Effect of Stereoregularity on the Thermal Behavior of Poly(methacrylic acid)s. 2. Decomposition at Low Temperatures

Massimo Lazzari,† Tatsuki Kitayama, and Koichi Hatada*

Department of Chemistry, Faculty of Engineering Science, Osaka University, Osaka 560, Japan

Oscar Chiantore*

Department of Inorganic Physical and Materials Chemistry, University of Torino, Via P.Giuria 7, 10125 Torino, Italy

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ABSTRACT: The effect of tacticity on the thermal degradation behavior under nitrogen of poly(methacrylic acid)s has been investigated. The structural changes occurring in the polymer chains during the first of the two stages of decomposition, at temperatures lower than 300 °C, were followed by FTIR and NMR. In this stage, the degradation of highly isotactic poly(methacrylic acid)s essentially consists of the formation of sequences of six-membered cyclic anhydrides by intramolecular dehydration. This process is likely to be favored by local conformations in which adjacent acid groups are fairly close. The presence of an increasing amount of syndiotactic units hinders the formation of cyclic anhydrides and shifts the decomposition at higher temperatures, making other reactions competitive, such as decarboxylation, formation of double bonds, and cross-linking. As a result, weight losses, solubility, and glass-transition temperatures of residues after the first degradation stage are proportional to their syndiotacticity.

Introduction

Stereoregularity is a fundamental microstructural feature in polymers that may directly affect their degradative behavior. However, the study of the effect of the tacticity on the mechanism of degradation has been rather limited by the availability of polymers in a wide range of stereoregularity to be used as model compounds.[1]

The role of tacticity has been first systematically faced in an exhaustive study on the thermal and photodegradation of poly(vinyl chloride) (PVC).[2] The extension of decomposition at low temperatures (i.e., the dehydrochlorination),[3] was pointed out to be dependent on the presence of tactic sequences, irrespective of whether they are isotactic or syndiotactic, and the initiation step was related to the occurrence during the polymerization of particular conformations at the end of some definite isotactic sequences. Further investigations on ultraviolet-degraded PVC[4] confirmed such sequences as labile sites. However, a recent study on thermal degradation supported the evidence that tacticity of macromolecules has no significant influence on the initial stage of PVC decomposition.[5] The difference in stability between isotactic and syndiotactic chains in the presence of oxygen has been studied to some extent only in the case of polypropylene (PP), and it was concluded that the higher stability of syndiotactic PP may be attributed to the different position of adjacent tertiary hydrogens, which are less susceptible to free radical or oxygen attack.[6,7]

Developments in living anionic polymerizations have provided a powerful tool for the synthesis of poly(methyl methacrylate) (PMMA) and other polymethacrylates with high stereoregularity and narrow molecular weight distributions.[8] In the case of PMMAs having the same end groups, the highly syndiotactic (*st*-) polymers have shown higher degradation temperatures than highly isotactic (*it*-) ones when molecular weights are lower than 25 000 and *vice versa* in the higher molecular weight range;[9,10] this behavior has been explained on the basis of a higher chain mobility of *it*-PMMA. Preliminary results on the thermal stability of a series of polymethacrylates available in a range of stereoregularity narrower than that of PMMA have also been reported.[9]

On the basis of the thermal degradative behavior, polymethacrylates can be classified into two categories. The first consists of polymers that degrade through a single step with quantitative formation of the monomer[11] and the latter of polymers that decompose through a more complex mechanism, where the first step essentially consists of the decomposition of the ester group with the formation of poly(methacrylic acid) (PMAD).[12] To elucidate the general effect of tacticity on the thermal degradation of polymethacrylates which undergo two-step decompositions, an accurate investigation on the behavior under an inert atmosphere of highly stereoregular PMADs has been therefore undertaken. In a previous paper we have reported the thermal analysis studies of three polymers with different tacticities.[13] For all the samples the same two-stage degradation behavior, already reported in many papers concerning PMADs with unknown tacticity,[14] has been observed. In the case of *it*-PMAD the first step of degradation essentially consisted of the formation of anhydride groups by dehydration, whereas in the atactic (*at*-) and *st*-polymers such a process was observed at higher temperatures where other degradation reactions are likely to take place at the same time. The order of stability for the second step of decomposition was *it*- > *at*- > *st*-PMAD. In this work the thermal degradation of PMAD has been investigated further by submitting a series of samples which cover a wide range of tacticity, to thermal

* To whom correspondence should be addressed.
† Current address: Department of Inorganic Physical and Materials Chemistry, University of Torino, Via P. Giuria 7, 10125 Torino, Italy.

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Table 1. Molecular Weights and Tacticity of Poly(methacrylic acid) Samples

			tacticity (%)[b]		
sample	M_n[a]	M_w/M_n[a]	*mm*	*mr*	*rr*
st1	10 300	1.4	0	3	97
st2	12 100	1.7	2	22	76
at1	10 400	1.2	29	16	55
at2	9 900	1.3	24	27	49
at3	12 200	1.6	33	29	38
it1	14 500	1.6	88	9	3
it2	10 400	1.5	95	4	1

[a] Determined by GPC. [b] Determined by ^{1}H NMR.

treatments under nitrogen. The structural changes occurring during the first step of decomposition have been followed by spectroscopic analysis, with a particular emphasis on the behavior of different tactic sequences. The comprehension of the mechanism of PMAD decomposition was also considered as a starting point for a better understanding of configurational effects on polymer degradation.

