

Rapid Stabilization of Acrylic Fibers Using Ammonia: Effect on Structure and Morphology

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SYNOPSIS

Acrylic fibers were stabilized, for subsequent carbonization, in oxidizing, inert, ammonia and mixed environments and the stabilized fibers were characterized using several techniques to determine the extent of reactions as well as the morphological changes. Ammonia was shown to accelerate stabilization of acrylic precursors that did not contain other effective initiators, such as acid comonomers. Two effects of ammonia—nucleophilic attack in initiating polymerization of nitrile groups and, possibly, the rapid disruption of lateral order in precursor morphology—combine to produce a significant enhancement in the rate of this intermediate step in the formation of carbon fibers. © 1993 John Wiley & Sons, Inc.

1. INTRODUCTION

Oxidative stabilization is a crucial part of the carbon fiber formation process from acrylic precursors. With stabilization being the rate-controlling step in carbon fiber manufacture, development of faster oxidation techniques is of great interest. The prospects for using ammonia as an accelerator for the stabilization process were investigated.¹ Acrylic fibers were stabilized in oxidizing, inert, and ammonia environments. Fibers stabilized for different times in these environments were characterized using several techniques to determine the extent of reactions, and ammonia was shown to have a pronounced accelerating effect on stabilization. However, stabilization did not go to completion in the absence of oxygen. Precursors containing acidic comonomers did not show the same ammonia-induced accelerating effect as seen with precursors containing no such comonomers.

Results of studies that were conducted to further elucidate the role of ammonia in the stabilization of different acrylic precursors are reported here. The changes in morphology and chemical structure of

different acrylic precursor fibers were followed with the progress of stabilization. Possible mechanisms for the accelerating effect of ammonia have been proposed.

2. EXPERIMENTAL

2.1. Precursors

A major part of this study was conducted using a commercial acrylic fiber containing 2% methyl acrylate (MA) as comonomer. Two additional precursors, a homopolymer and a terpolymer with 6% MA and 1% itaconic acid (IA), were also investigated.

2.2. Batch Stabilization

Batch stabilization was carried out using a tubular oven mounted on rails, as reported earlier.¹ The batch-stabilization studies on the MA-containing precursor were conducted at different temperatures with N₂, air, or air/ammonia environments, and temperatures of 250°C and higher were used. The atmosphere that was referred to as air/NH₄OH in the previous report,¹ generated by bubbling air through ammonium hydroxide, is labeled here as air/NH₃—H₂O, to identify the actual stabilization en-

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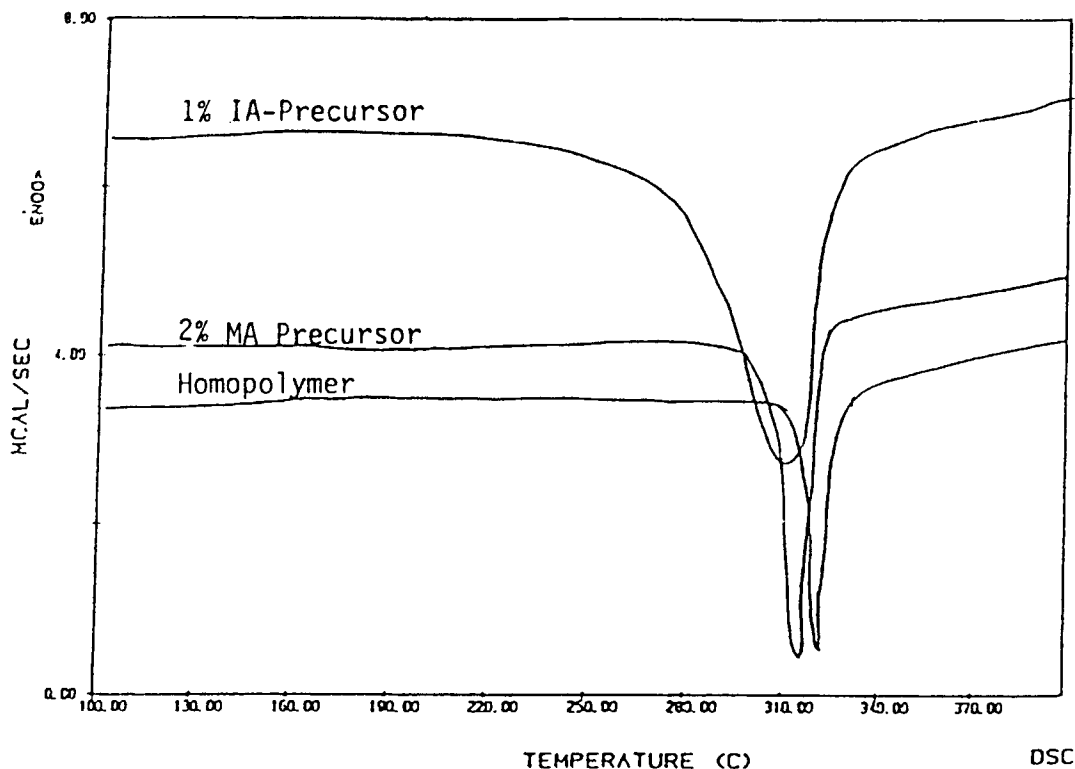


Figure 1 Normalized DSC scans for different precursors (in nitrogen, 20°C/min).

vironment rather than the source. Homopolymer precursor was stabilized at a maximum temperature of 250°C. The fibers containing itaconic acid comonomer were stabilized at 230°C, as the stabilization exotherm appeared in this case at a lower temperature compared to the homopolymer or the fiber with only MA as a comonomer. Calorimetric scans of the three precursors showing the exotherm obtained while heating at 20°C/min in nitrogen are shown in Figure 1.

2.3. Characterization of the Fibers

The following techniques were used to study the changes in structure and morphology of the acrylic fibers with the progress of stabilization.

2.3.1. Fourier Transform Infrared Spectroscopy

Infrared spectra of the samples were obtained using a Nicolet FTIR Model 60SX spectrometer. The microbeam, an auxiliary beam of the 60SX spectrometer that was obtained by employing a stepper motor-controlled beam condenser and a 35 μm pinhole, was used. Since the beam energy was concentrated, samples with low throughput could be examined by conventional transmittance measurements.

