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Mechanism and Kinetics of Stabilization Reactions of Polyacrylonitrile and Related Copolymers IV. Effects of Atmosphere on Isothermal DSC Thermograms and FT-IR Spectral Changes during Stabilization Reaction of Acrylonitrile/Methacrylic Acid Copolymer

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ABSTRACT: Structure formation during the stabilization reactions of the acrylonitrile/methacrylic acid (AN/MAA) copolymer under air, O_2 and N_2 was studied by an organized combination of isothermal DSC thermograms and FT-IR spectra. Under the oxidative atmosphere evolved heat was very large and the conjugated cyclic structure was formed as a stable structure. Particularly in pure O_2 gas the stabilization reaction attained to the most advanced state. Under N_2 the evolved heat was smallest and the resulted structure was thought to be a non-conjugated cyclic imine–enamine tautomerism structure.

KEY WORDS Polyacrylonitrile / Acrylonitrile–Methacrylic Acid Copolymer / Carbon Fiber / Stabilization / Differential Scanning Calorimetry / Fourier Transform Infrared Spectroscopy /

Acrylic fibers made of polyacrylonitrile (PAN) containing acidic comonomers such as methacrylic acid (MAA), itaconic acid or acrylic acid are the most commonly used precursors for carbon fibers because of excellent performances of PAN based carbon fibers.[1]

In the production processes of PAN based carbon fibers, stabilization process is most important, because the physical properties of carbon fibers are affected significantly by the conditions of stabilization process. A lot of studies have been reported concerning the stabilization of PAN since 1950.[2,3] According to these papers, acrylic fibers are converted to infusible and nonflammable fibers by heating at 200—300°C for about 1 h in an oxidative atmosphere during stabilization process. Only such stabilized fibers can be heated to carbonization temperature (1000—2000°C).[4]

In these several years, through an organized combination of isothermal DSC exothermic thermograms and FT-IR spectra we have studied the mechanism of stabilization reaction of PAN homopolymer, acrylonitrile (AN)/MAA and AN/acrylamide (AAM) copolymers obtained by aqueous suspension polymerization with a redox initiator,[3,5,6] and the following were indicated: (1) In isothermal DSC exothermic thermograms, induction periods are observed at early time region. During induction, initiation reaction of cyclization occurs. (2) MAA comonomer accelerates the stabilization to high degree where dehydrogenation is preferably accelerated. (3) AAM comonomer accelerates the stabilization only a little more than that of the PAN homopolymer.

In this way, we studied the roles of comonomers in stabilization and the rate of stabilization. It is said also that the precursor fibers are stabilized under an oxidative atmosphere, otherwise the resultant carbon fibers show only inferior performances.

To get information about the effects of atmosphere on stabilization, isothermal DSC thermograms and IR spectral changes were measured under air, N_2, and O_2 gas flows.

EXPERIMENTAL

Materials

The AN copolymer which contains about 1 mol% MAA was obtained by aqueous suspension polymerization with redox initiator. The weight averaged molecular weight was about 2×10^5. Triad tacticity was $mm = 0.27$, $mr = 0.50$, and $rr = 0.23$ when evaluated by ^{13}C NMR. The polymer powders filtered through a 400 mesh screen were used for DSC and FT-IR measurements.

DSC Measurements

Isothermal DSC measurements were carried as described previously.[3,5,6] SEIKO DSC 220C, a kind of heat-flux DSC, was used. To obtain an isothermal thermogram, sample pans were put quickly into the furnace maintained at predetermined temperatures. When the measurements were done under N_2 or O_2 gas flow, the DSC cell was covered with a specially designed box made of poly(methyl methacrylate) sheet (Acrylite) to prevent air leakage. The sample pan was placed for about 1 h in the box under N_2 or O_2 so as to purge air, and then put into the DSC furnace and measurement of isothermal DSC thermogram was started.

FT-IR Measurements

FT-IR measurements were carried out as described previously.[3,5,6] IR spectra of the samples treated thermally in DSC cell for predetermined periods were measured to get information about structural changes during stabilization. The samples heat-treated in DSC cell under N_2 or O_2 gas were taken out from the DSC cell into the above mentioned specially designed box and held at room temperature under N_2 gas to prevent the additional reaction under air flow.

