Glass-Transition Behavior of Poly(methacrylonitrile)

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ABSTRACT: The glass-transition temperatures (T_g) of some polymers reported in the literature have always been a source of great uncertainty. The values reported for poly(methacrylonitrile) (PMAN, 100 and 120°C) are well above the value determined in this study (67°C). It is clearly shown by FTIR and DSC work that formation of cyclic structures during the drying of PMAN, even at low temperatures, is the main reason for the high T_g values observed. The contributions of naphthydrine type cyclic structures and intermolecular crosslinks in the increase of the T_g are determined over an aging temperature interval of 90–300°C. The combined effects of intra- and intermolecular linking cause an increase in the T_g from 67 to 116°C. The hardness measurements also confirm the value determined by DSC. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1936–1943, 2001

Key words: glass-transition temperature; poly(methacrylonitrile); intramolecular cyclization; crosslinking

INTRODUCTION

A great amount of confusion, uncertainty, and even controversy exists for a number of polymer glass-transition temperature (T_g) values reported in the literature. To cite just a few examples, for polyethylene[1] the reported T_g values were between −15 and −130°C, for poly(vinylpyrrolidone)[2] they were 54–175°C, and for poly(acrylic acid)[3] they were 104–148°C. In addition to methodological factors causing this large discrepancy in the reported values, lack of detailed characterization of the polymers that were tested is another very important reason for the wide spread of T_g data, even for a particular polymer. Consequently, a number of research articles are being published every year to clarify these inconsisten-

cies. Although for some polymers there were numerous T_g determination type studies and more repeated values that were refined, for some others there are quite old values still being used without any attempt to correct or check the validity of existing T_g values. The latter is the case for poly-(methacrylonitrile) (PMAN). The earliest reported value for the T_g of PMAN is the one given by Nielsen[4] as 120°C, and a relatively recent study[5] considers the T_g as 100°C.

In our recent study related to PMAN we synthesized and tried to characterize a polymer and interpreted the results relevant to its thermal behavior by referring to the T_g value reported in the literature. Soon we noticed that at and around the T_g value reported in the literature (120°C), transparent PMAN samples in the form of chips or films turned slightly yellowish, indicative of reactions taking place in the polymer chains. We therefore undertook this study to clarify the thermal transition behavior of PMAN around this temperature and determine its T_g value.

EXPERIMENTAL

The PMAN samples used in this study were obtained by bulk polymerization of its monomer (Merck) at 30°C under a N_2 atmosphere. The initiator AIBN was used at 9.75 mmol concentration. Because this polymer is insoluble in its monomer, the polymerization was followed by a phase difference and 100% conversion was achieved in 55 days. These polymerization conditions were selected to obtain PMAN with very high molecular masses.

The small chip samples (2 mm) were washed with ether and held in a vacuum oven at 35°C for 4 days to purify the polymer, and then they were sealed in pyrex tubes under a 10^{-6} mmHg vacuum.

The glass-transition temperatures of the sample were determined by the DSC technique using a Du Pont 9900 thermal analyzer. Measurements were carried out at a heating rate of 10°C/min in a dynamic nitrogen atmosphere with a flow rate of 5 mL/min. A midpoint value of a reverse S was taken as the T_g value from the DSC thermograms.

A Nicolet FTIR spectrometer (model 520) was used to determine any changes in the chemical structure of the polymer upon heating to various temperatures during the T_g measurements. Spectra were taken from films prepared in acetone and dichloromethane solution.

The NMR spectra of the samples were obtained with a Varian T60-A spectrometer on deuterated acetone at 30°C.

A Waters 244 ALC/GPC chromatograph was used in the measurements of the molecular mass of the PMAN. Ultrastyragel columns of 10^3, 10^4, and 10^5 Å pore sizes connected in series and standard polystyrene (PS) samples obtained from Polysciences Inc. were used for calibration. The secondary calibration was done by using the following Mark–Houwink constants for DMF at 25°C: $K = 31.8 \times 10^{-3}$ and $a = 0.603$ for PS[6] and $K = 3.06 \times 10^{-3}$ and $a = 0.503$ for PMAN.[7] From SEC chromatograms the number-average (M_n = 237,000) and weight-average (M_w = 765,000) molecular weights and (HI = 3.2) were calculated for the PMAN sample used in the T_g measurements. The SEC chromatograms were between 20,000 and 3×10^6 molecular mass limits. No peaks due to unpolymerized monomers and/or oligomers were observed in the chromatograms.