The fiber samples were mounted as a very thin layer on cardboard pieces with holes punched in the center (Fig. 2). As the initially obtained spectra were "noisy," especially for stabilized fibers in the regions corresponding to water, special care was taken in drying the samples. The samples were dried by keeping them in a vacuum oven at 105°C for 2 h. They were then transferred immediately into a desiccator, containing a CaCl_2 agent, for storage. The microbeam sample chamber was continuously purged with dry air at all times. The sample was transferred from the desiccator quickly and properly mounted in the microbeam path. The sample cham-

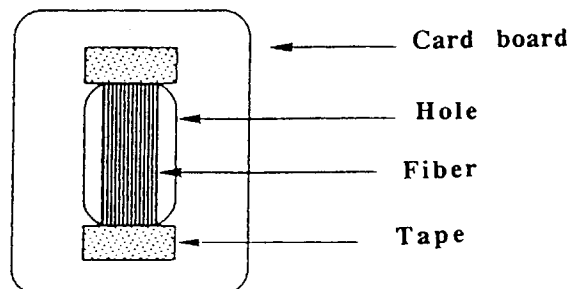


Figure 2 Sample holder and sample used in FTIR analysis.

ber was then purged again with dry air for 4 h before collecting the data. The data were collected, Fourier-processed, ratioed with the background, and plotted as absorbance spectra.

2.3.2. X-ray Diffraction

Both wide- and small-angle X-ray scattering measurements were made. The former gave information about the laterally ordered crystalline regions of the acrylic fibers, whereas the latter gave information about any larger-scale periodic structures. Both the measurements were carried out using a Rigaku Rotaflex Ru-200B Series X-ray unit and a Statton-type flat-plate camera with a vacuum chamber (Blake Industries) attached to it. Ni-filtered CuK_α (wavelength = 1.542 Å) radiation was used, at 45 kV and 100 mA. The samples were prepared by carefully placing the fibers as a parallel array on the sample holder (a frame with a central circular opening).

Wide-angle X-ray diffraction (WAXD) flat-plate photographs were obtained with a sample-to-film distance of 5 cm and an exposure time of 4 h. Small-angle X-ray scattering (SAXS) flat-plate photographs of the samples were obtained with a sample-to-film distance of 32.5 cm and an exposure time of 14 h.

2.3.3. Dissolution

Dissolution of the stabilized fibers was attempted in 50% concentrated sulfuric acid as the solvent. A small bundle of fiber was placed in a beaker containing about 25 mL of acid solution, warmed, and left overnight. Whether the fibers were observed to go into solution completely, slightly, or not at all was recorded.

2.3.4. Thermal Analysis

Calorimetric analysis of the fibers were carried out using a Perkin-Elmer DSC-4. The samples were purged with nitrogen during the scan and a heating rate of 20°C/min was used. For plasticized DSC, the samples were prepared with ~ 300% water as the plasticizer in special sealable capsules supplied by Perkin-Elmer (LVC 0319-0218). Heating and cooling rates of 10°C/min were employed.

2.3.5. Elemental Analysis

Some of the samples were analyzed for their elemental composition (C, H, N, and O). The measurements were carried out at Leco Corp. at St. Joseph, MI. For C, H, and N analyses, determinator CHN-800 was used with oxygen/helium as carrier

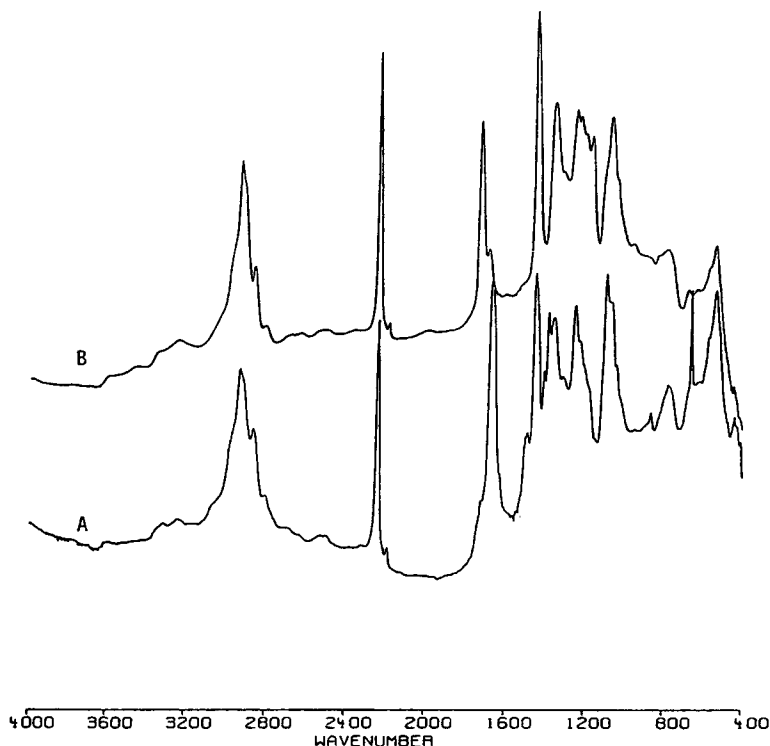


Figure 3 FTIR spectra of precursor fibers: (A) homopolymer and (B) copolymer containing 2% MA.

gas and acetanilide as the calibration standard. For oxygen analysis, determinator RO-478 was employed with nitrogen as the carrier gas and aminobenzoic acid as the calibration standard. About 2 mg of the sample was used in each case and it was dried at 105°C for 1 h before analysis.