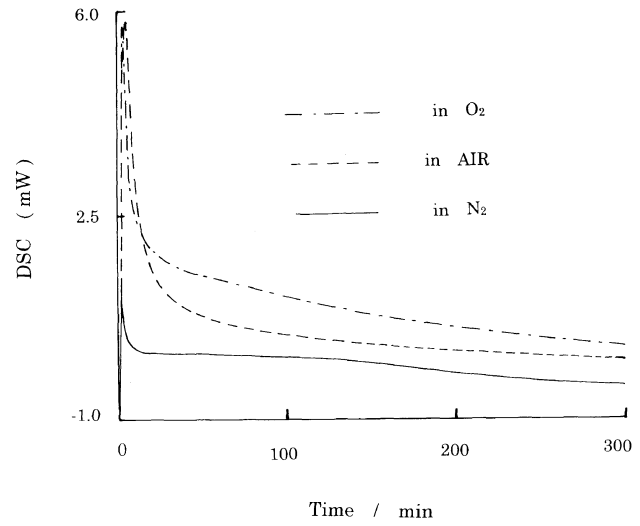

Figure 1. Isothermal DSC thermograms of the AN/MAA copolymer measured under air, O_2 and N_2 at 230°C. Sample weight, 4 mg.

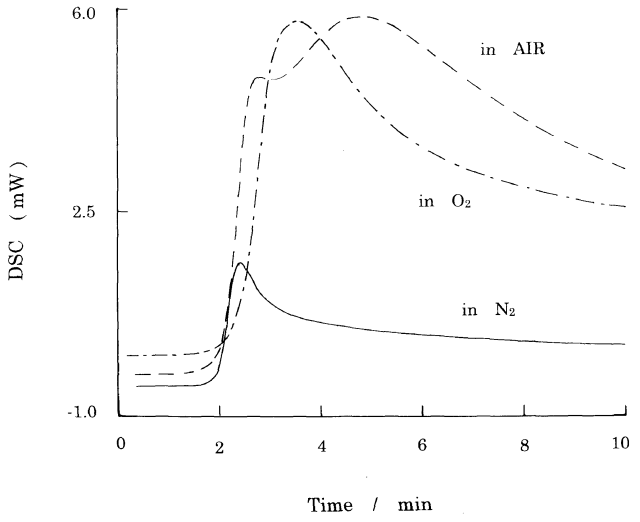

Figure 2. Early time region of isothermal DSC thermograms of the AN/MAA copolymer measured under air, O_2, and N_2 at 230°C.

RESULTS AND DISCUSSION

Effects of Atmosphere on Isothermal DSC Thermograms

Figure 1 shows the isothermal DSC thermograms of the AN/MAA copolymer measured at 230°C under air, O_2 and N_2 gas respectively. In Figure 2 are shown the same thermograms enlarged in the early time region. The isothermal DSC thermogram measured under N_2 shows the smallest exothermic peak at the earliest time among the three. The thermogram under N_2 shows a plateau extending from 10 to 130 min. After the plateau the heat flow continues to decrease very slowly. The thermogram under air flow shows a larger and broader exothermic peak at a later time than that under N_2 flow. In this case the exothermic peak is a little broader than the other two. The thermogram under O_2 shows the peak as large as that under air flow at an earlier time than that under air flow. After the exothermic peak, the heat flow is larger than the other two as seen in Figure 1.

In Figure 2, all thermograms show induction periods, which correspond to the initial flat parts at *ca.* 2 min.

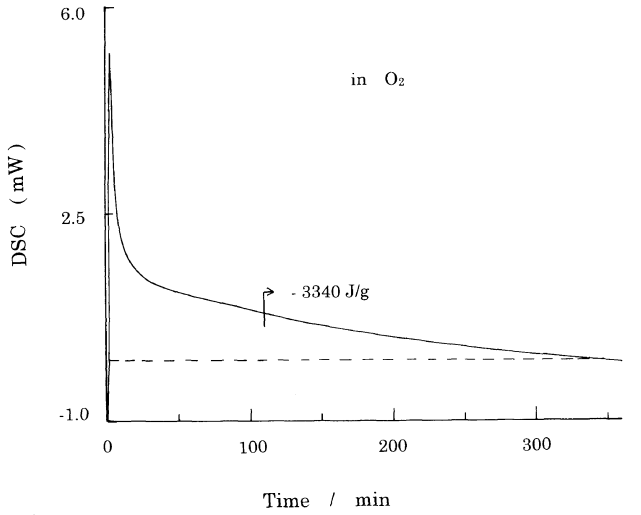

Figure 3. The evolved energy during stabilization under O_2 at 230°C.