The surface hardness of the PMAN samples was also determined over a temperature range by measuring their hardness with a Shore D durometer.

RESULTS AND DISCUSSION

Before attempting to determine the T_g of PMAN by the calorimetric method, a DSC thermogram of this sample was taken over a wide temperature range. Spectrum a in Figure 1 shows the thermogram of this polymer taken during initial heating from room temperature to 450°C. As is easily seen, there was an endothermic peak at around 70°C, which was immediately followed by an exothermic peak at 125°C. No change was observed until about 250°C, after which a slight ramp was observed in the baseline just before the large endothermic peak taking place at around 360°C. This last peak was attributed to the degradation of the polymer by comparing the dynamic thermogravimetric weight loss curve of the same sample heated to 600°C in another study[8] in which the degradative weight loss coincided with this peak.

Because we observed a slight color change for PMAN films heated to and slightly above 100°C, the sample was heated to 100°C, cooled to room temperature, and then reheated to 100°C again at the same rate. The thermograms of the first and second runs of this heating process are given in Figure 2. The thermogram of the second run depicts the typical reverse S-shaped curve corresponding to the glass transition. This clearly indicated that the first endothermic peak observed in Figure 1 (spectrum a) at around 70°C was due to an enthalpic relaxation process of the PMAN chains. When the typical glass-transition behavior of PMAN was analyzed from the second heating curve in Figure 2, its value at the inflection point was determined to be 67°C. This was in contradiction with the T_g value reported so far. The T_g values available in the literature are well above this value (e.g., 120°C given by Nielsen[4] and 100°C given by Nakamura et al.[5]). However, as is shown later in this article, it was possible to obtain these values as the T_g of PMAN, depending on the thermal history of the sample; but before investigating the effects of the thermal history and aging on the T_g of PMAN, the nature of the exothermic peak observed at around 125°C in Figure 1 (spectrum a) must be understood. The exothermic peak started at about 90°C and ended at approximately 150°C. We attributed this peak to the formation of intramolecular cyclic structures,
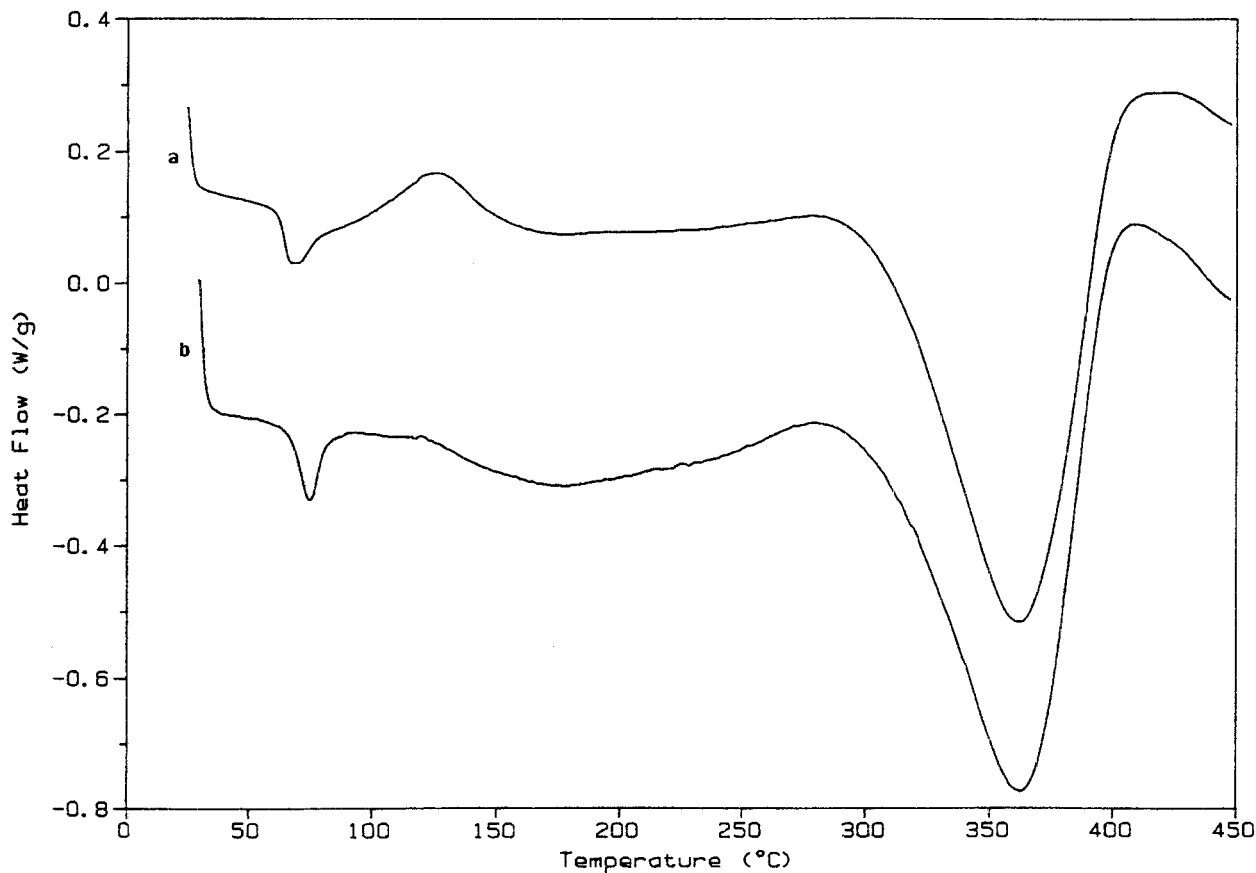
Figure 1   A DSC thermogram of PMAN taken up to 450°C (spectrum a). A thermogram of the PMAN sample aged for 3 days at 55°C that shows the decrease of the exothermic cyclization peak at around 125°C (spectrum b).

