Thermal Characterization of Poly(acrylic acid)

J. J. Maurer,* D. J. Eustace,[†] and C. T. Ratcliffe[‡]

Exxon Research and Engineering Company, Clinton Township,
Annandale, New Jersey 08801. *Received February 18, 1985*

ABSTRACT: A comprehensive thermal characterization of atactic (A) vs. syndiotactic (S) poly(acrylic acid) (PAA) was conducted. Tacticity assignments were based on infrared and solubility characteristics. The glass transition temperature (T_g) was ~105 °C for PAA(A) vs. ~125 °C for PAA(S). Thus, variations in polymer tacticity may be the cause of certain anomalous T_g values reported for PAA. Significant differences in the thermal stability characteristics of these polymers were observed via mass spectrometry. Maximum water evolution, due to anhydride formation, and carbon dioxide evolution, due to anhydride decomposition, occurred at ~170 and ~230 °C, respectively, in PAA(A) vs. ~200 and ~260 °C, respectively, in PAA(S). These differences may be directly related to tacticity or possibly an indirect effect due to enhanced hydrogen bonding in the PAA(S). A transition which occurs at 135 °C in PAA(A), but not in PAA(S), may reflect anhydride formation involving less reactive carboxyl groups, or some unidentified microstructure. In some PAA(S) samples, a weak transition of unknown origin occurs at a temperature similar to the T_g of PAA(A).

Introduction

There is a significant discrepancy or anomaly in the literature regarding the glass transition temperature (T_g) of poly(acrylic acid) (PAA). The value that is frequently observed for this polymer, herein termed $T_g(1)$, is in the range 102–109 °C.[1-3] However, other reports place the value, herein termed $T_g(2)$, in the 120–126 °C range.[4-6] Maurer et al. obtained a value of 102 °C via analysis of a series of poly(acrylamide-*co*-acrylic acid) copolymers vs. a value of 124 °C by direct DSC measurement of PAA.[6] Greenberg and co-workers suggest that this discrepancy may be due to a high degree of intermolecular hydrogen bonding involving "'bound' water acquired during the polymer preparation process".[5]

In the present study, PAA samples of low (~105 °C) vs. high (~125 °C) T_g are examined in terms of tacticity, as defined by the methods of Monjol and Champetier,[7] and thermal characteristics, as defined by differential scanning calorimetry (DSC), thermal gravimetric analysis (TG), and mass spectrometry (MS). This comprehensive thermal characterization was necessitated by the multiple features exhibited by DSC thermograms of PAA. Interpretation of these complex thermograms required careful consideration of several challenging issues, including (1) the strong affinity of PAA for water, which introduces questions relating to plasticization and free vs. bound water, (2) the need to identify drying conditions that will remove water without changing polymer composition via formation of inter- and/or intramolecular anhydride units, (3) the possibility of encountering enthalpy relaxation effects depending upon the thermal history of the polymer,[8] and (4) discrepancies in the literature regarding the temperature and nature of anhydride formation in PAA (Table I).

The objectivies of this paper are to (a) examine the relationship between T_g and tacticity of PAA, (b) distinguish T_g from several other features of the DSC thermogram, (c) interpret these additional features, and (d) comment on some apparently new aspects of the thermal characterization of PAA.

Experimental Section

Materials. Poly(acrylic acid) (PAA) samples were obtained from commercial sources and are described in Table II. Acid–base properties and potentionmetric titrations indicated that all samples were in the acid form and did not contain appreciable interfering impurities. The degree of ionization of water-soluble samples A-3, 3312, and 4551 varied with concentration according to $pH = (pK_0 + p[PAA])/2$, with $pK_0 = 4.6$.

Characterization of PAA Tacticity. (1) Infrared analysis was performed on solid samples (footnote *f*, Table II) in the form of KBr pellets in transmission mode on a Digilab FTS-15E spectrometer. Two hundred scans at a resolution of 4 cm^{-1} were signal averaged and spectra were stored on disks. Tacticity assignments were made on the basis of infrared band characteristics in the 900–1350-cm^{-1} region reported by Monjol and Champetier.[7] Specifically, syndiotactic poly(acrylic acid) (PAA(S)) is characterized by a strong absorption at 1240 cm^{-1} whereas atactic poly(acrylic acid) (PAA(A)) is characterized by a strong absorption at 1250 cm^{-1} and a shoulder at 1300 cm^{-1}. (2) The solubility of PAA is also influenced by tacticity, according to Monjol and Champetier.[7] At high molecular weight ($\geq 1 \times 10^6$) PAA(S) is insoluble in water or dioxane but is soluble in an 80% dioxane/20% water mixture, all at ambient temperature, whereas PAA(A) is soluble in all three solvents. At lower molecular weights the solubility difference appears to be one of degree, PAA(S) being less soluble than PAA(A) at a given molecular weight. PAA solubility was examined in this study at two concentrations (0.1% and 0.5%). Solutions were prepared from solid polymer or the initial concentrated solution via gently mixing for 6 days. The resulting solution was passed through a 0.45-μm Millipore cellulosic filter. Both PAA(A) samples (Table II) dissolved completely and passed readily through the filter, whereas the two PAA(S) samples were incompletely dissolved, exhibiting only limited solubility under these conditions.