The exothermic peaks of the thermograms obtained under O_2 and N_2 flow are apparently single. The exothermic peak under air flow is composed of a shoulder and main peak, this seems to suggest that in air the both reactions in N_2 and in O_2 occur simultaneously.

Figure 3 shows the isothermal DSC thermogram with total energy evolved during stabilization under O_2 gas. The base line was set as the DSC output level equal to that of the induction period. The evolved total energy is the smallest when the thermogram is obtained under N_2 gas, 1530 J g^{-1}. The one under O_2 gas is largest, 3340 J g^{-1}, and under air 2520 J g^{-1}. This means that stabilization under O_2 gas is highest, while that under N_2 gas lowest.

For stabilization under various gases the following statements may be presented. Under N_2 gas, the main reaction which evolves small amount of heat starts early and completes rapidly, but after that, a small exothermic reaction continues for about 200 min. The formation of stabilized structure is smallest in N_2. Under O_2 gas, several stabilization reactions seem to occur simultaneously a little later than that under N_2 gas. After the peak, the decrease of heat evolution is slower than the other two cases. So, in this case, the formation of the stabilized structure proceeds slowly but attains much greater degree than the other two cases. Under air, the exothermic peak consists of a shoulder and a main peak, so the reactions under N_2 and O_2 gas apparently occur simultaneously, but the decrease of the heat evolution after peak is faster than under O_2 gas flow. But, the second peak under air is observed later than the exothermic peak under O_2. Perhaps , this is because that O_2 in air is very little.

IR Spectral Changes during Stabilization

To clarify the difference of the structural change during stabilization under three atmospheres, the FT-IR spectra were measured along the exothermic DSC thermograms. Figure 4 shows the sampling points on the DSC thermogram, as an example, under air, *i.e.*, the samples were stabilized in DSC cell for the several predetermined periods from 1.6 to 600 min, and followed by FT-IR measurements. The assignments of the

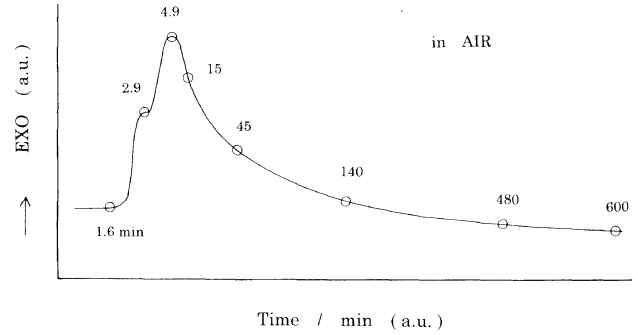

Figure 4. Sampling point for FT-IR measurement. Samples are stabilized in DSC cell to the pre-determined time point for FT-IR measurement.

Table I. Principal IR bands in solid and degraded PAN, AN/MAA, and AN/AAM copolymer structures

Functional groups	Wavenumber/cm^{-1}
NH_2	3390, 3356
NH	3230
CH_2	2945, 2920
CH	2895
C≡N (saturated)	2240
C=O (unreacted MAA)	1740
C=O (reacted MAA)	1700
C=O (amide)	1680
N–H (amide)	1620
C=N, C=C mixed	1620[a]
C=N, C=C, N–H mixed	1580[a]
CH_2	1450
CH, NH	1380
C–C, C–N mixed	1250
C=C–H	810

[a] These bands are often not resolved and appear at $1600 \pm 10\,cm^{-1}$.