Experimental Section

Materials. Trialkylsilyl methacrylates were used as protected monomers of methacrylic acid to prepare stereoregular PMADs, since trialkylsilyl esters are easily hydrolyzed to form a carboxylic function.[15] The synthetic procedures have been detailed elsewhere.[16,17] The molecular characteristics of the polymers synthesized are reported in Table 1, in the order of decreasing syndiotacticity. Highly *it*- i.e., (**it1** and **it2**) and highly *st*-PMADs were synthesized by the polymerization of trimethylsilyl methacrylate with *t*-C_4H_9Li in toluene at −78 °C in the absence and in the presence of bis(2,6-di-*tert*-butylphenoxy)methylaluminum, respectively; **st2** was prepared under the same conditions by using a combination of *t*-C_4H_9Li/(*n*-$C_4H_9)_3Al$ (Li/Al = 1/3). **at2** was prepared by procedures similar to *t*-C_4H_9MgBr in toluene at −40 °C. Finally, **at1** and **at3** were obtained by polymerization of dimethylisopropylsilyl methacrylate and *tert*-butyldimethylsilyl methacrylate with *t*-C_4H_9MgBr in toluene at −60 and −78 °C, respectively. Termination with HCl(aq)/methanol(1 M) converted quantitatively poly(trialkylsilyl methacrylate)s to PMADs. PMADs were also converted to PMMA by the reaction with diazomethane in chloroform,[18] and the resulting polymers were subjected to tacticity determination by ^{1}H NMR and molecular weight determination by gel permeation chromatography.

Measurement. Molecular weights and their distributions were determined on a Jasco 880-PU chromatograph equipped with Shodex GPC columns, KF-802.5 and KF-80M, using THF as an eluent. The GPC chromatogram was calibrated against standard polystyrene samples.

Thermogravimetric measurements were performed with a Rigaku TG 8110 under a 50 cm^3/min nitrogen flow. Differential scanning calorimetry was carried out under a nitrogen flow (30 cm^3/min) with a Rigaku DSC 8230. Both units were driven by a thermal analysis station TAS 100.

FTIR spectra were collected on a 8399 Jasco instrument with a 2-cm^{-1} resolution, and samples were measured in the form of KBr pellets. ^{1}H NMR spectra were measured on a JEOL JNM-GSX270 spectrometer. ^{13}C NMR spectra were measured in dimethyl sulfoxide-d_6 at 110 °C on a Varian Unity-Inova 500 spectrometer (125 MHz for ^{13}C nuclei), using the solvent signal as an internal standard.

Results and Discussion

Thermal Characterization. The tacticity dependence of the temperatures of decomposition processes, already noticed in the previous part of this research,[13] has been investigated for a wider series of PMADs having the same end groups, almost the same number-average molecular weight, M_n, and with a higher variety of tacticity distribution. Samples with M_n between 9900 and 14 500, going from highly isotactic (*mm* = 95%) to highly syndiotactic (*rr* = 97%) through polymers with a lower content of *mm* or *rr* triads, have been prepared and used for this study (Table 1).

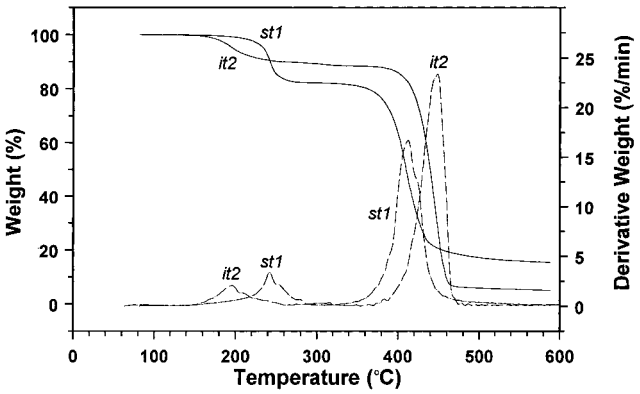


Figure 1. Thermogravimetric curves (solid lines) and corresponding derivative curves (dashed lines) of highly *st*- (**st1**) and highly *it*- (**it2**) PMADs under nitrogen flow, at a heating rate of 10 °C/min.

Table 2. Thermogravimetric Analysis Parameters of Poly(methacrylic acid) Samples[a]

sample	T_{in} (°C)	$T_{I,max}$ (°C)	W_I	$T_{II,max}$ (°C)	W_{II}
st1	220	244	17.8	410	65.0
st2	216	240	16.0	405	65.5
at1	197	225	12.8	426	74.2
at2	210	224	12.7	427	77.8
at3	197	220	12.2	428	74.4
it1	176	199	11.5	440	76.4
it2	177	194	10.7	446	83.4

[a] Parameters: T_{in}, temperature of beginning of volatilization, corresponding to a derivative weight of 1%/min. $T_{I,max}$ and $T_{II,max}$, temperatures of maximum volatilization rates of the first and second decomposition processes; W_I and W_{II}, percent weight losses at the first and second decomposition processes.

Thermogravimetric analysis under a nitrogen flow with a linear temperature programming of 10 °C/min has been performed and the curves of weight loss and the corresponding derivative curves of **st1** and **it2** are shown in Figure 1 as an example. The thermogravimetric parameters of all the samples are summarized in Table 2.