Preparation of Solid Polymer Samples. Preparation of equivalent sample types for PAA(A) and PAA(S) was complicated by the aforementioned influence of tacticity on solubility and by the different forms of the original samples (Table II). The following modes of preparation of solid polymer samples were attempted and/or utilized as appropriate: (a) casting a thin film from a dilute (~0.1 wt %) aqueous solution; (b) vacuum evaporation of a 1% aqueous solution of PAA(A) prepared by dilution of the 25% aqueous solutions or of partially dissolved PAA(S) (original mixture: water plus sufficient PAA(S) to prepare a 1% solution, assuming polymer was completely soluble); (c) freeze-drying the polymer systems from (b). Because of its limited solubility, PAA(S) was used primarily in the as-received solid form, except for drying to remove water. Use of dioxane as a solvent for PAA(S) was not explored because of potential complications relating to incomplete removal of this solvent.

Thin films are ideal for thermal mechanical analysis (TMA), e.g., via a penetrometer probe. However, they present sample preparation and handling difficulties in DSC and TG–MS experiments and are difficult to prepare reproducibly, as were vacuum-evaporated samples. In contrast, freeze-dried samples, which can be prepared in relatively large quantities, gave the best reproducibility in DSC experiments; hence, this method of sample preparation was utilized, where applicable, for the more detailed DSC studies of PAA.

Drying of PAA Solid Samples. A range of drying conditions (temperature, time, and atmosphere) was explored. On the basis of this background and other factors, a standard temperature of

---

[†] Present address: Polaroid Corp., New Bedford, MA 02741.

[‡] Present address: Union Oil of California, Science Division, Brea, CA 92621.

0024-9297/87/2220-0196$01.50/0

Table I
Thermal Decomposition Characteristics of Poly(acrylic acid)

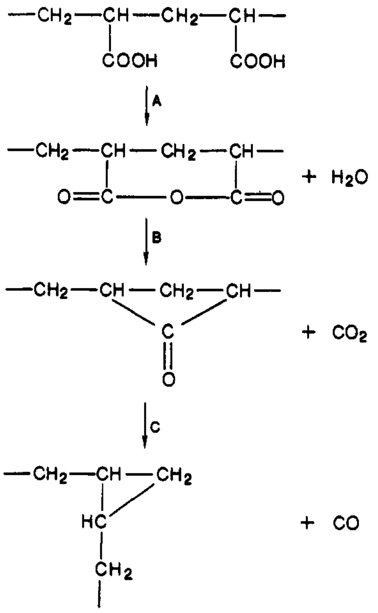
decomp sequence	decomp step	temp, °C	ref
	A, B	160–240	11
	A, B	125, 140, 155, 170	3
	A, B, C	150, 250, 300, 350	12
	A, B	150, 200, 250	13
	A, B	221	14

Table II
Source and Properties of Poly(acrylic acid) Samples

code	source	orig form	MW × $10^{-6\,a}$	tacticity[b]	T_g,[c,d] °C	solubility[e]
3312	Polysciences	solid	~0.25	syndiotactic	119–125	insoluble
6500	Polysciences	solid	~1.0	syndiotactic	118–127	insoluble
4551	Polysciences	25% solution[f] (aqueous)	~0.3	atactic	98–103	soluble
A-3	Rohm and Haas	25% solution[f] (aqueous)	~0.1	atactic	102–107	soluble

[a] Viscosity-average molecular weight; supplier's value. [b] Based on infrared analysis by method of Monjol and Champetier.[7] [c] Samples predried 17 h at 93 °C; nitrogen atmosphere. Heating rate: 2 °C/min. [d] Range observed for various sample histories. [e] Solubility procedure described in Experimental Section. [f] Solid polymer obtained via vacuum evaporation of a 1% aqueous solution until no further weight loss.

93 °C was selected. Samples were dried at this temperature in a vacuum oven, a nitrogen-purged oven, the DSC unit (nitrogen atmosphere), or the TG unit (in flowing helium) for various time periods as indicated elsewhere. The principal concern in selecting the preferred drying history for a given sample was to achieve efficient removal of water while avoiding potential complications due to enthalpy relaxation effects or anhydride formation. More severe drying conditions were also explored to examine the effects of anhydride formation on the thermal characteristics of PAA.

During the initial phase of this study, samples intended for DSC analysis were placed in DSC pans and covered by a crimped lid. Prior to placement in the drying oven, several holes were pierced in the lid to enable volatilization of water from the container. This procedure was intended to minimize water pickup by the dried sample during transfer from the oven to the DSC cell. In the latter stages of this study, the crimped lid was not employed for reasons to be discussed elsewhere in this paper.

Samples to be evaluated via TG–MS analysis were predried in the TG crucible via the following procedures: (a) the system was evacuated to 10^{-2} Torr; (b) samples were then typically held in the unit for 16 h at 93 °C in a flowing dry helium atmosphere. Other studies suggest that 2–3-h drying at these conditions would be adequate for freeze-dried samples. Shorter times would be preferred in order to minimize the possibility and extent of anhydride formation.

Thermal Analysis. (1) DSC. A DuPont DSC and 990 thermal analyzer system was used. Samples were contained in pierced-lid or open DSC pans. Typical conditions were as follows: 2 °C/min heating rate; 15–20 mg of sample; nitrogen atmosphere; samples predried as previously described. **(2) TG/DTG.** A Mettler 2000C thermal analysis system was employed. Conditions were as follows: (a) 50 mg of PAA weighed into an α-Al_2O_3 crucible; (b) samples predried in the unit at 93 °C as previously described; (c) system then programmed from 93 to 350 °C at 2 °C/min in a flow of dry helium (20 cm^3/min through the top of the reaction chamber down to the sample), with changes in weight monitored on a strip chart recorder. The content of the evolved gases and helium was monitored by differentially pumping approximately 10% of the gas from the chamber through a 0.125-mm i.d. stainless steel capillary tube and sampling from this tube with a Varian leak valve into the mass spectrometer. **(3) MS.** A UTI Model 100 mass spectrometer equipped with a Spectra Link unit to allow multiple masses (16, 17, 18, 27, 28, 44) to be analyzed[9] was used.