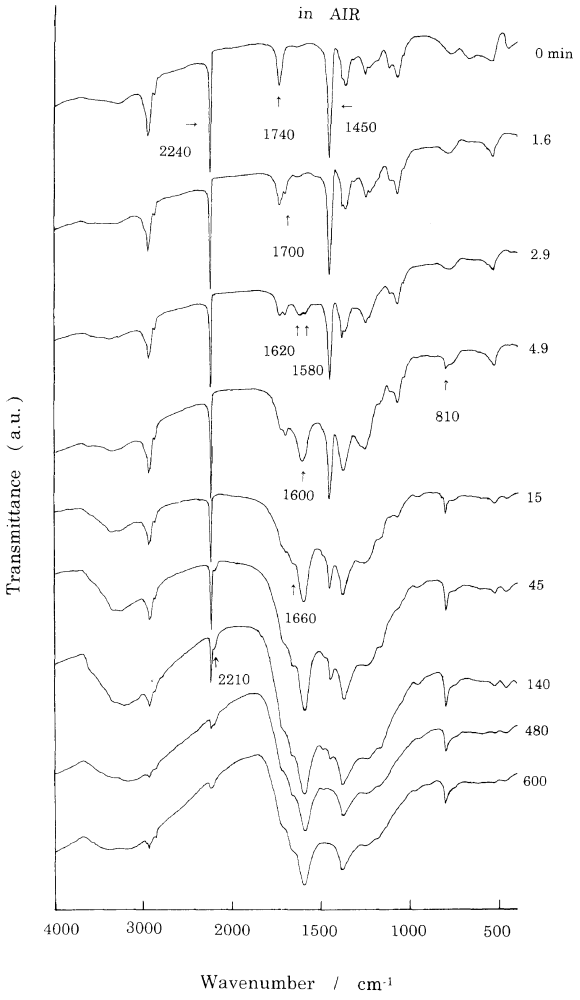

Figure 5. IR spectral change during stabilization under air 230°C.

main IR bands of the degraded PAN and AN/MAA copolymers are summarized in Table I with reference to Fochler *et al.*[7] and Sivy *et al.*[8]

Figure 5 shows changes of the IR spectra measured for the sample stabilized under air. At first, the 1740 cm^{-1} ν(C=O) band intensity of the unreacted MAA decreases and simultaneously the 1700 cm^{-1} ν(C=O) band of the reacted MAA appears and increases in intensity. Then, 1580 and 1620 cm^{-1} ν(C=C) and ν(C=N) bands begin to be observed and several minutes later the 1580 and 1620 cm^{-1} bands converge into the 1600 cm^{-1} band. At the same time the 810 cm^{-1} γ(C–H) band of >C=C–H group appears. Then the 1660 cm^{-1} band assigned to acridone ring[9] appears. Then the 1740 and 1700 cm^{-1} bands disappear at about 45 min of stabilization, and at almost the same time the 2210 cm^{-1} band, assigned to the α, β-unsaturated nitrile groups,[10] begins to be observed. As time of stabilization in DSC cell becomes longer, the 1600 and 810 cm^{-1} bands increase in intensity, while the 2240 cm^{-1} nitrile and 1450 cm^{-1} methylene $\delta(CH_2)$ bands decrease.

Figure 6 shows changes of the IR spectra measured for the samples stabilized under O_2 gas. The spectral changes resemble that observed under air flow, but the decrease of the intensity of the 1450 cm^{-1} methylene band is a little faster than in the air, and the 2240 cm^{-1} nitrile band decreases as fast as in air. Appearance of the 1600, 810, and 1660 cm^{-1} bands seems to be a little earlier than under air. Also at around 45 min of stabilization, the 2210 cm^{-1} band begins to be observed.

Figure 7 shows changes of the IR spectra when the samples were stabilized under N_2 gas flow. The spectral changes are different from those under air or O_2. The 1700 cm^{-1} ν(C=O) band of the reacted MAA increases in intensity a little faster than the other two. The 1740 and 1700 cm^{-1} bands disappear around 45 min of stabilization. Then the band of β-iminonitrile[10] at 2198 cm^{-1} begins to appear. Though the nitrile band decreases in intensity as fast as under air or O_2, the methylene bands at 1450 and 2910 cm^{-1} decrease much more slowly. The 1575 and 1620 cm^{-1} bands continue to grow without converging into 1600 cm^{-1} band. The rather strong bands which are not observed under air or O_2 are observed at 3360, 3200, 2920, 2850, 1255, 1145, 790, and 745 cm^{-1} even after 1000 min of the stabilization treatment. All these bands except 790 cm^{-1} band are assigned to the vibrational modes of the degraded PAN under reduced pressure as shown in Table II.[10] The 790 cm^{-1} band may be assigned to the vibration of the group analogous to that of the 810 cm^{-1} band.