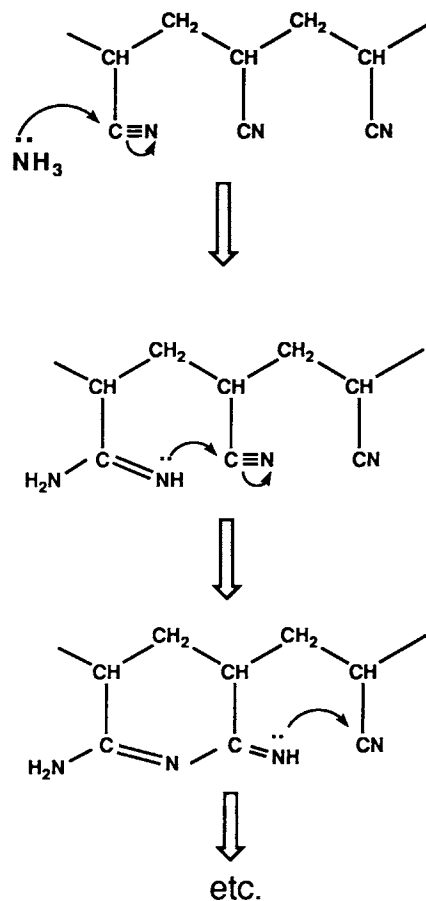
3. RESULTS AND DISCUSSION

3.1. Changes in Chemical Structure

The combination of chemical reactions taking place during stabilization and their relative importance remain unclear. Depending on the composition of the polymer, the stabilization environment, and the temperature profile, different reactions take place, rendering it difficult to determine the exact reaction paths and the final chemical structures. The present case is further complicated because of possible additional reaction mechanisms with ammonia in the stabilization environment. FTIR spectroscopy was used to evaluate the differences in the reaction paths between air and air/ammonia environments in stabilization. Figure 3 shows the FTIR spectra of the two precursors: the homopolymer and the methyl acrylate-containing copolymer. The band due to the ester C=O group in the copolymer at 1730 cm^{-1} is not seen in the homopolymer, but the homopolymer spectrum does show a carbonyl band at 1672 cm^{-1} . The latter peak has been assigned to the spin finish on the fiber.² With carbonyl being a strongly absorbing species in IR, even a low concentration of a compound containing this functionality on the fiber surface produces an intense peak. The 2% MA precursor fiber did not have any finish on it.

With both the homopolymer and the 2% MA copolymer, evidence for faster stabilization was seen with ammonia in the environment. Although a mechanism has been proposed for initiation with MA, it is still considered to be a poor initiator.³ DSC scans (Fig. 1) showed that the temperature for initiation of the stabilization exotherm was not much lower for the 2% MA precursor compared to that for the homopolymer. These data also show that IA is a more effective initiator than is MA, a fact first reported by Grassie and McGuchan.⁴

Even in the absence of an added initiator, defect structures that may be formed during polymerization or at a later stage can initiate cyclization. A defect that has been shown to exist is the ketonitrile-type species, which can initiate the reaction by enolization.⁵ Self-initiation is another possibility at these



Scheme 1 Proposed mechanism for initiation of cyclization by ammonia.

temperatures, although there is little support in the literature for such a mechanism.⁶ For example, Cook showed, from well-defined model compound studies, that pure PAN would not cyclize and that self-initiation apparently did not take place upon heating.⁷

The ionic mechanism can play a major role in the initiation of cyclization. KCN and NaCN have been found to be strong initiators of the PAN nitrile cyclization reaction.⁶ One such scheme has been previously proposed and later confirmed by FTIR studies by Coleman and Sivy.⁸ The presence of ammonia in the environment provides nucleophilic NH_3 to initiate the cyclization reaction via the activated pair of unshared electrons in the range of stabilization temperatures (Scheme 1).

The accelerating influence of ammonia on stabilization can be seen spectrophotometrically from the relative rates of disappearance of nitrile functionality at 2240 cm^{-1} , and the formation of the new band at 1580–1600 cm^{-1} , assigned to C=N and C=C sequences in the cyclic structure (Figs. 4 and

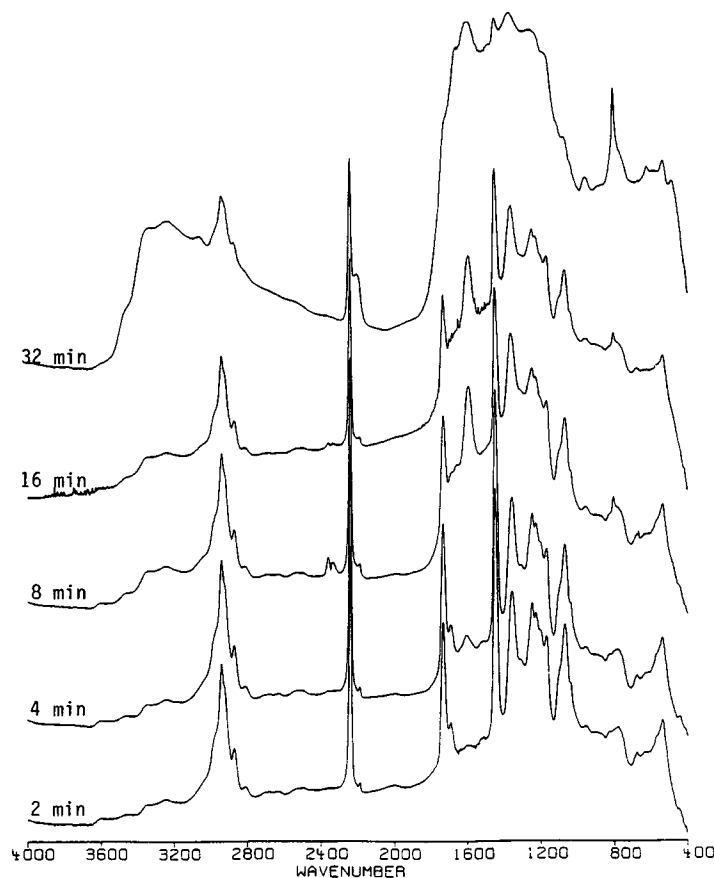


Figure 4 FTIR spectra of 2% MA precursor stabilized in air at 260°C.

5). Since cyclization can be initiated at many more sites in the presence of NH_3 nucleophile, the structure reaches the "stabilized state" much faster than in the absence of ammonia. The formation of amide-type species in the structure is confirmed by higher absorption in the corresponding range (3250 and 3400 cm^{-1} , assigned to NH and NH_2 , respectively) with samples stabilized in the presence of ammonia, especially in the early stages.

Similar effects were also seen with the homopolymer precursor fiber. Figures 6 and 7 compare the spectra of the homopolymer fiber stabilized in air and air/ammonia, respectively. The new peak around 1600 cm^{-1} , due to formation of conjugated sequences, appears in a shorter stabilization time in the presence of ammonia when compared to that in air alone. The increase in intensity of the 1600 cm^{-1} peak is accompanied by reduction in intensities at the 2240 cm^{-1} (nitrile) and 1450 cm^{-1} (CH_2) regions and also an increase in absorption in the 3230–3400 cm^{-1} (NH and NH_2) region. All these changes seen in the FTIR spectra happened much faster during stabilization of the homopolymer in the presence of

ammonia. These faster kinetics are the result of nucleophilic action of ammonia to initiate nitrile polymerization as suggested in Scheme 1.