Results and Discussion

Anhydride Formation in PAA. The thermal history of each PAA sample is an important issue in this thermal characterization study. PAA has been reported to convert to anhydride over a wide temperature range (Table I)[3,11-14] and then to ketone and hydrocarbon at higher temperatures. On the basis of experiments at 170 °C, Eisenberg et al.[3] found that the T_g of PAA (103 °C) increases with increasing anhydride content. The pure linear anhydride had an extrapolated T_g of 140 °C. They also concluded that anhydride formation occurred primarily via an intramolecular route. Therefore, it was necessary to examine the time and temperature dependence of anhydride formation in the polymers used in this study. This provided the basis for selecting conditions that would dry the polymers without leading to changes in T_g, due to anhydride formation.

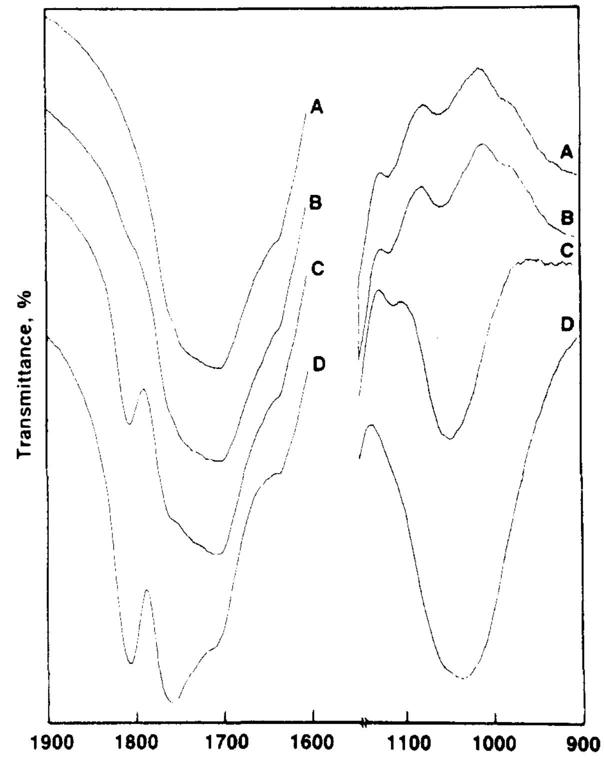


Figure 1. Influence of thermal history on anydride formation in PAA(A):A-3. Spectra are displaced for clarity. (A) Control; (B) 16 h at 93 °C; (C) 16 h at 113 °C; (D) 16 h at 123 °C.

The influence of drying temperature on anhydride formation in freeze-dried PAA(A):A-3 is shown in Figure 1. The simultaneous appearance of bands at 1806, 1757, and 1030 cm^{-1} and the disapperance of bands at 1708 and 1243 cm^{-1} are consistent with the conversion of carboxylic acid to anhydride. No anhydride is evident at 83 °C. Anhydride is just barely detectable at 93 °C, significant at 113 °C, and substantially increased at 123 °C. At similar thermal histories, anhydride formation in freeze-dried PAA(S):3312 appears to occur at a slower rate vs. PAA(A):A-3 (Figure 2).

DSC experiments indicated that T_g of PAA(A):A-3 samples dried for 16 h at 93 °C changed only slightly (2–5 °C, or one-tenth to one-quarter of the difference between the two stereoregular forms) vs. the nondried control. On the basis of this study, a standard drying condition of 16 h at 93 °C was used except as noted.

DSC Characterization of PAA(A). In the initial phase of this investigation, DSC samples, contained in a pierced-lid DSC pan, were dried in an oven or the TG–MS unit as described elsewhere and quickly transferred to the DSC unit. DSC analysis revealed an extremely complex thermogram (Figure 3). Interpretation of the multiple events shown in Figure 3 and determination of their relationship to polymer tacticity are the primary objectives of this paper. The transition at region A, which occurs around 105 °C, was interpreted as the T_g of PAA(A). This value is in good agreement with a T_g value of 102 °C obtained for PAA by Maurer et al.[6] via analysis of the T_g vs. composition data for poly(acrylamide-*co*-acrylic acid) in terms of the Gordon–Taylor–Wood equation. The present value (105 °C) is also in agreement with other literature values for the T_g of PAA.[1-3] Further, infrared analysis, by the method of Monjol and Champetier,[7] indicated that this polymer is predominantly PAA(A).

The apparent transition or endotherm at region B is interesting since it occurs around 125 °C, which is similar to the second T_g value, $T_g(2)$, that has been reported for PAA. This is considered fortuitous, however, since it will be shown that region B of the thermogram appears to involve strongly bound water. Region C might also be due to bound water, but anhydride formation must also be considered as a factor since Eisenberg et al.[3] detected anhydride in samples aged in the 125–170 °C range. Possibilities regarding the origin of the endotherm at region D include both anhydride formation and degradation.[3,11-14]