These data of IR spectra show differences in stabilization. Under N_2 gas the nitrile oligomerization proceeds as likely as under air or O_2 gas, but the dehydrogenation occurs only a little. Therefore, the stabilized structure does not become fully conjugated. As shown in

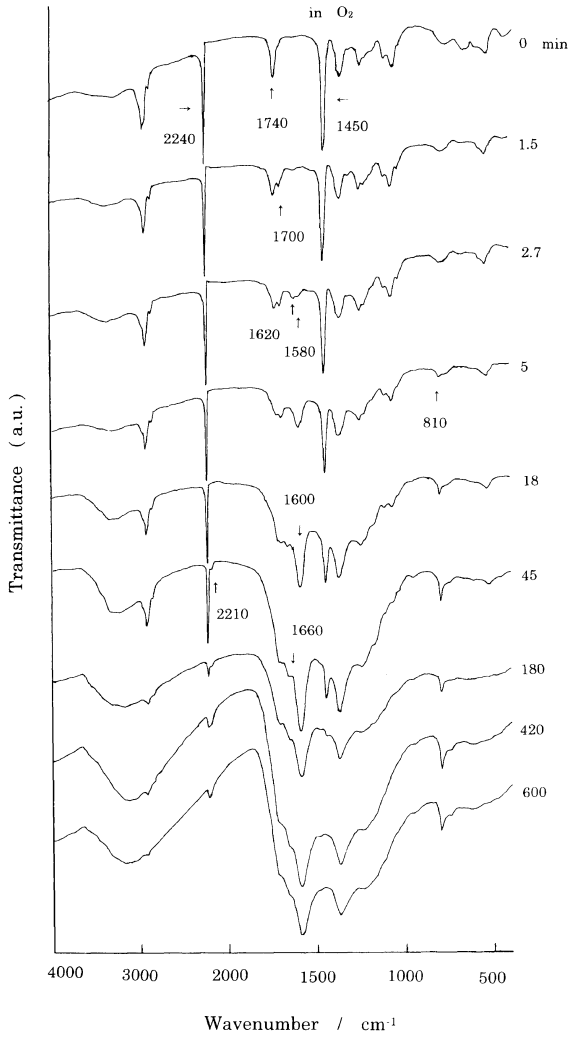

Figure 6. IR spectral change during stabilization under O_2 at 230°C.

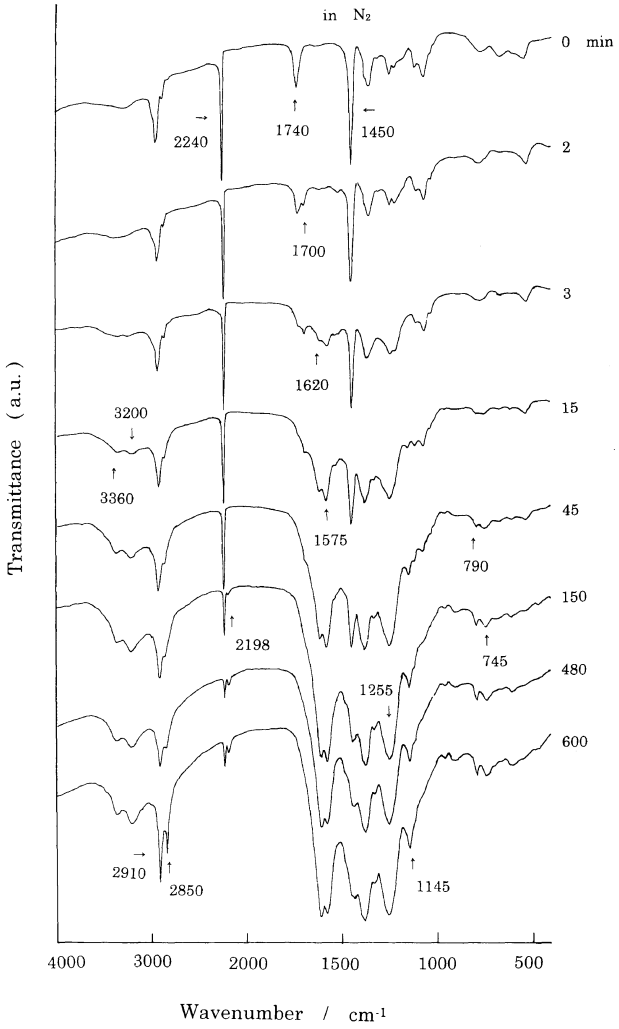

Figure 7. IR spectral change during stabilization under N_2 at 230°C.