which were called a naphthydrine type by Nakamura et al.[5] (Scheme 1).

At relatively low temperatures (90–140°C) this cyclization took place intramolecularly as we determined from the solubility of PMAN; at higher temperatures (above 150°C) the intermolecular cyclization and crosslinking took place as reflected by the insolubility of these latter samples in structures II and III in Scheme 1. It was also observed that the time–temperature superposition principle applied here and partial cyclization took place even for samples aged for long periods of time at relatively low temperatures. Because the cyclization process was observed to proceed over a temperature range of 90–150°C, the samples heated to various temperatures in this interval were expected to possess a different extent of cyclic structures that would affect the T_g values.

In order to be able to find a relation between the T_g values of the samples having different thermal histories and corresponding chain struc-

tures, a detailed FTIR study was performed on PMAN films. The changes in intensity of bands arising from —CH and —CH$_3$ groups are shown in Figure 3 in the 2100 and 3200 cm^{-1} regions of the spectrum. Upon heating the PMAN films to the temperatures indicated in the figure, a continuous decrease in the peak of the —CN band area at 2220 cm^{-1} was observed. Normalization of the CN peak areas was done by dividing the CN peak areas by the peak area corresponding to the band observed between 532 and 606 cm^{-1}. The last peak was chosen as the reference, because its area was not affected by temperature changes. The decrease in the normalized peak area of the nitrile group is given in Table I. The small peak observed at 3061 cm^{-1} due to the —CH$_3$ group also decreased, which was assumed to be consumed during the intermolecular linking reaction. The dynamic thermogravimetry of samples also revealed the removal of —CH$_3$ groups from the polymer backbone.[8] The temperature at
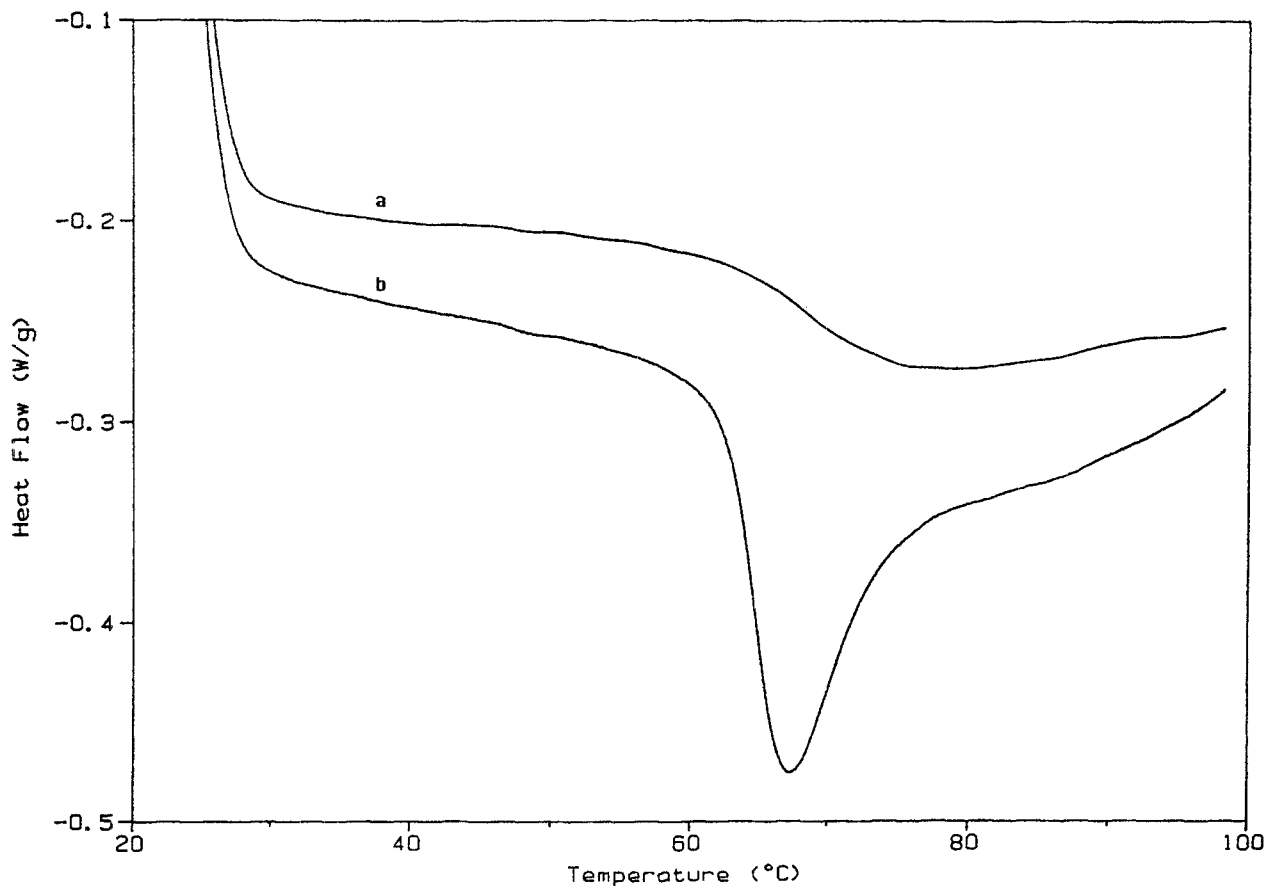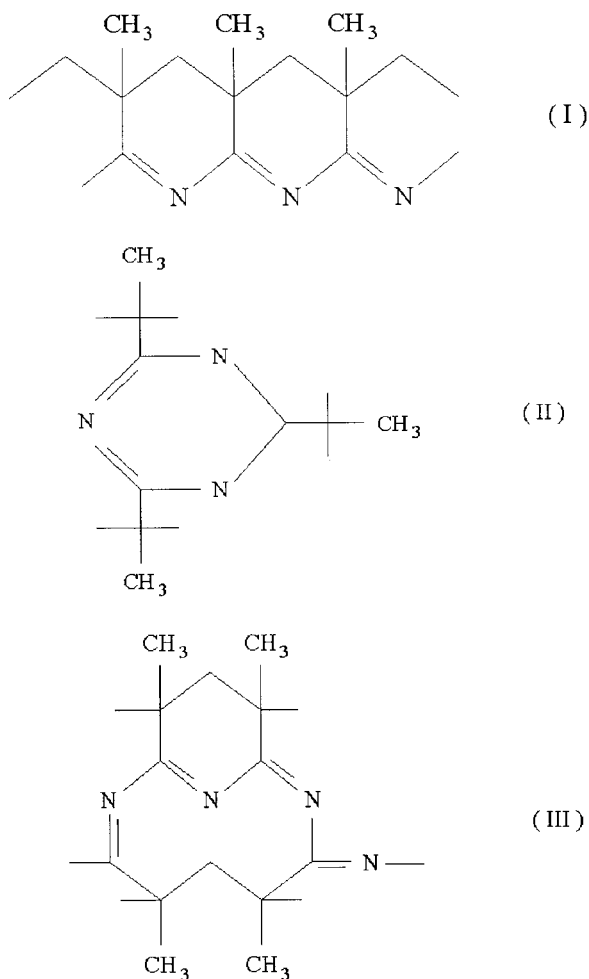
Figure 2 A thermogram of the first (spectrum a) and second (spectrum b) heating runs of PMAN heated to 100°C.