Particularly in the case of the first decomposition process, a clear dependence on the syndiotacticity is visible for both the temperatures of the maximum of the volatilization rate and the weight losses. At the same time, the temperature at the beginning of volatilization depends on the isotactic content. The degradation at a low temperature mainly consists of the elimination of water between pairs of carboxylic groups[14b,e] and the increase in the content of *rr* triads seems to hinder such a process. The dehydration shifts to a range of temperatures where other decomposition reactions take place at the same time, and consequently the overall weight loss exceeds the maximum yield of water which is 10.5%, corresponding to half of the moles of the repeating units.

Differential scanning calorimetry (DSC) measurements under programmed heating in nitrogen indicated the endothermic nature of the decomposition processes. In the case of the sample with higher syndiotacticity, **st1**, an exothermic peak centered at about 290 °C, in correspondence with the end of the first stage of

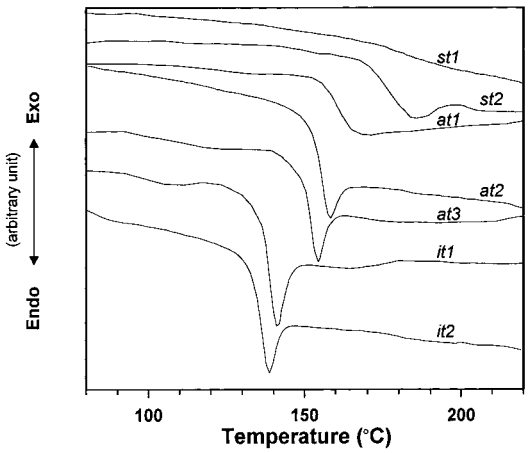


Figure 2. DSC traces under nitrogen flow at a heating rate of 20 °C/min of PMADs previously treated up to 300 °C.

Table 3. Glass-Transition Temperatures and Solubility of PMADs Treated up to 300 °C

		solubility[b]	
sample	T_g (°C)[a]	water[c]	DMSO
st1		i	i
st2	170	i	i
at1	156	i	ps
at2	150	i	ps
at3	148	i	ps
it1	136	i	ps
it2	129	ps	ps

[a] Extrapolated peak onset temperature of glass transition. [b] Solubility: ps, partially soluble; i, insoluble. [c] Water or aqueous hydrogen chloride.

degradation,[13] confirmed decomposition processes apart from the elimination of water, giving rise to the formation of more stable structures. In general, these exothermic reactions have been observed for PMADs with different molecular weights when the content of syndiotactic units is higher than 95%.[19]

The structures formed owing to thermal treatments up to 300 °C have also been subjected to second runs at a heating rate of 20 °C/min (Figure 2). Glass transitions are visible for all the polymers except **st1** and the corresponding temperatures, T_g, are reported in Table 3 together with the results of a survey on the solubility in water and dimethyl sulfoxide (DMSO).[20] A direct correlation between the tacticity and both the T_g and the results of the solubility tests is clearly visible. Starting from a sensible supposition on the relative chemical similarity of the structures formed by all the polymers, both the enhancement of T_g and the increasing difficulty in its determination with the increase of syndiotactic content may be explained on the basis of general considerations of chain flexibility. In the case of the above series of PMADs, the presence of syndiotactic sequences may be related, as confirmed by solubility tests, with the formation of cross-linking points during the degradation, which hinder the rotation around the backbone bonds and thus stiffen the chain. At the same time, the restriction of the main-chain motion gives rise to a broader temperature range of the sample baseline step, introducing an inaccuracy into the measurement of T_g.[21]

FTIR Spectroscopic Studies. To provide a precise understanding of the spectral changes related to the structural modification of the PMADs during the degradation and, in particular, during the first step of

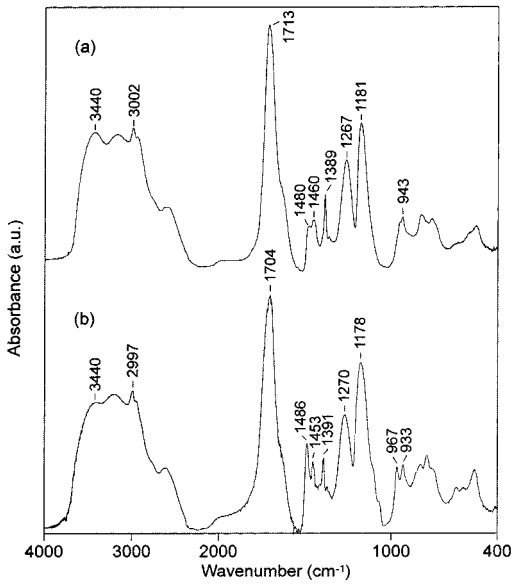


Figure 3. FTIR spectra of **it2** (a) and **st1** (b).