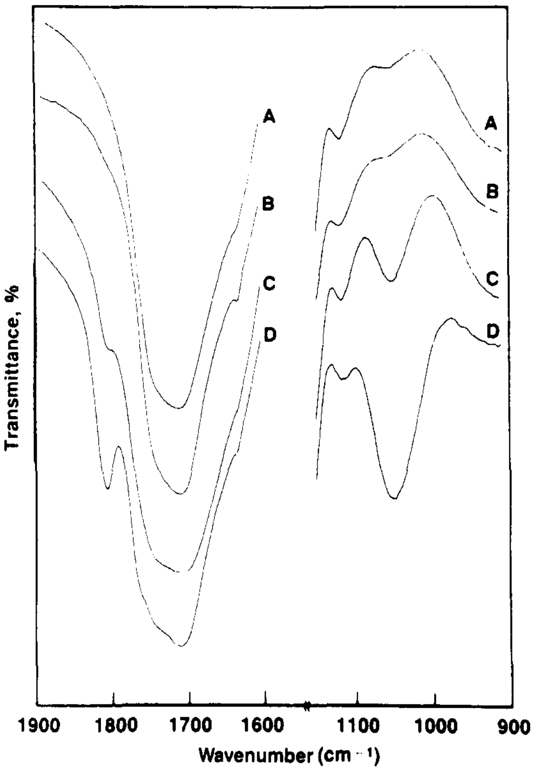


Figure 2. Influence of thermal history on anhydride formation in PAA(S):3312. Spectra are displaced for clarity. (A) Control; (B) 16 h at 93 °C; (C) 16 h at 113 °C; (D) 16 h at 123 °C.

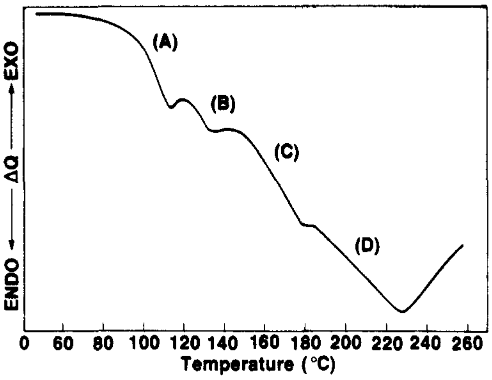


Figure 3. DSC thermogram for PAA(A):4551 (encapsulated sample (pierced lid); predried 20 h in a 93 °C oven). Regions A–D are described in the text.

Thermal History Effects. The influence of thermal history on PAA(A) and PAA(S) is shown in Figure 4. The initial thermogram for PAA(A):4551, Figure 4A, indicated T_g at ~102 °C and a second endotherm at ~123 °C, which is similar to region B of Figure 3. The initial DSC scan used to generate the thermogram of Figure 4A was terminated at 160 °C, the sample was cooled in place to ~25 °C, and the sample was immediately rerun to generate the thermogram shown in Figure 4B. Two effects are noted in comparing thermograms A and B. The principal effect

Table III
Influence of Thermal History on Thermal Characteristics of Poly(acrylic acid)

	PAA(A):A-3			PAA(S):3312		
drying temp,[a] °C	$T_g(1)$[b]	T_x[c]	endotherm min, °C	$T_g(1)$[b]	$T_g(2)$[b]	endotherm min, °C
93	108	135	168	108	124	205
103	115	135	167	118	128	205
113	120	135	169		127	206
123		135	189		128	207

[a] Predried 16 h (open DSC pan) in a TG unit; see Experimental Section. [b] Defined in the Introduction. [c] T_x is the 135 °C "transition" in PAA(A); origin not yet established.

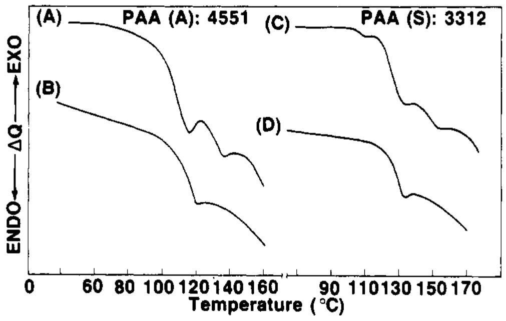


Figure 4. Influence of thermal history on thermograms of PAA(A):4551 and PAA(S):3312 (encapsulated sample (pierced lid); predried 22 h in a 93 °C oven): (A, C) original runs; (B, D) recycled in place.

is the absence of the "transition" at ~125 °C. This would be consistent with the removal of residual, tightly bound water from the original sample. A T_g value of 108 °C was observed in the recycle run, which suggests that a small amount of anhydride formation may have occurred in the original run. Alternatively, this may reflect kinetic effects associated with the thermal history applied to the sample.

A similar DSC recycle experiment for PAA(S):3312 is also shown in Figure 4. The initial thermogram exhibits three interesting characteristics: (a) a weak transition near ~105 °C, (b) a major transition at ~119 °C, which is tentatively interpreted as T_g of PAA(S), and (c) an endotherm above T_g, here at ~140 °C.

Only the proposed T_g of PAA(S) is evident in the recycle run (D). The slightly higher T_g value (~123 °C) may reflect kinetic effects due to the particualr thermal history employed or a small amount of intramolecular anhydride formation.[3] Absence of the 105 °C "transition" in the recycle experiment may be due to kinetic effects and the weakness of the transition in the original run. Finally, loss of the endotherm above T_g is interpreted as due to removal of tightly bound water in the original sample. This interpretation is supported by the observation that the endotherm above T_g is *not* observed in original runs of PAA(A):4551 or PAA(S):3312 when the samples are predried, and run, in *open* DSC pans.