In the case of fibers containing MA, nucleophilic attack can also occur at the comonomer sites (Scheme 2), generating new functionalities and leading to enhanced cyclization and other reactions. As seen from the FTIR spectra, the band at 1730 cm^{-1} (due to C=O from the acrylate group) disappears rapidly (in less than 4 min) in the presence of NH_3 . The absorption intensity of this band is reasonably high even after 16 min of stabilization in air alone (Fig. 8).

Another possible, but less likely, mechanism is radical initiation. No attempt was made in this study to experimentally verify the formation or presence of radicals. However, earlier researchers have reported free-radical-type reactions during stabilization, and one possible way, suggested by Grassie,⁶ is by radical initiation from an acrylamide intermediate.

The FTIR spectra indicate that cyclization reactions occur much faster in the presence of am-

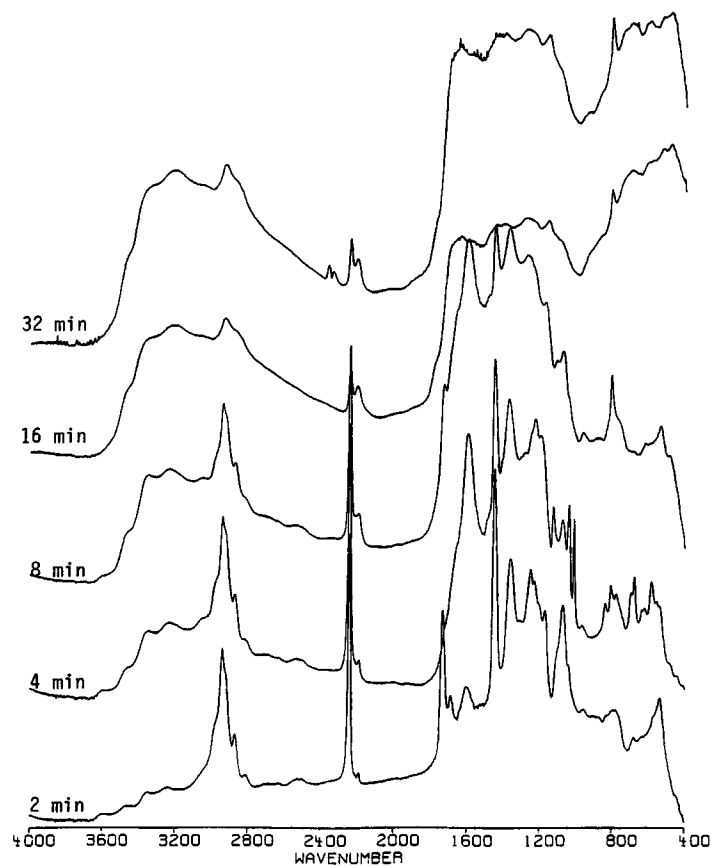


Figure 5 FTIR spectra of 2% MA precursor stabilized in air/ NH_3 / H_2O at 260°C.

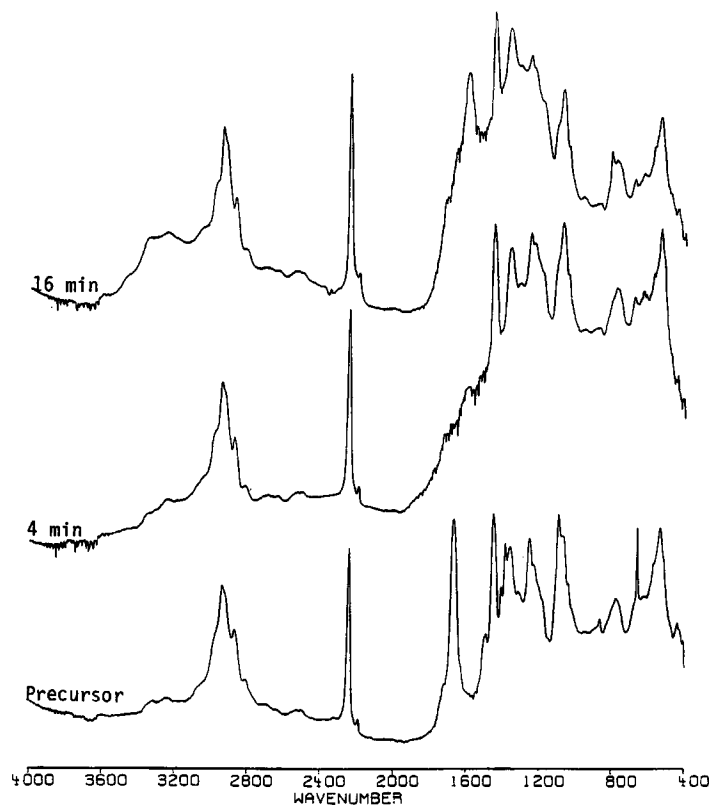


Figure 6 FTIR spectra of homopolymer PAN stabilized in air at 250°C.

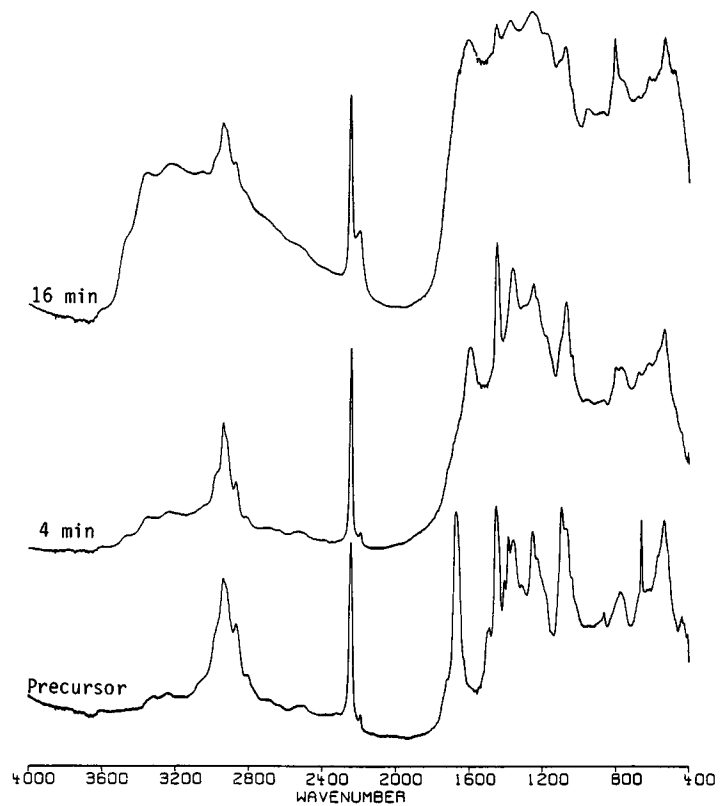


Figure 7 FTIR spectra of homopolymer PAN stabilized in air/ammonia at 250°C.