which an appreciable decrease was observed in the CH_3 groups (i.e., 150°C) corresponded to the formation of insoluble structures. The decrease in the intensity of the nitrile groups coincided very well with an increase in the intensity of a new band appearing at 1127 cm^{-1} (Fig. 4). This band became significant for the sample heated above 150°C, which is the onset temperature of thermal gelation. The chemical structure that gave rise to this band was assumed to be C—N type groups. The precursor of this group was most probably —C≡N type structures that formed during the initial heating process, which caused intramolecular cyclization.

The change in the side chain structures of PMAN through cyclization affects the physical properties of PMAN from two different aspects. First, because of the formation of a conjugated double in the cyclic moieties, the polymer discolors; this was observed, even with the naked eye. Second, cyclic structures forming in the side chains decrease the chain flexibility that further

causes an increase in the T_g. To confirm this latter expectation, second heating runs of PMAN samples initially heated to various temperatures (100, 110, 120, 140, 165, 200, and 250°C) were recorded and are given in Figure 5. The samples used in this figure were first heated to the indicated temperatures and then immediately cooled to room temperature and reheated. The T_g values shifted to higher temperatures that are observed in this figure are given Table I.
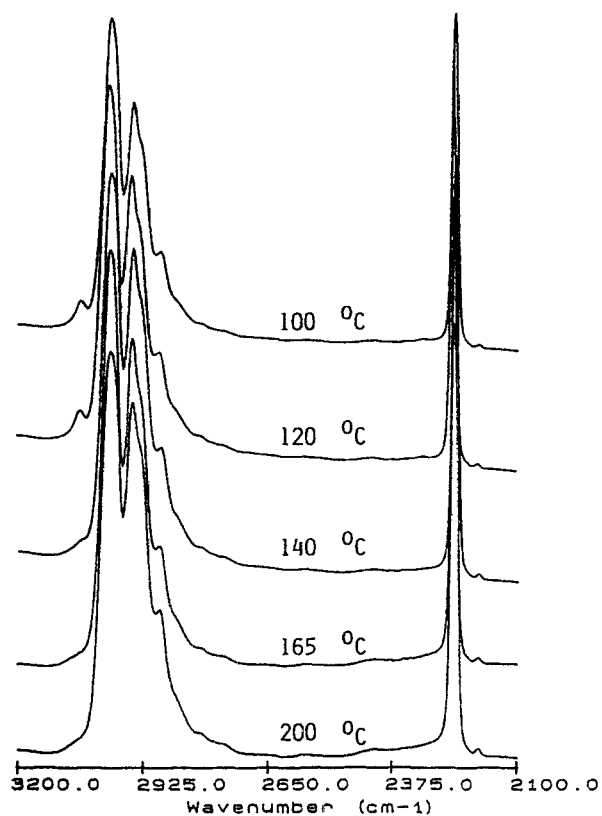
A quite similar effect of chain stiffening on the T_g was also recently reported for polyacrylic.[3] Upon formation of an anhydride type cyclization in the side chains, the T_g of polyacrylic increased from 111 to 148°C. The drying conditions seriously affected the glass-transition behavior of PMAN. The T_g of a sample kept at 55°C for 3 days was found to shift to 74.5°C. The pale yellow color observed for this sample together with an increase in the T_g value clearly indicated the formation of cyclic structures, even at these low temperatures. Spectrum b in Figure 1 shows the com-

Scheme 1 (I), (II), (III)

Scheme 1 The scheme of the intermolecular and crosslinking structure of PMAN after heating.

Figure 3 The FTIR spectra (2100–3200 cm^{-1}) of PMAN films heated to 100, 120, 140, 165, and 200°C.

plete DSC thermogram of this sample aged for 3 days at 55°C. The exothermic peak initially observed at 125°C in spectrum a in Figure 1 is absent in the thermogram given in spectrum b that was attributed to the formation of intramolecular cyclic structures. Following the relatively flat baseline after the endothermic relaxation peak, a fall in the baseline was observed prior to the decomposition peak. In previous work[4,5] the drying of the samples was conducted above 80°C, a temperature well above the T_g that we determined. This explains why they could not observe the enthalpic relaxation and consequently the high T_g value they found. The starting point of the fall in the baseline that corresponds to 100–120°C in Figure 1 (spectrum b) was most probably considered as the T_g of their samples.