The nature of the weak transition at ~105 °C (curve C of Figure 4) is interesting but uncertain. It occurs at about the same temperature as, and has a thermal history dependence (Table III) similar to, the T_g assigned to PAA(A). These observations suggested that this apparent transition might reflect the presence of a small amount of atactic PAA microstructure in a predominantly syndiotactic polymer. Two reviewers of this paper have observed that this is very unlikely since it would imply phase separation of the two systems over regions of ca. 50-Å minimum. In an attempt to rationalize the presence of this apparent transition at ~105 °C two additional, speculative proposals have been considered. The first is that the transition at ~105 °C is the actual T_g of the polymer which is being obscured by another "transition" of unknown origin at ~119 °C. This is considered unlikely because the transition at ~119 °C is the major transition, displays the anticipated thermogram characteristics of a T_g, and remains strong following recycle from above "T_g". Also, a T_g value in the 118–127 °C range was observed in several PAA(S) samples whereas the transition in the ~105 °C region was not noted in some of these polymers. The second speculative proposal is that this polymer might be a blend consisting of a major amount of PAA(S) and a minor amount of PAA(A). Evaluation of this proposal would require additional information regarding the general phase behavior of such blends as well as the synthesis and composition of PAA(S):3312.

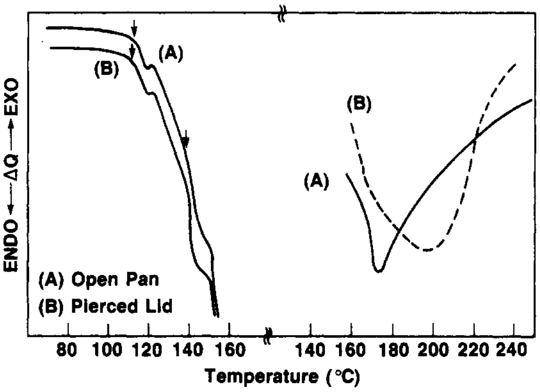


Figure 5. Influence of sample type and mode on thermogram of PAA(A):A-3 (freeze-dried polymer; predried 16 h at 93 °C in a TG unit): (A) open pan; (B) encapsulated (pierced lid). (Arrows identify features described in the text.)

Influence of Sample Type and DSC Mode. The next phase of this study involved consideration of the influence of two key experimental variables on the thermogram characteristics of PAA(A) and PAA(S). These experiments, which are illustrated in Figure 5, employed a high DSC sensitivity to enable definition of several complex thermal characteristics of these PAA samples in the temperature range from about 80 to 150 °C. The more intense endotherms that occur above about 150 °C have been plotted at reduced sensitivity, shifted upward on the ΔQ axis, and shown separately for ease of presentation (similar comments apply to Figures 6 and 7). One of the important findings from this study was that use of a freeze-dried sample apparently enables removal of the "bound water" from PAA(A) during predrying in either the pierced-lid (B) or open-pan (A) mode (Figure 5). Note T_g (at ~108 °C), the absence of the endotherm at about 123 °C, (vs. Figure 4), and the transition at ~135 °C for *both* sample modes. These features are indicated by the arrows in Figure 5. However, another influence of sample mode is evident above the ~135 °C transition. It appears that loss of volatiles, presumably water from anhydride formation, is retarded in the pierced-lid system. Therefore, the use of freeze-dried samples and the *open*-pan DSC mode were

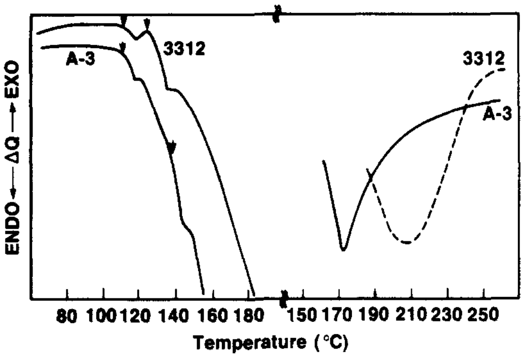


Figure 6. Comparison of thermograms for PAA(A):A-3 and PAA(S):3312 (freeze-dried polymer; predried 16 h at 93 °C in a TG unit (open pan)). (Arrows identify features described in the text.)

chosen as standard DSC conditions.

Comparison of PAA(A) vs. PAA(S). These standard conditions were employed to compare the thermal characteristics of PAA(A):A-3 and PAA(S):3312 as shown in Figure 6. Several key features of these thermograms are indicated by the arrows in Figure 6. PAA(A):A-3 exhibits a T_g at ~108 °C, a pronounced transition around 135 °C, and a large endotherm, presumably due to loss of volatile material, whose minimum occurs at ~170 °C. The 135 °C transition is similar to the value that Eisenberg attributes to linear intramolecular anhydride. For reasons to be described subsequently, it is considered unlikely that this transition is due to the complete conversion of PAA to the linear anhydride in the present case. PAA(S):3312 exhibits a weak transition around 108 °C, similar to that shown in Figure 4, and a strong transition (taken to be T_g), at ~124 °C. A transition is not observed in the 135 °C region. Finally, the large endotherm, whose minimum occurs at ~210 °C, is again attributed to loss of volatile material. This comparison indicates several pronounced differences between these PAA(A) and PAA(S) samples. An interesting question here is whether the higher T_g, the absence of a 135 °C transition, and/or the higher temperature endotherm compared to PAA(A) might be a consequence of enhanced hydrogen bonding in PAA(S). With regard to the 135 °C transition, there is also the question of whether it is obscured by, or not resolved from, the T_g of PAA(S).