Table 4. Vibrational Assignments for PMADs

isotactic		syndiotactic		
Cm^{-1}	I[a]	Cm^{-1}	I[a]	assignment[b]
3440	v	3440	v	ν (O−H) free groups
∼3200	m	∼3200	m	ν (O−H) associated with water
3002	w	2997	w	ν_a (C−H) CH_3
2950	w	2950	w	ν_a (C−H) CH_2
∼2620	w	∼2620	w	ν (O−H) bonded groups
1713	s	1704	s	ν (C=O)
1480	sh	1486	m	δ_a (C−CH_3) planar deformation
1460	w	1453	w	δ (CH_2) + δ (CH_3) out of plane
1389	m	1391	m	δ_s (CH_3) planar deformation
1267	s	1270	s	ν (C=O) or δ (O−H)
1181	s	1178	s	related to 1270
943	m	967	m	γ (C−CH_3)
		933	m	δ (O−H) out of plane deformation
836	m	836	w	γ (CH_2)

[a] Intensity: v, variable; w, weak; m, medium; s, strong; sh, shoulder. [b] Vibrations: ν, stretching; δ, bending; γ, rocking; $_s$, symmetric; $_a$, asymmetric.

decomposition, a careful band assignment for undegraded polymers is necessary. The interpretation of the FTIR spectra of samples with different tacticities has been made, paying particular attention to the effect of stereoregularity on the vibration bands.

The FTIR spectra of undegraded highly *it*-PMAD (**it2**) and highly *st*-PMAD (**st1**) are given in Figure 3. FTIR spectroscopic investigations of stereoregular PMADs are not available, but on account of a similarity in the main chain, the band assignment reported in the literature for PMMA and in particular for its methyl and methylene groups[22−24] has been used as a starting point for an unambiguous interpretation of the tacticity-related absorptions of the samples used in this investigation.

The vibrational assignment for *it*- and *st*-PMADs are summarized in Table 4. Spectra of samples with lower stereoregularity may be approximately interpreted on the basis of the data reported in the table, considering the peaks as an overlapping of components with different tacticities.

In the region between 3600 and 2500 cm^{-1}, besides the C−H stretchings at about 3000 and 2950 cm^{-1}, three other absorptions related to the hydroxyl groups may be seen. The bands at ca. 3200 and 2600 cm^{-1} are due to the stretching vibrations of free and bonded OH

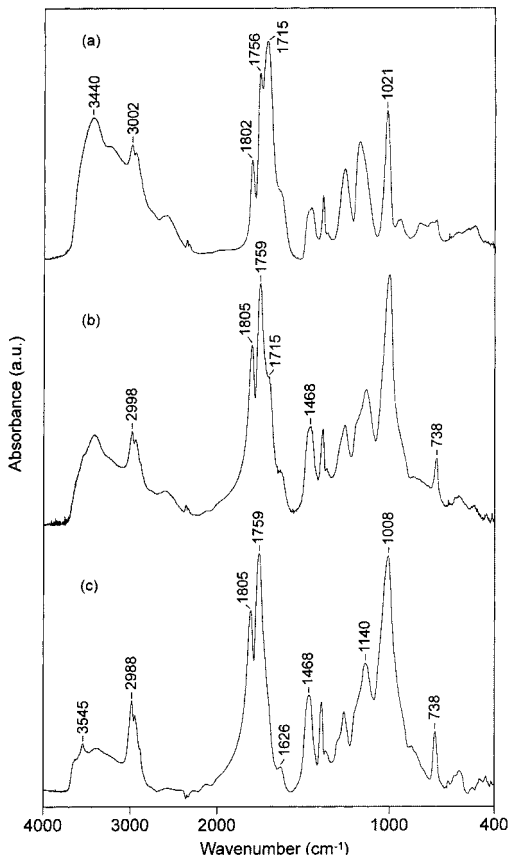


Figure 4. FTIR spectra of **it2** after treatments up to temperatures of ca. 180, 200, and 300 °C, corresponding at weight losses of 2% (a) and 5% (b), and at the end of the first process of decomposition (c), following the conditions reported for thermogravimetric analysis in Figure 1.

groups, respectively. The broad peak with a maximum at about 3440 cm^{-1}, depending on both the drying conditions of the samples and the accuracy in the preparation of the KBr pellets, has been ascribed to the presence of some water molecules bonded to carboxylic groups.[14h]

In the carbonyl stretching region, the shift of the isotactic band toward higher wavenumbers than those of the syndiotactic one (1713 and 1704 cm^{-1}) is possibly due to a different degree of hydrogen bonding. Moreover, the asymmetry of this peak, shown in all the samples independently on the tacticity, may be a further indication of association between water molecules and COOH groups. The effect of stereoregularity is evident in the fingerprint region, as in the case of PMMA.[23] It is particularly clear on the deformations of methyl and methylene groups and on rocking vibrations of methylene groups (at 1480, 1460, and 943 cm^{-1} and 1486, 1453, and 967 cm^{-1}, for *it*- and *st*-polymers, respectively) and because of a band overlapping, is mainly reflected as a change in the ratio of intensities of some absorptions.