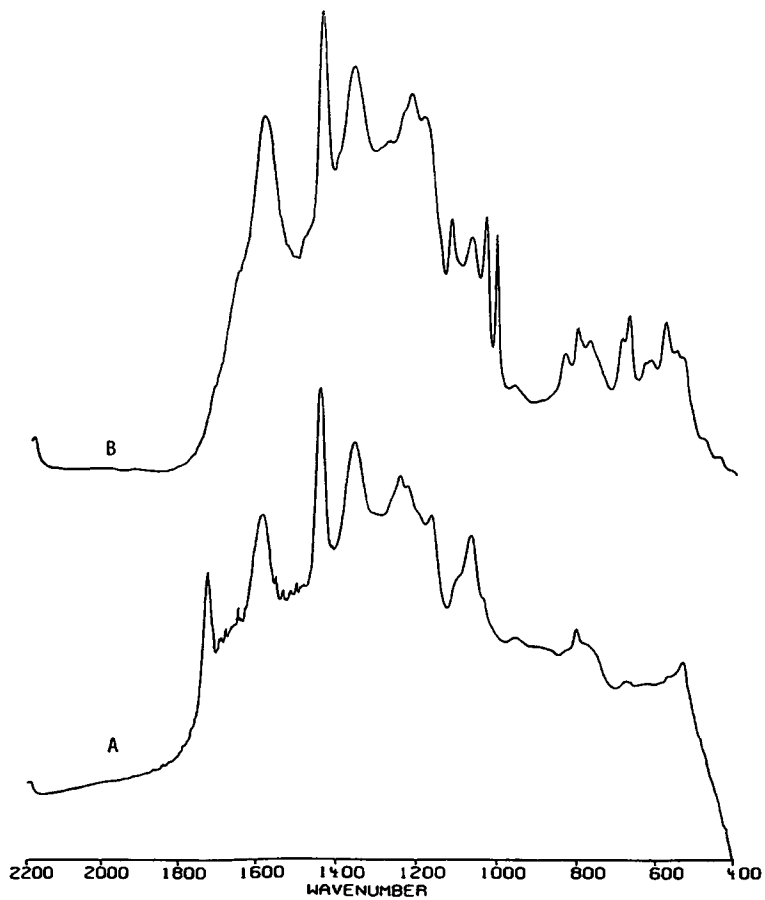


Figure 8 FTIR spectra of 2% MA precursor stabilized at 260°C (A) in air for 16 min. and (B) in air/NH₃/H₂O for 4 min.

Table I Oxygen and Nitrogen Contents (w/w) Obtained from Elemental Analysis of Different Samples (2% MA Precursor)

Sample	% Nitrogen	% Oxygen
Precursor	24.7	2.2
16 min in air	24.8	3.2
64 min in air	21.7	11.5
256 min in air	20.1	20.6
16 min in air/NH ₃ /H ₂ O	23.9	7.8
64 min in air/NH ₃ /H ₂ O	23.1	10.5
256 min in air/NH ₃ /H ₂ O	24.4	9.8

monia, but do not reveal much regarding the possible differences in the final chemical structure of the stabilized fiber. Elemental analysis (Table I) showed that the oxygen content of the ammonia-stabilized samples did not increase beyond 10% (w/w) with prolonged heating, whereas the samples stabilized in air alone achieved reacted oxygen contents higher than 20%. Reasons for this difference in limiting oxygen contents are not clear. The amount of nitrogen was higher by 3–4% in the case of fibers stabilized in the presence of ammonia. With ammonia in the environment, the number of sites where initiation occurs will be higher, causing further increase in nitrogen content. As can be seen from Scheme 2, the reactions of NH₃ with the existing MA functionality is also accompanied by the elimination of oxygen from the comonomer and, in its place, addition of an amine group. However, this effect alone cannot account for the full extent to which the apparent oxygen concentration is lowered in the ammonia-stabilized fiber compared to the fiber stabilized only in air.

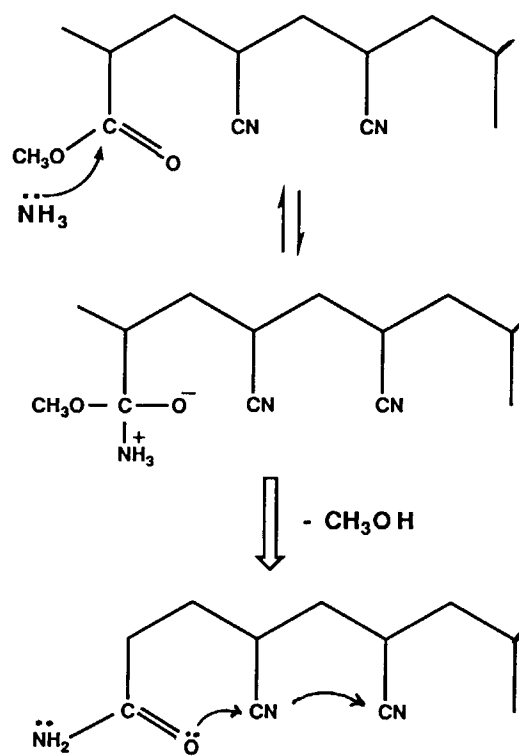
As an example, two possible structures, one by stabilization in air and another by stabilization in the presence of ammonia, were assumed and the oxygen and nitrogen contents in them were calculated. The proposed structures are based on earlier published structures.⁹ Nitrogen and oxygen contents for the air-stabilized fibers from a typical structure (Scheme 3) are 21 and 16%, respectively. For the ammonia-stabilized fiber, with an otherwise comparable structure (Scheme 4), the elemental compositions are 27% N and 11% O. These values are comparable to experimentally observed values. It should be acknowledged, however, that these speculated structures are simplified ones without any intermolecular cross-linking and thus the calculated elemental concentrations may differ from the experimental values. They are presented here only to

exemplify the possible structures that can account for the lower apparent oxygen content in ammonia-assisted stabilization.