A final point of interest here concerns the observed difference in T_g for PAA(A) vs. PAA(S). This polymer system may represent an exception to an empirical rule proposed by Karasz and MacKnight.[17,18] These authors indicate that the T_g of monosubstituted vinyl polymers of the type CH_2CHY is not influenced by tacticity. The present study suggests such an effect in PAA. However, as noted earlier, this may be an indirect effect due to hydrogen bonding and thus not a true exception to the rule. Burfield and Doi have recently reported that the T_g of polypropylene is also influenced by tacticity.[19]

The 135 °C Transition in PAA(A). Various authors recommend the practice of heating a polymer to about 10 °C greater than T_g, cooling the sample below T_g, and then determining T_g from the thermogram of a recycle run.[1,15] The effect of thermal history on T_g and the 135 °C transition of PAA(A) was studied in a similar manner as illustrated in Figure 7. Key features of the thermograms are indicated by the arrows in Figure 7. PAA(A):A-3 was first held at 125 °C for 1 h. This temperature was chosen to bring the sample about the T_g of PAA(A), but below 135 °C, before cooling to ~40 °C. Upon reheating the sample to 150 °C (Figure 7A), one notes a diffuse T_g region (T_g ≃ 113 °C) and the transition at ~135 °C. Recycling this sample (Figure 7B) reveals a sharper T_g region (T_g ≃ 118 °C) but the 135 °C transition is not detected.

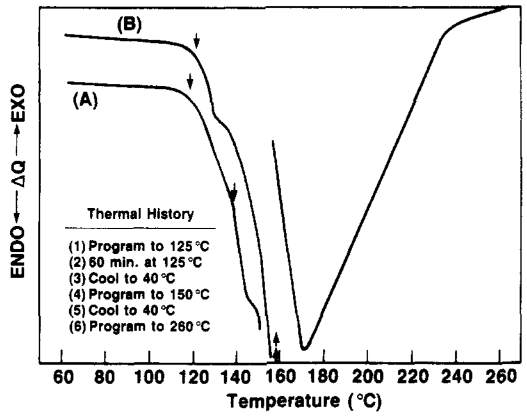


Figure 7. Influence of thermal history on the 135 °C region of PAA(A):A-3 (freeze-dried polymer; open pan; no predrying). (Arrows identify features described in the text.)

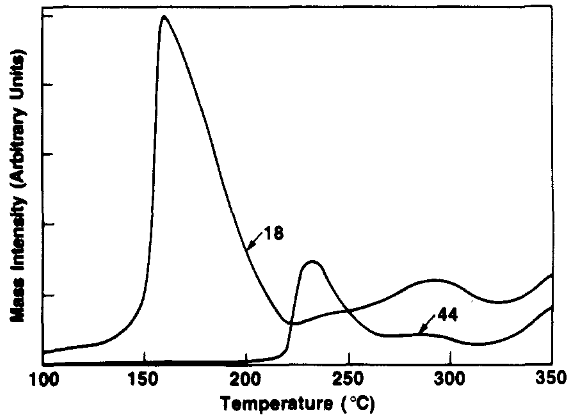


Figure 8. Analysis of water and carbon dioxide evolution from PAA(A):A-3 (freeze-dried polymer; predried in a TG unit for 16 h at 93 °C (open crucible)).

The small change in T_g following the recycle run suggests that there has not been a major increase in intramolecular anhydride formation, since Eisenberg et al.[3] indicate that T_g should increase to a limiting value of 140 °C as anhydride formation progresses. Further the T_g value of Figure 7B is similar to the value before the sample was heated through the $T_{135\,°C}$ region. Thus the event at 135 °C has not had a significant effect on T_g of the polymer. It is not possible from these data to identify the exact nature of the process or event that occurs at 135 °C. However, one may speculate that it may be due to intramolecular anhydride formation involving a small amount of less reactive carboxyl groups or to other microstructures (e.g., isotactic or head-to-head vs. head-to-tail units in the polymer chain,[16] etc.)

Volatiles Analysis via Mass Spectrometry. In order to determine the nature of the processes responsible for the endotherms noted above T_g for PAA(A) and PAA(S), TG–MS experiments were conducted in which the polymers were dried in a TG unit and the volatiles were analyzed by an MS system as previously described. Some comments regarding (a) the water content of these polymers and (b) the temperature at which water evolved *from the polymer* is detected are appropriate before proceeding to an interpretation of the TG–MS data.

Information regarding the water content of the dried polymers is available from the TGA trace of sample weight vs. temperature which is obtained during the TG–MS

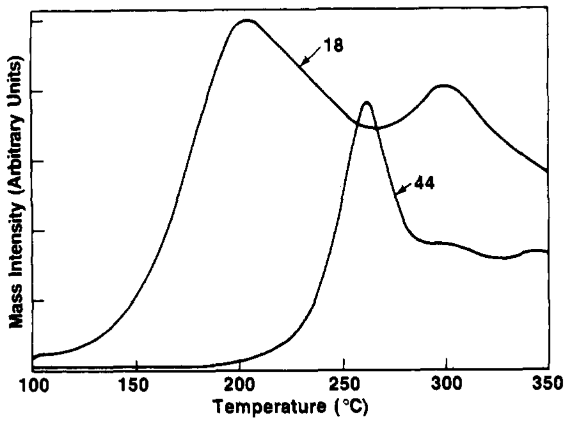


Figure 9. Analysis of water and carbon dioxide evolution from PAA(S):3312 (vacuum-dried polymer; predried in a TG unit for 16 h at 93 °C (open crucible)).

experiment. For PAA(A):A-3, Figure 8, a weight loss of 2.5% was observed during the isothermal predrying step (16 h at 93 °C). In the subsequent programmed heating step, during which the MS data are obtained, a weight loss of only 0.06% (based on the sample weight at the end of the predrying step) was observed during heating from 100 to 130 °C. This small weight loss may include some water arising from anhydride formation. For PAA(S):3312, Figure 9, the corresponding weight losses were 0.4% in the predrying step and 0.09% during the programmed heating step.