PMADs have been subjected to treatments under a nitrogen flow at a heating rate of 10 °C/min up to temperatures corresponding to weight losses of 2 and 5%, and at the end of the first process of decomposition. The FTIR spectra of *it*-PMAD after treatment up to ca. 180, 200, and 300 °C shown in Figure 4 can be compared to those of the untreated polymer in Figure 3a. In the first spectrum corresponding to a weight loss of 2% (Figure 4a), the formation of an anhydride is confirmed through the appearance of absorptions at 1802, 1756 and 1021 cm^{-1},[14c,h] with the first two peaks assigned to asymmetric and symmetric stretching of carbonyl groups, respectively, and the latter due to C−O−C stretching vibrations.[25]

The continuation of decomposition leads to advances of anhydride formation (Figure 4b), and the ν C=O absorption at 1715 cm^{-1}, due to initial carboxylic groups, is hardly visible as a shoulder. The differentiation between open-chain and cyclic anhydrides is possible on the basis of the relative intensities of the two carbonyl absorptions: in the first case, the higher frequency band is always the more intense of the two and *vice versa* in the latter.[25] In the above spectra, the twin peaks at 1759 and 1805 cm^{-1}, with the lower frequency peak being more intense, indicated that the structure is dominated by cyclic anhydrides and the same frequencies are in good agreement with the formation of six-membered glutaric-type rings.[26]

The shifts of bands related to methyl groups, from 3002 to 2988 cm^{-1} and from 1460 to 1468 cm^{-1}, respectively, with an increase of intensity in the latter, are the consequence of their reduced mobility following the formation of rings on the main chain. In a previous study on PMAD prepared by radical polymerization, the sharp peak at 738 cm^{-1} has been attributed to aromatization of cyclic structures.[14h] However, by taking into account FTIR spectra of glutaric anhydrides, the above absorption can undoubtely be related to six-membered glutaric-type rings, even though a precise assignment was not possible.[27]

At 300 °C the transformation is almost complete and only a small absorption at 3545 cm^{-1}, due to isolated COOH groups, is still visible. Moreover, a new band at 1626 cm^{-1} shows that olefinic unsaturations were also formed, and whose origin will be explained below for the interpretation of degraded *st*-PMADs spectra. The main peak of the two peaks in the C−O−C stretching region between 1200 and 1000 cm^{-1} shows a shift during the heating treatment, from 1021 cm^{-1} at ca. 180 °C to 1008 cm^{-1} at 300 °C; this feature may be related to the progressive stiffening of the chain, owing to the formation of longer sequences of cyclic anhydrides.

The FTIR spectra of *st*-PMAD (**st1**) recorded at different degrees of degradation, corresponding to treatment up to ca. 215, 230, and 300 °C, are shown in Figure 5. By comparing the spectra of degraded *it*- and *st*-PMADs having the same weight losses of 2 and 5% (Figures 4a,b and 5a,b, respectively), several deductions may be inferred. In the first phases of decomposition the same structural changes occur in both samples. However, in the case of *st*-PMAD, the intensities of peaks assigned to cyclic anhydrides are lower than those in the spectrum of *it*-PMAD with the same weight loss and this difference in the degree of anhydridization indicates a different mechanism of degradation. The evaluation of variations in the intensity of the broad absorptions in the range of OH stretchings appears difficult, but the relevant decrease of the peak at 933 cm^{-1}, due to OH out of plane deformation and the identification of CO_2 among the products evolved during the decomposition at 280 °C,[13] suggests the decomposition of COOH groups by decarboxylation as well.

The spectrum of **st1** at the end of the first stage of weight loss (Figure 5c, obtained for treatment up to 300 °C), shows a more complicated pattern than that of **it2** after the same treatment (Figure 4c). The variety of

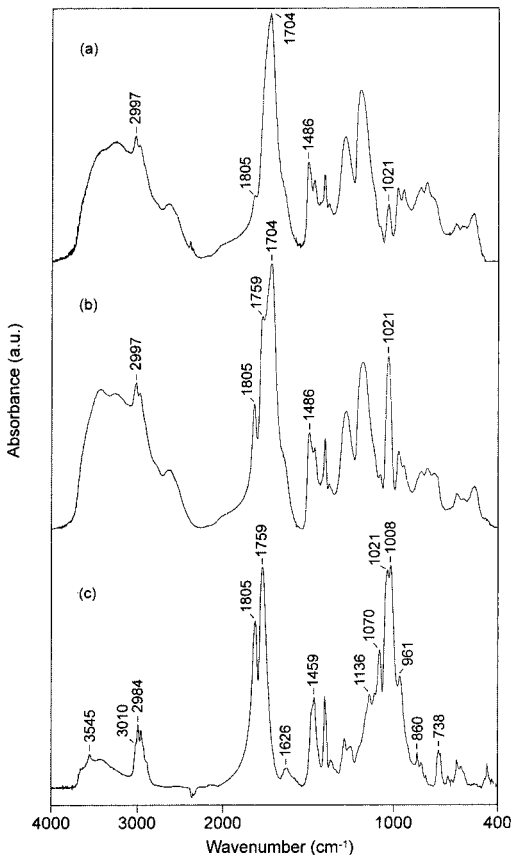


Figure 5. FTIR spectra of **st1** after treatments up to temperatures of ca. 215, 230, and 300 °C, corresponding to weight losses of 2% (a) and 5% (b), and at the end of the first process of decomposition (c), following the conditions reported for thermogravimetric analysis in Figure 1.

signals in the range of C−O−C stretchings can tentatively be explained by the contemporary presence of both sequencies of cyclic anhydrides, as in **it1**, and isolated rings. In comparison to the undegraded samples seen in Figure 3b, apart from the shift of CH_3-related absorptions owing to stiffening, new peaks are visible at 3010, 1626, and 860 cm^{-1}, whose assignments agree well with the formation of double bonds, $CR_1R_2{=}CHR_3$. Spectra of *at*- samples subjected to the same treatments as above showed behavior between that of highly *it*- and highly *st*-PMADs, with the formation of both sequences and isolated cyclic anhydrides, together with the appearance of unsaturations.

