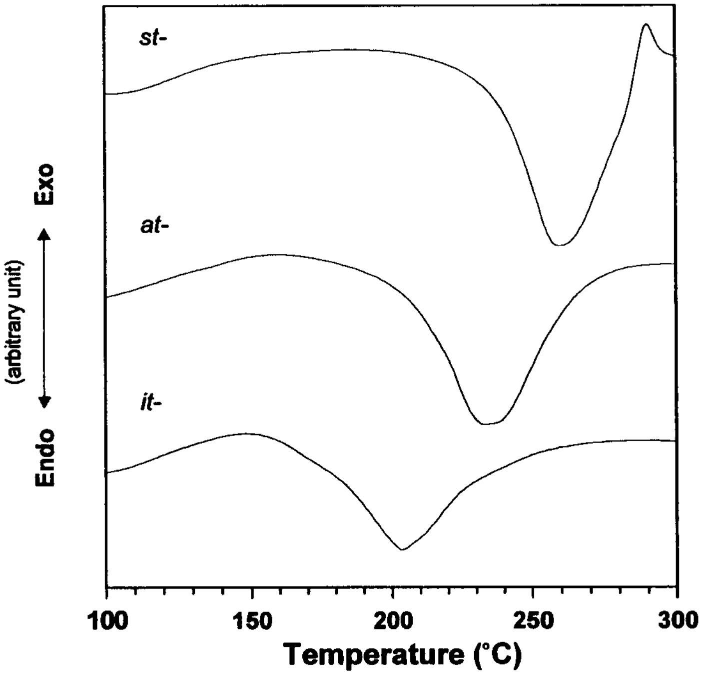

Figure 3. *DSC curves of PMADs under nitrogen flow, at a heating rate of 10°C/min up to 300°C.*

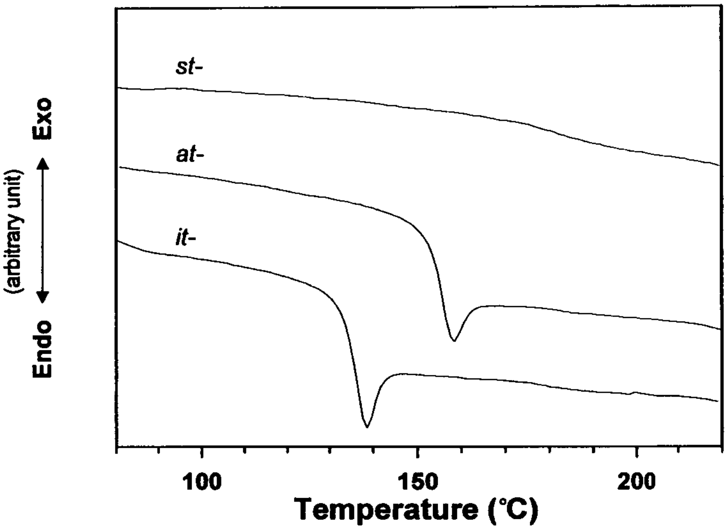

Figure 4. *DSC curves of PMADs, second runs under nitrogen flow at a heating rate of 20°C/min.*

Second runs at a scan rate of 20°C/min are shown in Figure 4, where the peaks of glass transition are observed for the structures formed by *it*- and *at*-PMADs, at 132 and 151°C, respectively. After the first run, the *st*-PMAD became insoluble in the usual solvents such as water and dimethyl sulfoxide while *it*- and *at*-PMADs were still soluble in these solvents.

Conclusions

It may be inferred that the first stage of the degradation of *it*-PMAD gives rise to the anhydride formation almost quantitavely, favored by the steric arrangement of neighboring carboxyl groups, and the resulting new polymer shows its proper glass transition. In the macromolecules with lower isotacticity, elimination of water between two adjacent units becomes more difficult and the anhydridization shifts at higher temperatures where other decomposition processes may take place at the same time. Particularly in *st*-PMAD, decarboxylation together with the formation of insoluble cross-linked structures have been revealed.

The investigation of structural changes by FTIR spectroscopy and ^{13}C-NMR is in progress and will be published soon [30]. A detailed account of the dependence of the degradation reactions on the stereoregularity will be also proposed in the subsequent publication.

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