Figure 14(c), imine–enamine tautomerism occurs, and 1620 (C=N) and 1575 (C=C) cm^{-1} bands thus do not converge into single 1600 cm^{-1} band under N_2 gas 1000 min later. Under air or O_2, the stabilized molecules become fully conjugated, so the 1620 and 1580 cm^{-1} bands converge into the 1600 cm^{-1} band.

Comparison of Structural Changes

Figures 8, 9, and 10 show intensity changes of the main IR bands during the stabilization in DSC cell under air, O_2 and N_2 respectively. The 1450 cm^{-1} $\delta(CH_2)$ band intensity decreases rapidly in O_2 flow but maintains intensity even at 1000 min stabilization in N_2 gas. The 2240 cm^{-1} $\nu(C\equiv N)$ band intensity decreases at the same rate during stabilization in the three gases. This means that the cyclization reaction, *i.e.*, the nitrile oligomerization, proceeds at the same rate in spite of differences of stabilization atmospheres. The bands around 1600 cm^{-1} behave very differently for the three atmospheres. In the air and O_2, the 1580 and 1620 cm^{-1} bands are observed separately in the early period and then these bands fuse into the 1600 cm^{-1} single band immediately. In N_2, the 1575 and 1620 cm^{-1} bands can be observed even after 1000 min stabilization. Oxygen is considered to affect strongly the formation of the conjugated structure. The 1660 cm^{-1} $\nu(C=O)$ band assigned to acridone ring appears early when the sample is stabilized under air or O_2, but under N_2 the 1660 cm^{-1} band can not be observed even after the 1000 min stabilization.

Table II. Infrared bands attributable to PAN thermally degraded under reduced pressure

IR bands/cm^{-1}	Tentative assignment
3390	$\nu(NH_2)$
3356	$\nu(NH_2)$
3230	$\nu(NH)$
2930	$\nu(CH_2)$
2870	$\nu(CH_2)$
2240	$\nu(C\equiv N)$
2198	β-iminonitrile
1610	mixed mode, predominantly $\nu(C=O)+\nu(C=C)$
1575	mixed mode, predominantly $\nu(C=C)+\delta(NH)$
1485	$\delta(CH_2)$
1450	$\delta(CH_2)$
1385	CH or NH in-plane bending
1325	CH in-plane bend
1250	$t(CH_2)$
1150	mixed mode, $\gamma(CN)+\gamma(NH)$
792	
750	$\gamma(CH_2)$

Figures 11, 12, and 13 emphasize the early times of Figures 8, 9, and 10. In the case of stabilization under O_2, the 1620 and 1580 cm^{-1} bands converge into 1600

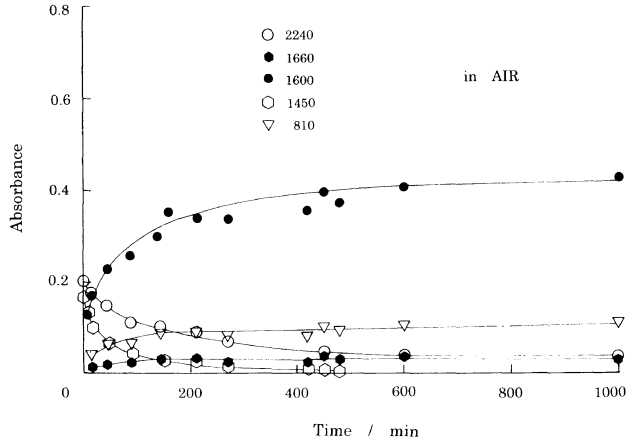

Figure 8. Intensity changes of main IR bands during stabilization under air at 230°C.