Highly polar CN groups in the side chains impart a hydrophilic character to PMAN. Conse-

quently, absorption of humidity is expected to change the T_g of this polymer. To clarify this effect, a PMAN sample was kept at a relative humidity of 100% at 25°C for period sufficient to establish equilibrium. The T_g of such a sample was determined to be 45°C in the first run; reheating of this sample revealed a T_g value very close to that of pure anhydrous polymer (i.e., 67°C).

Table I Change in T_g Values and Loss in Normalized Absorbance Values of CN Bands When Heating PMAN Samples

Initial Heating Temp. (°C)	Loss in Normalized Absorbance in CN (%)	T_g
100	9.60	74
110	20.20	80
120	25.20	86
140	30.40	88
165	35.00	94
200	40.40	112
300	45.20	116
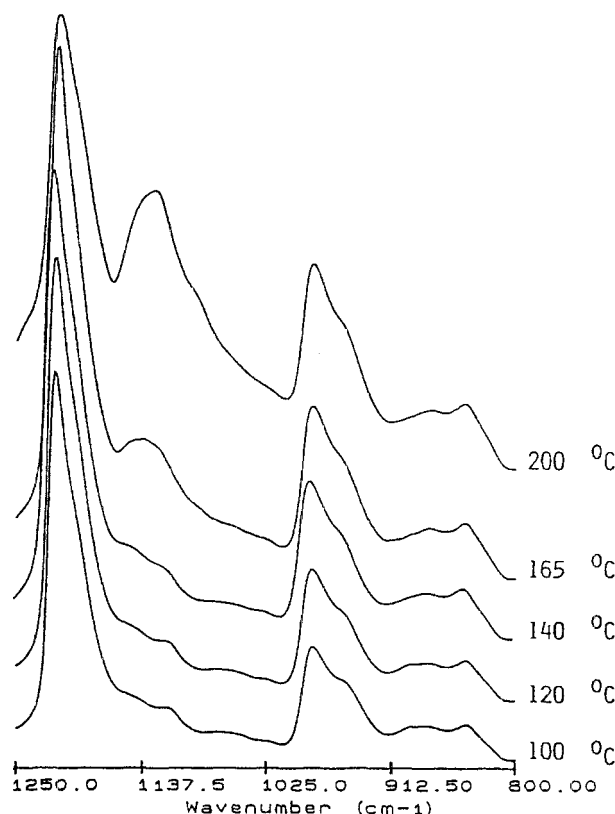
Figure 4 The FTIR spectra $(800–1250 \text{ cm}^{-1})$ of PMAN films heated to 100, 120, 140, 165, and 200°C.

If we return to the explanation of the shift in the T_g values listed in Table I, we can say that there were two different types of contributions to the observed increase in their values. In addition to the incorporation of hard segments of naphthydrine type structures in the main chain during the initial low temperature treatments of the samples, at relatively high temperatures the thermally induced crosslinking reactions also became significant. The T_g value of 112°C observed for PMAN heated to 200°C was for a completely insoluble polymer sample. However, the first four T_g values reported in Table I reflect only the effect of increasing cyclic segments on the T_g of PMAN.

In the following discussion we distinguish the additive effects of these two contributions on the observed T_g for samples heated above 120°C. It is very well established that long sequences of cyclic structures form on the backbone of PMAN chains during low or high temperature aging of the samples. These chains then can be considered as random copolymers with various lengths of ladder-like cyclic structures followed by linear chain segments. If the decrease in the intensity of the

nitrile band can be taken as a measure of the extent of cyclization, then from a plot of $1/T_g$ versus the percentage of decrease in CN absorbance, one can follow the effect of chain stiffening on the T_g. When the simple relation

$$1/T_g = w_1/T_{g1} + w_2/T_{g2}$$

is applied to the data given in Table I, extrapolation made by the least squares method to 0% (instead of weight fraction) yields a T_{g1} of 67°C for a PMAN sample with no cyclic structures. From the slope of the same line the inverse T_{g2} is found. The value found for T_{g2} (i.e., 1300°C) theoretically corresponds to the glass transition of a fully cyclisized, ladderlike methacrylonitrile polymer.