The presence of an exothermic peak seen in the DSC trace of **st1**[13] has been related to the formation of double bonds that takes place in the same range of temperatures, and whose concentration is the highest among the samples analyzed. It may be supposed that a series of endothermic processes is always present in all the polymers, together with an exothermic process responsible for the formation of unsaturations as well. However, only in the case of highly *st*-PMAD is the intensity of such an exothermic process high enough to be revealed as a sharp peak in the DSC trace resulting from superimposition of elementary processes.

NMR Spectroscopic Studies. Although NMR spectroscopy is the most widely used analytical means that provides quantitative data on tacticity,[28] its applications on the study of stereoselective degradation are still rather limited. One of the main reasons is certainly the formation of insoluble polymer networks that often occurs during the degradation itself, in contrast to the technical need of soluble samples for high-resolution analysis. In our case, *at*- and *it*-PMADs were still partially soluble in organic solvents after the first stage of degradation (Table 3), allowing the use of NMR in order to focus on the transformation occurring at low temperatures on different sequences. ^{1}H NMR spectroscopy has been found to be unsuitable for an accurate determination of tacticity in PMADs, and consequently neither for the discrimination of preferential transformations; moreover, reactions on C=O functionalities cannot be directly detected by this technique. However, through a comparison of the ^{1}H NMR spectra of **at3** and **it2** treated up to 280 °C with those of the corresponding undegraded samples, more general information on the degradation behavior was obtained. The observed huge broadening of the signals due to the methyl and methylene hydrogens has been related to the stiffening of

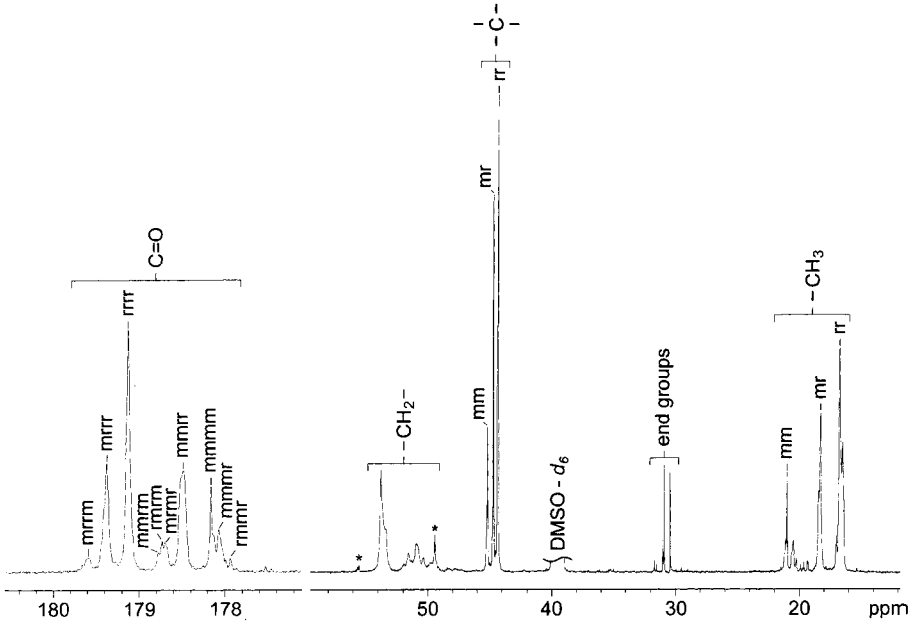


Figure 6. ^{13}C NMR spectrum of atactic PMAD (**at2**). Marks denote signals due to impurities.

Table 5. ^{13}C NMR Signals of Stereoregular PMAD Measured in DMSO-d_6 at 80 °C

carbon	triad	chemical shift (ppm)
C═O	*mm*	177.8−178.3
	mr	178.3−178.9
	rr	178.9−179.8
methylene		49.0−54.0
quaternary	*mm*	45.1
	mr	44.7
	rr	44.3
end groups		30.4−31.8
methyl	*mm*	21.0
	mr	18.3
	rr	16.8