The data indicate that these samples were essentially dry at the beginning of the programmed heating phase of the TG-MS experiment. They also suggest that T_g differences observed for similarly dried PAA(A) and PAA(S) polymers are not likely to be due to differences in residual water content.

Inspection of Figures 8 and 9 indicates water evolution beginning at 100 °C, even though the TGA traces show that weight loss during programmed heating does not begin until about 110 °C. The initial water evolution around 100 °C is due to a very small amount of background water which is virtually impossible to eliminate in this type of equipment. This problem is conventionally handled by running a "blank" experiment in which no sample is present and comparing the MS trace for mass 18 with that obtained from a similar experiment in which the sample is present. In order to verify this approach, we have conducted such an analysis for our system. Comparison of the mass 18 (water) evolution vs. temperature curve for the blank vs. that for PAA(A):A-3 and PAA(S):3312 showed that the water evolution was identical up to ca. 110 °C, i.e., no water loss from the polymer up to this temperature.

The TG–MS experiments are highly informative as shown for PAA(A):A-3 in Figure 8. Substantial water evolution commences near ~130 °C and reaches a maximum rate around 170 °C. This temperature is in good agreement with the position of the DSC endotherm minimum at about 170 °C (Figure 6). Very little CO_2 evolution is noted until most of the water evolution was completed around 215–220 °C. The CO_2 evolution peak occurs near ~230 °C. Assuming that the water evolution is due primarily to anhydride formation, the data suggest that this process commences in about the 130–150 °C region under these conditions.

A similar experiment was conducted with freeze-dried PAA(S):3312. MS data are shown in Figure 9. Water evolution again starts around 130, but proceeds more gradually and is more diffuse than in PAA(A):A-3. The maximum rate of water evolution occurs near 200 °C, which is in good agreement with the DSC endotherm minimum (~205 °C) (Figure 6). These data suggest that anhydride formation commences in the same region (~125–150 °C) as in PAA(A):A-3 but proceeds much more gradually than in the atactic polymer. The maximum CO_2 intensity in the MS experiment appears at ~260 °C, which is a substantially higher temperature than that of the PAA(A):A-3. Both the water maximum and the CO_2 maximum occur about 30–35 °C higher in the syndiotactic polymer vs. the atactic polymer. As in the case of the T_g differences observed for these polymers, these effects might conceivably be a direct consequence of the tacticity differences or an indirect effect related to stronger polymer–polymer interaction through hydrogen bonding in the syndiotactic polymer.

Influence of Thermal History on PAA Thermogram Characteristics. The influence of drying temperature on transition temperatures and endotherm characteristics is compared for PAA(A) and PAA(S) in Table III. For the atactic polymer, drying at 93 °C has had little effect on T_g as previously noted. Therefore there does not appear to have been a major amount of anhydride formation. As the drying temperature is increased to 103 °C and to 113 °C, T_x (as defined in Table III) and the endotherm minimum remain invariant. However, T_g of the polymer steadily increases, presumably due to the formation of additional anhydride.[3] At a drying temperature of 123 °C, T_g and T_x merge, and the endotherm minimum increases to 189 °C. The latter feature may reflect decomposition of the anhydride.

The effect of drying temperature on PAA(S) is also interesting. At drying temperatures of 93 and 103 °C, the value and response to heating rate of the lowest transition are similar to that of the T_g of PAA(A) as previously noted. At drying temperatures above 103 °C, this transition is not evident, presumably because it is merged with or masked by the T_g of PAA(S).

Several other aspects of the data in Table III are also of interest: (a) with the exception of the 123 °C dried PAA(A-3) system, the endotherm minimum remained essentially constant in both systems over a broad range of drying conditions. This suggests that drying temperature has not had an appreciable effect on anhydride formation or decomposition characteristics in either system; (b) unlike PAA(A-3), the T_g of PAA(3312) does not appear to be significantly influenced by anhydride formation. Alternatively, this T_g invariance may indicate that the amount of anhydride formation is much less, under these conditions, in the syndiotactic vs. the atactic polymer; (c) the invariance of the 135 °C transition in PAA(A) again suggests that it does not correspond to the pure linear anhydride. Note that this transition is clearly resolved from T_g even though substantial T_g increases are noted, presumably due to intramolecular anhydride formation. As previously noted, the 135 °C transition is believed to reflect some other microstructure, or anhydride formation due to a small amount of some less reactive carboxyl groups.

Summary and Conclusions

Thermal characterization procedures have provided important insight regarding the microstructure and thermal stability of PAA. A key component of this study was the definition of procedures that enabled resolution of several challenging problems relating to water content and anhydride formation in PAA. These complictations were overcome by the use of multiple techniques (DSC, TG–MS, and IR) in combination with rigorous definition of sample type and thermal history effects.

The thermal characteristics of PAA(A) and PAA(S) appear to differ significantly with regard to the glass transition temperature (T_g) and thermal stability, i.e., the temperatures at which maximum water evolution (due to anhydride formation) and carbon dioxide evolution (due to anhydride decomposition) occur in the TG–MS experiment. These differences may be a direct consequence of tacticity or possibly an indirect effect due to enhanced hydrogen bonding in the syndiotactic polymer. In either case, variations in polymer tacticity may be the cause of a T_g discrepancy which appears in the literature regarding poly(acrylic acid).