When the T_g of PMAN samples initially heated to the temperatures given in Table I were plotted against the percentage of decrease in the CN absorbance (Fig. 6), the curve obtained could be broken down into two linear sections. The initial linear part up to a 33% decrease in CN corresponded to data of soluble polymers. Samples heated beyond 150°C were insoluble, indicating the presence of crosslinked structures. The increase in the slope of the second linear section clearly showed the combined effects of cyclization and the crosslinking reaction on the observed T_g values of the PMAN samples in which the effect of crosslinking predominated.

The tacticity of PMAN was calculated from the peak areas in the NMR spectrum to complete the characterization of the samples. The results were 27% isotacticity, 21% syndiotacticity, and 52% heterotacticity. These were in good agreement with the results of Hirai et al.[9] whose polymerization conditions were almost identical to this study. The stereoregularity of the PMAN obtained in this study was therefore not a potential factor affecting the observed T_g.

The T_g value of a high molecular weight poly(acrylonitrile) (PAN) sample prepared in this laboratory was determined to be 100°C. This value was consistent with the literature values, which were between 80 and 104°C.[10,11] If the structural state of PAN is compared with PMAN, the only difference is the replacement of H by CH_3 on the main chain; its affect on the T_g is interpreted in two ways. Rigid, bulky, and inflexible substituents on carbon chains impedes the rotation about single bonds in the main chain and decreases the flexibility of the chain. This effect results in the raising of the T_g value of the polymer, for exam-
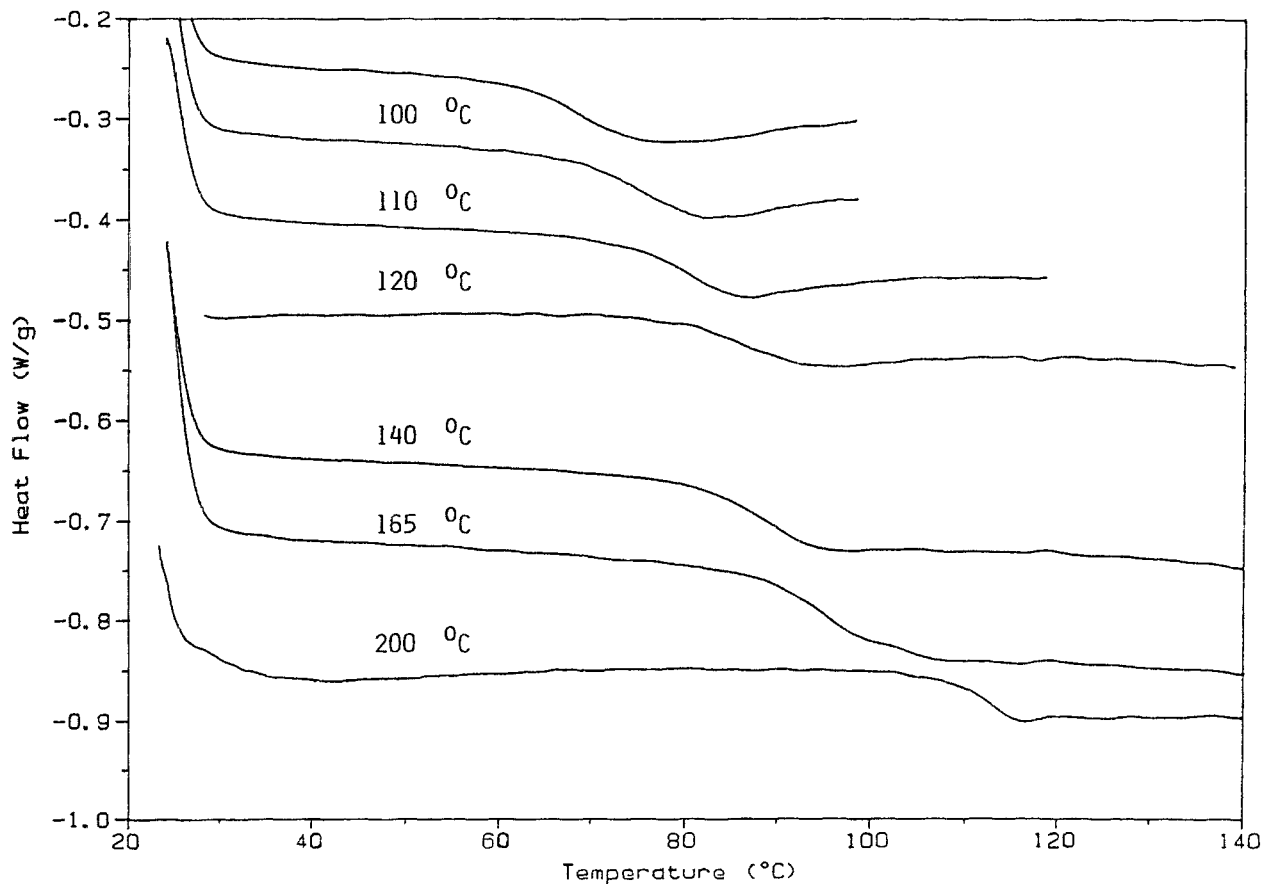
Figure 5   The DSC thermograms of PMAN samples initially heated to 100, 110, 120, 140, 165, and 200°C.