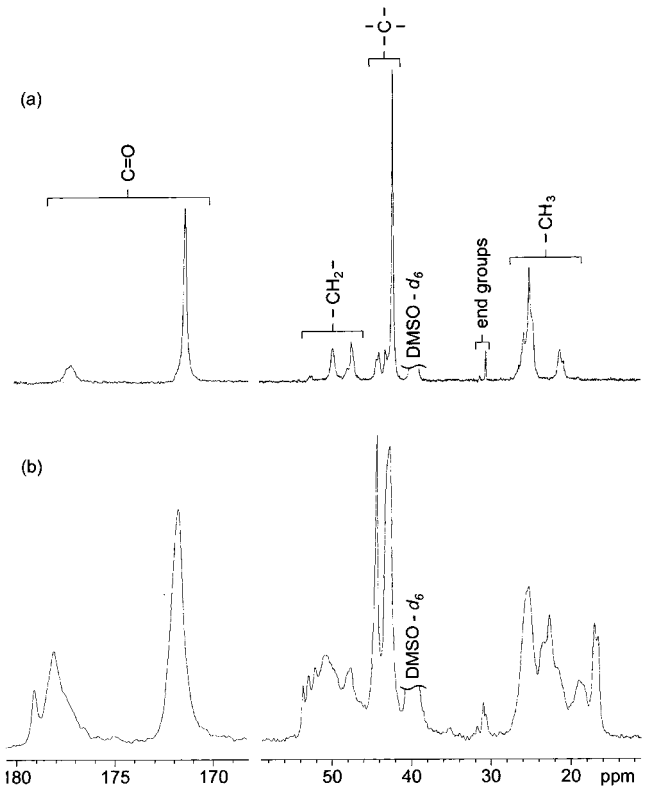


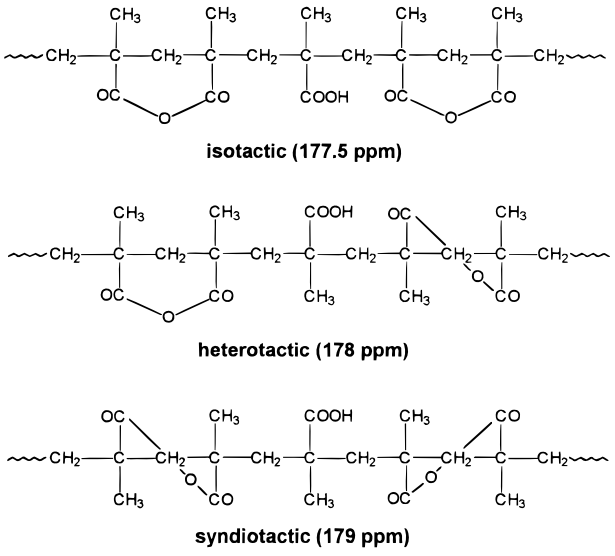
Figure 7. ^{13}C NMR spectra of **it2** (a) and **at2** (b) after treatment up to 280 °C under nitrogen flow, at a heating rate of 10 °C/min.

the polymer chains already pointed out by DSC measurements.

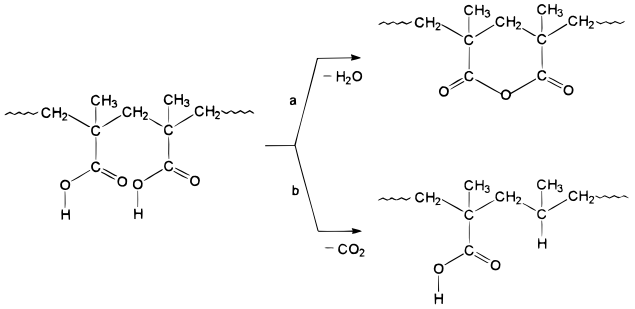
In the case of ^{13}C NMR, chemical shifts of C═O carboxylic carbons are sensitive up to pentad sequences[17] and *mm*, *mr*, and *rr* triads can also be distinguished from quaternary and methyl carbon signals. As an example, the spectrum of **at2** is shown in Figure 6 and the corresponding chemical shift assignments are reported in Table 5. ^{13}C NMR spectra of **at2** and **it2** treated up to 280 °C under a nitrogen flow at a heating rate of 10 °C/min are reported in Figure 7. In both polymers the substantial spectral changes may be explained by reactions of carboxylic groups. In **it2** (Figure 7a), the C═O region shows the appearance of a new peak at 171.2 ppm together with a signal of lower intensity centered at about 177.5 ppm. These changes correspond to the formation of anhydrides from the carboxylic acid groups. Several types of anhydrides can theoretically be formed in this polymer. However, on the basis of the chemical shifts reported for ^{13}C solid-state NMR[14b] and several model compounds in solution (succinic anhydride, a model of a five-membered ring, 2,4-dimethylglutaric anhydride, a model of a six-membered ring, and isobutyric anhydride, an example of open structures),[29] the resonance at 171.2 ppm can be assigned to carbonyl groups from the formation of a six-membered glutaric anhydride-type ring. The narrowness of this signal also confirms the absence of other types of anhydrides, with open or cyclic structures, already suggested by FTIR spectroscopy. The peak at ca. 177.5 ppm is due to residual carboxylic groups. Moreover, the intensity ratio of the anhydride signal to the carboxylic acid signal gives a cyclization extent (ca. 80%) in good agreement with the maximum value expected in the case of the statistical formation of a cyclic anhydride. The effect of cyclization on the polymer chain is also reflected in the signals of carbons not directly involved in the decomposition. For example, the methyl resonance shifts to about 25 ppm, owing to the cyclization of adjacent acid functionality but, at the same time, residual acid α-methyls are still visible at ca. 21 ppm. The splitting of quaternary carbon resonances may be similarly explained.

The spectrum of degraded **at2** (Figure 7b) shows a more complicated pattern. In the C═O region, apart from the peak at ca. 172 ppm because of the formation of an anhydride, the remaining signals centered at ca. 179 and 178 ppm, the latter with a shoulder at a lower frequency, are related to the presence of residual acid groups. Taking into account both the chemical shifts reported in Table 5 for acid functionalities with a different stereoregularity, and the behavior of *it*-PMAD, the signals of residual acid groups in Figure 7a,b were