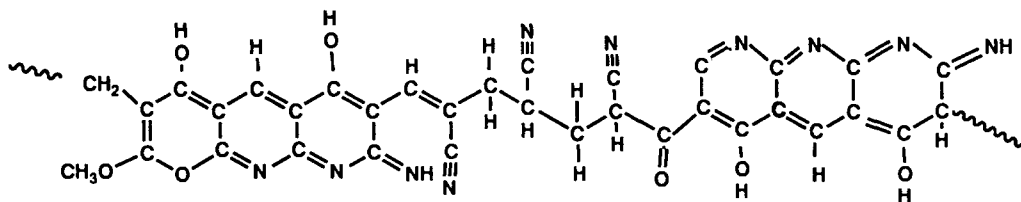
When fibers stabilized in different environments were studied for dissolution in 50% sulfuric acid, samples stabilized in nitrogen dissolved completely, samples stabilized in air or in air/ammonia did not dissolve, and samples stabilized in anhydrous ammonia showed only partial dissolution (Table II). Apparently, some intermolecular cross-linking occurs during stabilization in anhydrous ammonia, but not as much as in the presence of air. Since many more growing species exist in the presence of ammonia, the statistical probability of intermolecular cyclization increases. If free-radical formation occurs during cyclization reactions, the possibility of cross-linking increases, leading to the formation of undissolvable structures. One possibility of formation of free radicals is from the intermediate acrylamide, via a mechanism proposed by Grassie and McGuchan.⁴

3.2. Changes in Morphology

As the linear structure is chemically transformed into a planar structure via ring formation and aro-



Scheme 2 Proposed action of ammonia on MA and initiation of cyclization.



Scheme 3 Proposed structure of air-stabilized acrylic fiber. Adapted from Clarke and Bailey.⁹

matization during the process of stabilization, the morphology of the fiber also changes. Morphological changes occurring during stabilization in different environments were followed by X-ray diffraction and plasticized melting and recrystallization studies.

Figure 9 shows the WAXD photographs of the 2% MA precursor and samples stabilized in different environments for 16 min. As reported by earlier workers, the precursor shows the diffraction arcs due to (100) and (200) reflections corresponding to d -spacings of 5.2 Å ($2\theta = 17^\circ$) and 3 Å ($2\theta = 29.5^\circ$).² Lack of all but equatorial arcs in these cases indicates only two-dimensional order. Previous studies using X-ray diffraction have shown that the intensity of the main equatorial reflection at $2\theta = 17^\circ$ shows an initial increase followed by a continuous decrease with prolonged stabilization.¹⁰

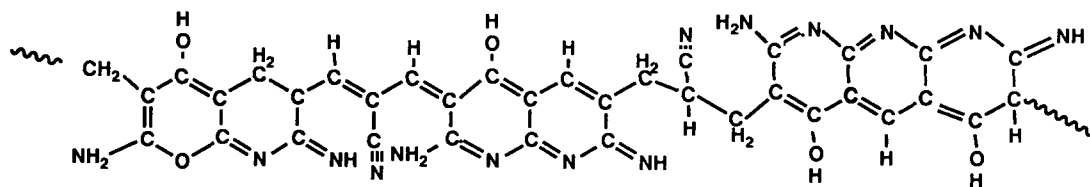
As stabilization progresses, both (100) and (200) diffraction arcs disappear, with the simultaneous appearance of a diffraction halo due to amorphous scattering, often called the (002) arc of carbon,² and the disappearance of the exotherm in thermal analysis. It is evident from the X-ray analyses that crystalline structures in the precursor disappear after about 16 min of stabilization in the presence of ammonia. On the other hand, the crystalline reflections disappear only after thermal treatment for about 1 h in the case without ammonia in the environment.

Morphological consequences of stabilization were also examined through small-angle X-ray scattering studies. The meridional scattering, showing the existence of a long period, appears in the initial stages of stabilization of acrylic precursors and then dis-

appears with further progression of the stabilization reactions. Figure 10 is a typical SAXS pattern of a partially stabilized fiber showing the meridional scattering. This has been attributed by earlier researchers to preferential occurrence of the reactions initially in the laterally disordered regions of the fibers, causing the electron density of these regions to be different from the laterally ordered, as yet unstabilized, regions.¹¹ The results from SAXS studies are summarized in Table III. SAXS of samples stabilized in the presence of ammonia for just 4 min showed the characteristic meridional scattering, whereas samples stabilized in air or nitrogen did not show such a scattering even after 16 min. Again, the evidence supports faster stabilization in the presence of ammonia.

X-ray diffraction photographs of the homopolymer fiber stabilized in air and in air/ NH_3 - H_2O are compared in Figure 11. The WAXD photographs of precursor and samples stabilized for 64 min in air and air/ NH_3 - H_2O are shown. The disruption of crystals is once again seen to occur much faster in the presence of ammonia, consistent with the earlier observations for the 2% MA copolymer.

Figure 12 shows the WAXD photographs of an acrylic precursor fiber containing 6% MA/1% IA, stabilized in air and air/ NH_3 - H_2O for 32 min. The accelerating effect of ammonia in disrupting crystals is also seen with this precursor, in spite of the fact that ammonia did not show any accelerating effect on the solid-state stabilization reactions. The plasticized DSC results (Table IV) also confirm the observations from the X-ray diffraction studies that



Scheme 4 Proposed structure of the air/ammonia-stabilized acrylic fiber derived from the Clarke and Bailey model.⁹

Table II Results from Dissolution Studies in 50% Sulfuric Acid of 2% MA Precursor Stabilized in Different Environments at 260°C

Stabilization Time (min)	Stabilization Environment			
	Air	Nitrogen	Ammonia	Air/NH ₃ /H ₂ O
4	Diss.	Diss.	Diss.	Sl. Diss.
16	Sl. Diss.	Diss.	Sl. Diss.	No
32	No	Diss.	Sl. Diss.	No
64	No	Diss.	Sl. Diss.	No

Diss., dissolved. Sl., slightly.

the crystals disappear much faster with stabilization in the presence of ammonia. Ammonia showed the same effect on a precursor containing the acid comonomer as on the homopolymer and the 2% MA precursor. However, such rapid disruption of crystalline order did not accelerate the chemical stabi-

lization process in the case of precursors containing acid comonomers.