Thermal characterization has also revealed three additional features of PAA: First, for certain combinations of sample type and thermal history, bound-water effects are noted in both tactic forms of the polymer; second, a weak transition, of undetermined origin, occurs in some PAA(S) polymers at a temperature similar to the T_g of PAA(A); third, a pronounced transition of unknown origin occurs at ~135 °C in atactic PAA. On the basis of studies of thermal history effects, this transition does not appear to involve intramolecular anhydride formation. Speculative proposals regarding its origin include some type of less reactive carboxyl groups or an as yet undetermined type of microstructure.

Acknowledgment. We are pleased to acknowledge valuable comments and suggestions concerning this research made by Professor William J. MacKnight, University of Massachusetts. Karen Graf, Gerald Harvey, and Richard Salher are thanked for assistance in the infrared, DSC, and TG–MS studies, respectively.

References and Notes

(1) Brandrup, J., Immergut, E. H., Eds.; *Polymer Handbook*, 2nd ed., Wiley: New York, 1975; Chapters 2 and 3.

(2) Greenberg, A. R.; Kusy, R. P. *J. Appl. Polym. Sci.* **1980**, *25*, 1785.

(3) Eisenberg, A.; Yokoyama, T.; Sambalido, E. *J. Polym. Sci., Part A-1* **1969**, *7*, 1717.

(4) Klein, J.; Heitzmann, R. *Makromol. Chem.* **1978**, *179*, 1895.

(5) Greenberg, A. R.; Rehrl, M. D.; Letendre, D. In *Proceedings of the 12th North American Thermal Analysis Society Conference*; Buck, J. C. Ed.; **1983**, 500.

(6) Maurer, J. J.; Schulz, D. N.; Siano, D. B.; Bock, J. In *Analytical Calorimetry*; Johnson, J., Gill, P. S.; Eds.; Plenum: New York, **1984**, *5*, 43.

(7) Monjol, P.; Champetier, G. *Bull. Soc. Chim. Fr.* **1972**, *4*, 1302.

(8) Petrie, S. E. B. *J. Polym. Sci., Part A-2* **1972**, *10*, 1255.

(9) Ratcliff, C. T. In *Proceedings of the 13th North American Thermal Analysis Society Conference*; McGhie, A. R., Ed.; **1984**, 90.

(10) Ellis, T. S.; Karasz, F. E.; Moy, P. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1981**, *22*, 121.

(11) Roux, F. X.; Audebert, R. A.; Quivoron, C. *Eur. Polym. J.* **1973**, *9*, 815.

(12) McGaugh, M. C.; Kottle, S. *J. Polym. Sci., Polym. Lett. Ed.* **1967**, *5*, 817.

(13) Kabanov, V. P.; Dubnitskaya, V. A.; Khar'kov, S. N. *Vysokomol. Soedin.* **1974**, *A17*, 1604.

(14) Girard, H.; Monjol, P.; Audebert, R. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1974**, *C279*, 597.

(15) Chiantore, O.; Costa, L.; Guaita, M. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 303.

(16) Otsu, T.; Quach, L. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 2377.

(17) Karasz, F. E. In *Preparation and Properties of Stereoregular Polymers*; Lenz, R. W., Ciardelli, F., Eds.; Reidel: Dordrecht 1979; p 449.

(18) Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1968**, *1*, 537.

(19) Burfield, D. R.; Doi, Y. *Macromolecules* **1983**, *16*, 702.

Self-Similar Structure of an Adsorbed Polymer Layer: Comparison between Theory and Scattering Experiments

Loïc Auvray* and J. P. Cotton

Laboratoire Léon Brillouin,[†] CEN-Saclay, 91191 Gif-sur-Yvette Cédex, France.

Received June 17, 1986

ABSTRACT: We compare the predictions of the scaling theory of polymer adsorption to the neutron-scattering experiments that we have performed on a large molecular weight monodisperse poly(dimethylsiloxane) strongly adsorbed on mesoporous silica in the presence of pure cyclohexane. The contrast variations method has enabled us to isolate in the scattering vector range $10^{-2} < q < 10^{-1}$ Å^{-1}, chosen to probe the inner structure of the adsorbed layer, both the silica polymer cross-structure factor, $S_{pg}(q)$, related to the Sine–Fourier transform $\phi(q)$ of the polymer concentration profile $\phi(z)$, and the intrinsic structure factor of the layer, $S_{pp}(q)$. The prediction that the structure of the adsorbed layer is self-similar, with a concentration profile decreasing as $z^{-4/3}$, interprets the experimental observation that $\phi(q)$ increases as $q^{0.35\pm0.1}$ in the q range investigated. The contribution to $S_{pp}(q)$ of the fluctuation of polymer concentration in the layer, recently discussed, has, however, not been detected.

I. Introduction

One of the most beautiful predictions of the scaling theory of polymer adsorption[1] is that, in a good solvent, neutral linear long flexible chains strongly adsorbed on a solid wall build a self-similar diffuse layer (Figure 1). At a distance z from the solid, where the average polymer volume fraction is $\phi(z)$, the layer is assimilated to a semidilute solution of correlation length $\xi[\phi(z)]$, predicted to be simply equal to z. The relation $\xi(\phi) = a\phi^{-3/4}$, established for the bulk solutions,[2] then leads to a very singular polymer profile:

$$\phi(z) = (a/z)^{4/3} \qquad (a < z < R) \tag{1}$$

a is a microscopic length comparable to the monomer size, and R is of the order of the Flory radius of the chains $R = aN^{3/5}$ (N, number of monomers per chain).

So far, this prediction has not been confronted directly by experiment because many techniques[3] used to study adsorbed layers such as spectroscopic techniques[4-6] (in-

---

[†] Laboratoire commun CEA-CNRS.