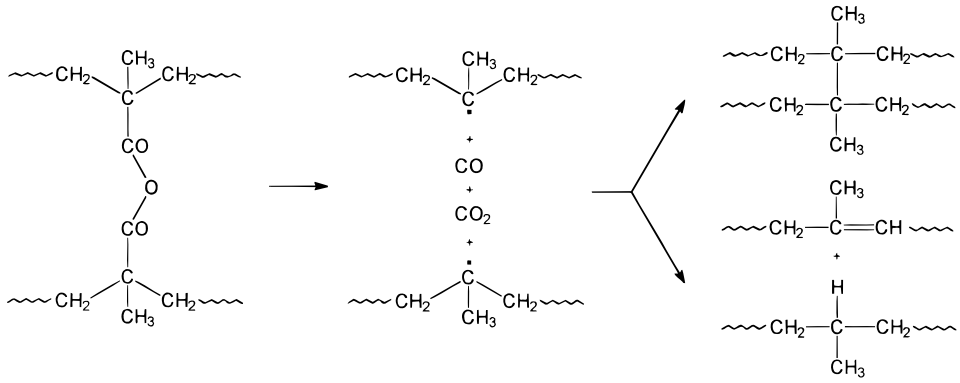
Scheme 1



Scheme 2



Scheme 3



assigned to isolated −COOH left from the anhydridization of isotactic (177.5 ppm), heterotactic (178 ppm), and syndiotactic sequences (179 ppm), as shown in Scheme 1. Therefore, the relative intensity of COOH signals in degraded **at2** compared to the values of its tacticity (*mm*:*mr*:*rr* = 24:27:49) suggests a preferential decomposition of acid groups in isotactic sequences, leaving an amount of isolated residual groups smaller than those in the case of heterotactic and syndiotactic sequences. Similar features may be argued on the basis of the signals of residual α-CH_3 with different stereoregularities.

Mechanism. A common feature for all the samples irrespective of their tacticity is the formation of only one type of stable anhydride (i.e., six-membered glutaric type by intramolecular dehydration) in the whole range of temperatures corresponding to the first step of decomposition. As the temperatures at the beginning of weight loss were related to the content of *mm* triads, it may be supposed that the very labile structures are some local conformations in isotactic sequences, in which adjacent acid groups are fairly close. At the same time, the presence of an increasing amount of syndiotactic units shifts the formation of cyclic anhydrides at higher temperatures where other reactions become competitive.

The evolution of CO_2 since the beginning of decomposition, mainly seen in highly *st*-PMAD but only partially in *at*-PMAD,[13] may be explained through a process of decarboxylation assisted by an adjacent acid group (Scheme 2). A unimolecular mechanism was rejected on the basis of the presence of residual acid groups in all the samples. Both decarboxylation and dehydration were explained through reaction mechanisms involving a common preliminary step. Because of the ionic nature of PMADs and the relatively low temperature of reaction, a transition state involving the formation of a carboxylate anion and the corresponding trigonal carbocation, as in the preliminary step of nucleophilic substitution at a carboxyl group, can be taken into account. However, a radical mechanism was not excluded. In the case of highly *it*-PMAD the decomposition mostly occurs by route **a**, with the formation of sequences of cyclic anhydrides, and only a few isolated COOH groups are left; whereas in other PMADs the feasibility of route **b** is proportional to their *rr* content.

The absence of open-chain type of anhydrides in degraded samples may be ascribed to their instability once formed rather than any hindrance on forming. The formation of intermolecular anhydrides can reasonably occur when the more favorable intramolecular process is almost completed and the residual acid groups still meet the necessary steric requirements, in strict connection with the flexibility of the chain. Two main factors are responsible for an easier formation of open-chain anhydrides in *st*-PMAD compared with *it*-PMAD. The first one is the higher accessibility of isolated acid functionalities in *st* sequences, and the latter is related with the lower segmental mobility of partially degraded *it*-PMAD, where sequences of cyclic anhydrides stiffen the chain, compared to the situation in *st*-PMAD where the extent of cyclization is less. It is therefore suggested that intermolecular anhydrides decompose as soon as they are formed, with the evolution of CO and CO_2,[30] giving rise to diradicals whose fate depends on steric and thermodynamic factors (Scheme 3). The general mode of free radical decay corresponds to mutual deactivation, by either recombination, with the formation of insoluble cross-linked structures, or disproportionation, with the formation of double bonds, $CR_1R_2{=}CHR_3$, as shown by FTIR.

Conclusions

It has been shown that the degradation of PMAD is more sensitive to stereoregularity than in the case of other polymethacrylates (e.g., PMMA). In PMAD, the first step of decomposition involves reactions on lateral carboxyl groups, making the tacticity of sequences an essential factor for the direction of degradative paths. The degradation at low temperatures of highly *it*-PMADs essentially consists of the formation of sequences of adjacent six-membered cyclic anhydrides with a few isolated carboxylic groups left, giving rise to an almost regular poly(methacrylic anhydride)-type structure, which is thermally stable up to temperatures of about 400 °C. An increasing syndiotactic content makes other reactions competitive, such as decarboxylation, the formation of C=C bonds, and cross-linking involving macroradicals. As a result, the weight losses and the solubility of residues after the first degradation stage are proportional to their syndiotacticity, with the utmost effect on highly *st*-PMAD. Moreover, the formation of unsaturation on the main chain is also likely to destabilize the structure with regard to treatments at higher temperatures.

And finally, the effect of stereoregularity on the thermal behavior of PMADs may be associated to the cases of PVC and PP oxidation, where differences of stability were explained by configurational and conformational effects or by different positions of labile sites, rather than the case of PMMA degradation, where chain mobility was thought to be the key factor.

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