4. CONCLUSIONS

Ammonia, acting as a nucleophile under stabilization conditions, initiates nitrile polymerization. As

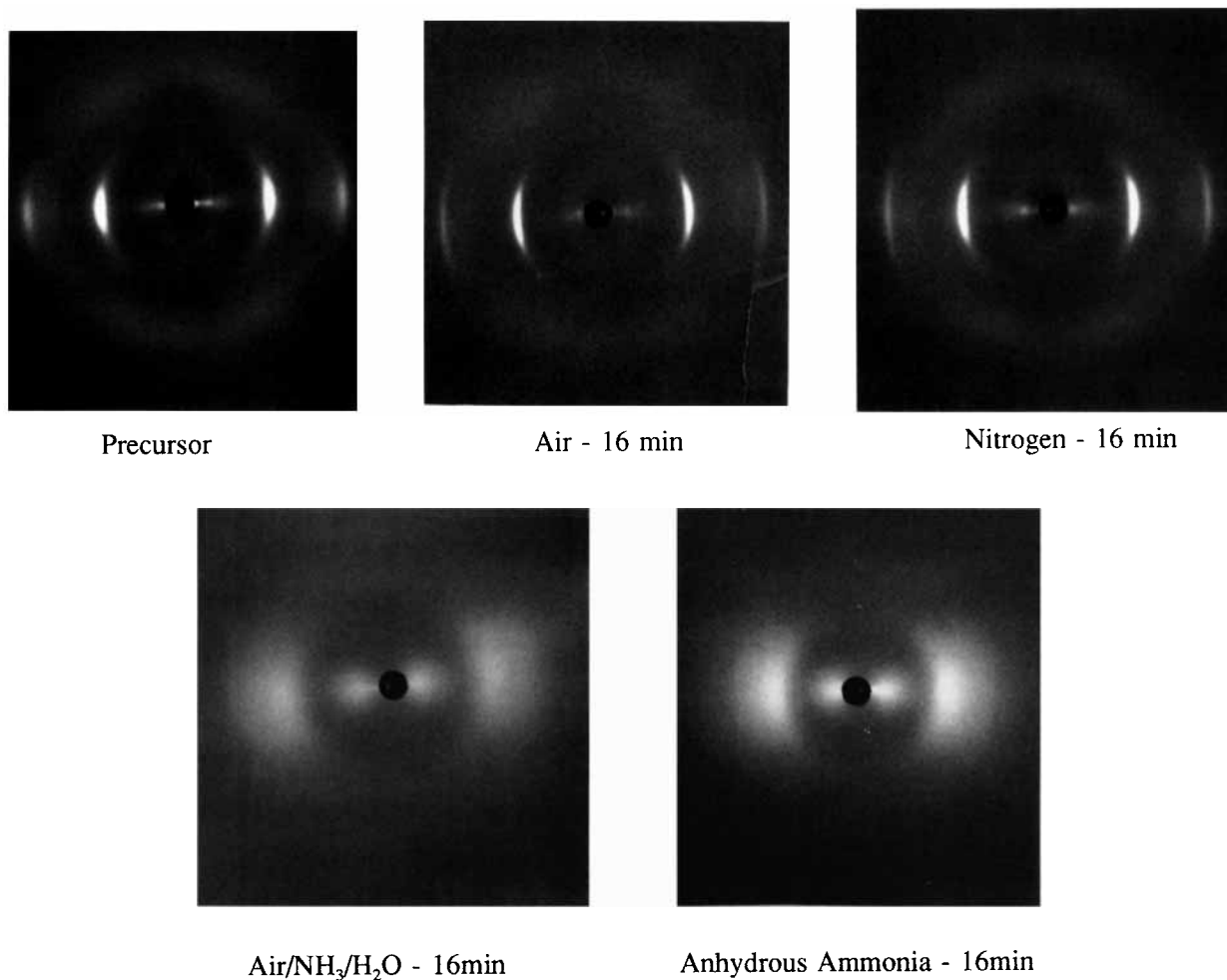


Figure 9 WAXD photographs of 2% MA precursor fibers stabilized in different environments.



Figure 10 SAXS photograph of a partially stabilized 2% MA precursor fiber showing the two-point pattern along the meridian.

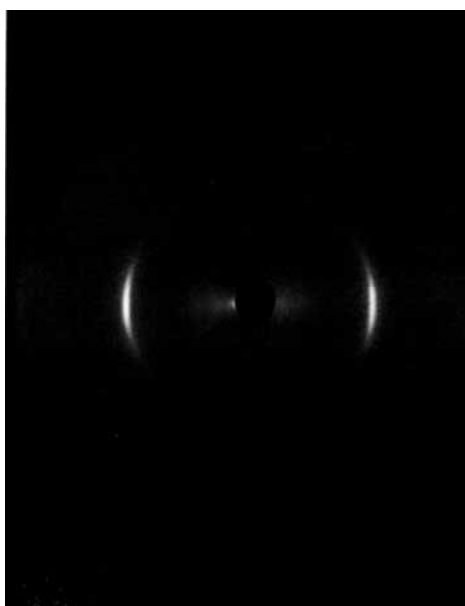
the initiation is faster and can occur at multiple sites, stabilization reaction sequences proceed much faster, intra- as well as intermolecularly. In the case of fibers containing MA and no acidic comonomer, nitrile polymerization can also be initiated by secondary functional groups produced by reaction of ammonia at comonomer sites, leading to further acceleration. With ammonia in the stabilization en-

Table III Results from SAXS Studies of 2% MA Precursor Stabilized in Different Environments at 260°C Indicating the Presence or Absence of the Two-point Pattern