ple, poly(methyl acrylate) was $10°C^{12}$ and poly(methyl methacrylate) was $103°C.^{13}$ However, the size of the substituent may not be directly related
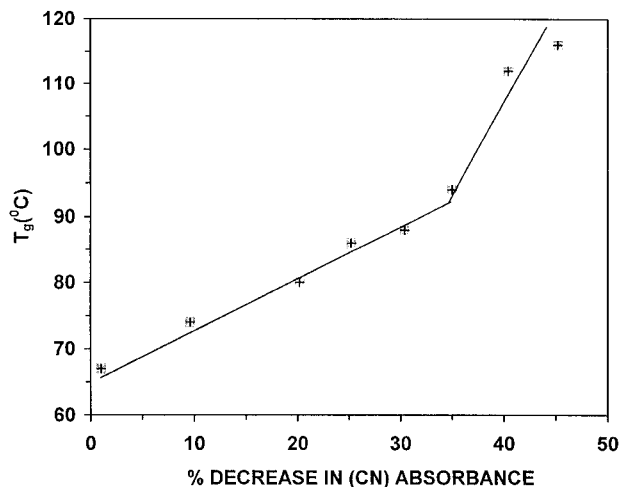

Figure 6   The change of the T_g values with the percentage of CN losses of PMAN.

to the T_g. Introducing flexible side groups like an alkyl chain causes an increase of intermolecular distances; consequently, free volume predominates and the T_g value is lowered; for example, polypropylene was $17°C^{14}$ and polyisobutene was $-73°C.^{15}$

Because of the high electron affinity of CN groups, the CH_3 groups in PMAN are weakly connected to the main chain; consequently, CH_3 most probably produces a flexible side group effect and a free volume increase predominates the other possible effect of CH_3, which may stiffen the polymer. This affirmed that the T_g value of PMAN could be expected to be lower than the T_g of PAN.

In an oxygen diffusion study of $PMAN^{16}$ two different diffusion activation energy values were obtained at about 60°C, which could be explained as different energy requirements above and below the T_g value. This T_g value was very close to 67°C.

To confirm the T_g value found in the DSC measurements, the surface hardness of the PMAN disks was determined as a function of temperature as a final check. Figure 7 shows the change
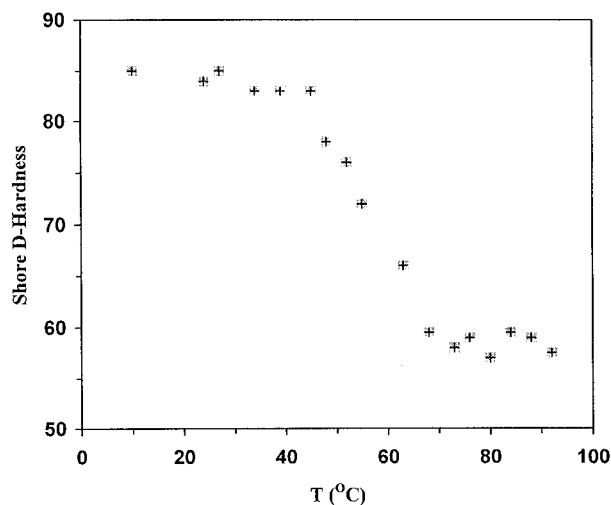
Figure 7 The change of the Shore D hardness of PMAN samples with the temperature.

in the surface hardness of PMAN with temperature as determined by a Shore D durometer. As can be seen, the hardness of PMAN showed a sudden drop between 60 and 70°C. The temperature corresponding to a sharp decrease in hardness ($\approx$65°C) was in very good accordance with the value determined from DSC measurements.

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