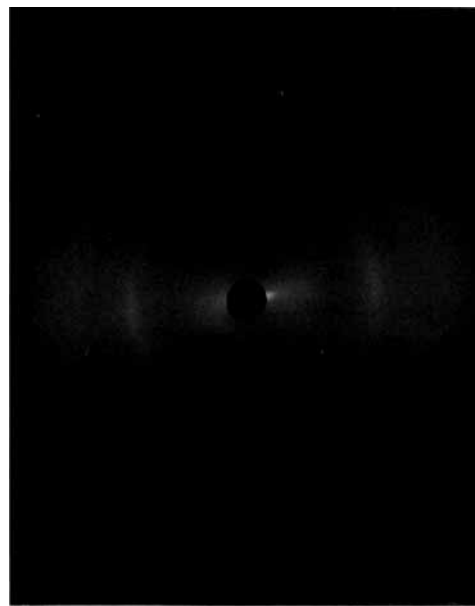
Stabilization Time (min)	Stabilization Environment		
	Air	Air/NH ₃ /H ₂ O	Ammonia
4	No	Yes	Yes
16	No	Yes	No
32	Yes	No	No
64	Yes	No	No

Yes, pattern seen. No, pattern not seen.

vironment, faster disappearance of C=O groups (from MA comonomer) was observed via FTIR spectroscopy. For the 2% MA precursor, air/ammonia-stabilized samples approached limiting oxygen content lower than for fibers stabilized in air alone. The reaction of ammonia with this acrylic copolymer, to initiate cyclization and produce new functional groups, left amine-imine and amide-type structures at the reaction sites. The presence of such species in the structure led to increased nitrogen content in the stabilized structure.



A



B

Figure 11 WAXD photographs of homopolymer PAN fiber stabilized (A) in air for 64 min. and (B) in air/NH₃/H₂O for 64 min.

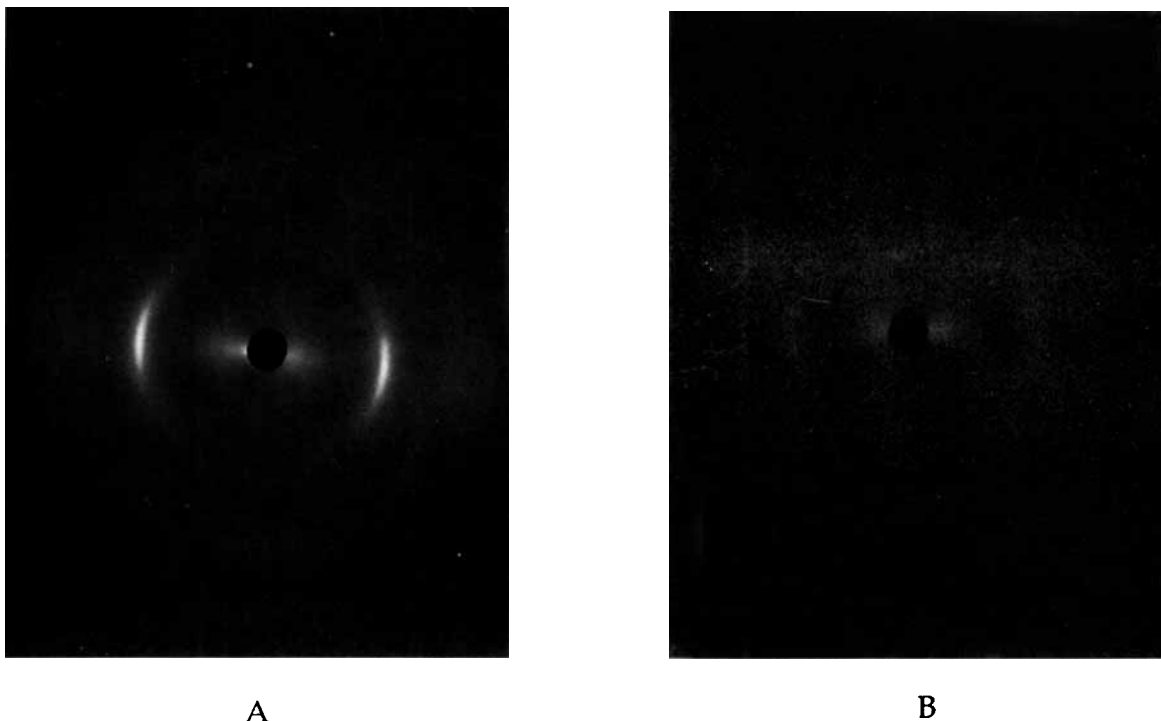


Figure 12 WAXD photographs of 6% MA/1% IA precursor stabilized (A) in air for 32 min and (B) in air/NH₃/H₂O for 32 min.

Lateral order disappeared much faster during stabilization in the presence of ammonia. The rapid decrease in order with ammonia in the environment occurred both in the presence and absence of oxygen and with all the precursors used in this study. Ammonia, because of its affinity for the highly polar nitrile groups, can form a complex with the latter.

No accelerating effect of ammonia was observed with precursors containing acid comonomers. Rapid initiation of stabilization by the nucleophilic acid groups appeared to be more than sufficient to overwhelm any influence of ammonia in these precursors. However, plasticized DSC and X-ray diffraction studies showed that the lateral order disappeared much faster in the presence of ammonia even in the fibers with an acid comonomer. The mechanism and the role of such disruption of crystalline order, if any, in the solid-state stabilization process remain unclear.

Ammonia, a known byproduct of the stabilization reactions, has an accelerating effect on the stabilization kinetics of nonacidic acrylic precursors when intentionally introduced into the stabilization environment. It is clear that the nucleophilic action of ammonia's unshared pair of electrons in initiating

the intra- and interchain polymerization of nitrile groups and the conversion of any poorly initiating acrylate functionality in the precursor to a fast initiating acrylamide functionality are the predominant sources of this acceleration.

Table IV Enthalpic Changes (cal/g) in Plasticized Melting and Recrystallization during Stabilization of 6% MA/1% IA Precursor

Stabilization Time (min) ^a	Stabilization Environment			
	Air		Air/NH ₃ /H ₂ O	
	Hm	Hc	Hm	Hc
8	8.4	4.1	7.1	4.6
16	5.4	2.9	2.8	1.7
32	2.6	0.7	n.d.	n.d.
64	n.d.	n.d.	n.d.	n.d.

Hm, heat of melting; Hc, heat of crystallization; n.d., not detected.

^a Stabilized at 230°C.

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