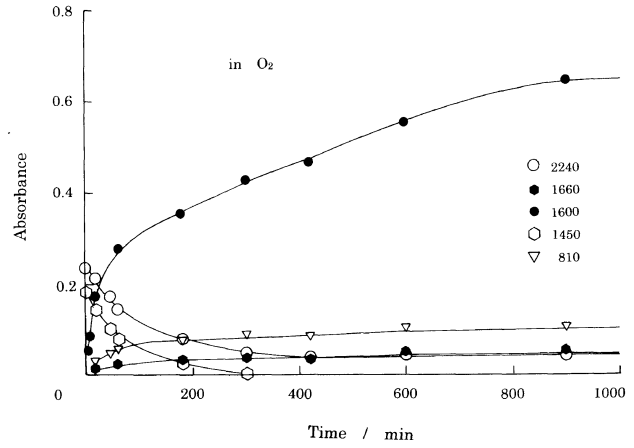

Figure 9. Intensity changes of main IR bands during stabilization under O_2 at 230°C.

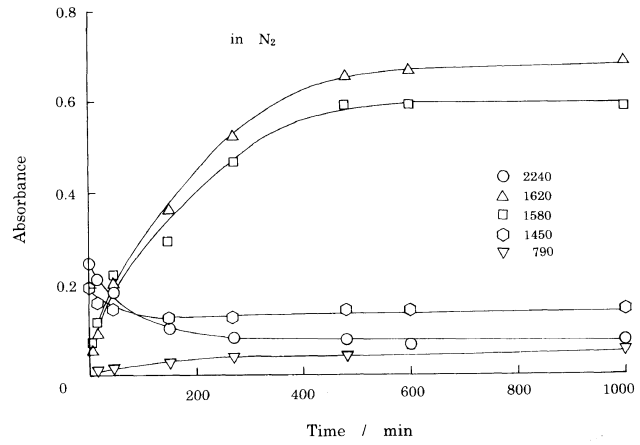

Figure 10. Intensity changes of main IR bands during stabilization under N_2 at 230°C.

cm^{-1} band at about 3 min stabilization, earlier than the case under air, and the 810 cm^{-1} band appears within 3 min. But, the 1700 cm^{-1} ν(C=O) band of the reacted MAA becomes stronger a little later than that in the N_2 atmosphere. The 1740 and 1700 cm^{-1} bands can be observed after the 45 min stabilization in all atmospheres.

From the above-mentioned data and by referring to the mechanism presented by Sivy and Colemann,[11]

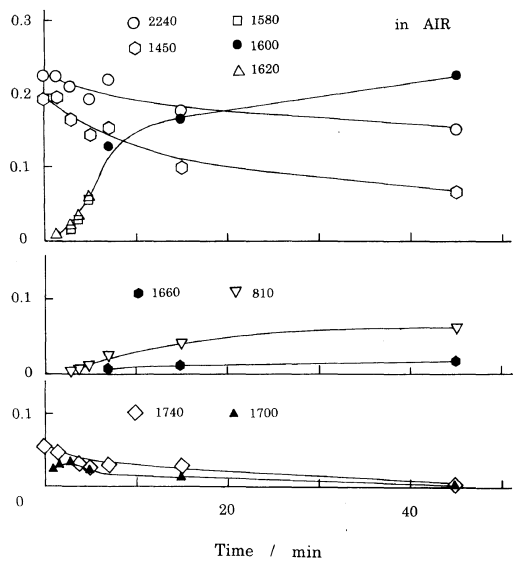

Figure 11. Early time region of intensity changes of main IR bands during stabilization under air at 230°C.

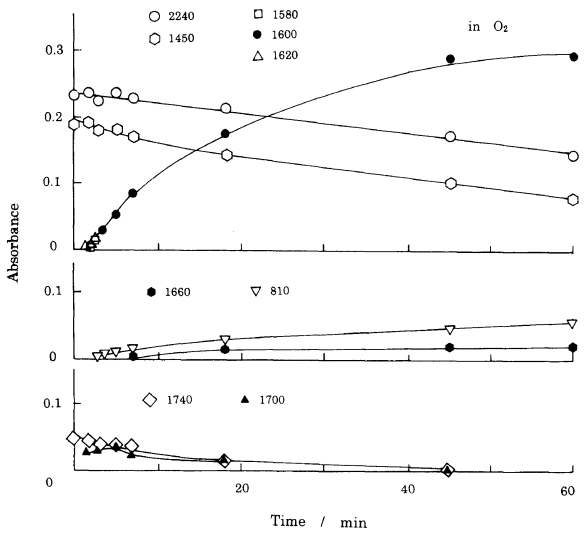

Figure 12. Early time region of intensity changes of main IR bands during stabilization under O_2 at 230°C.

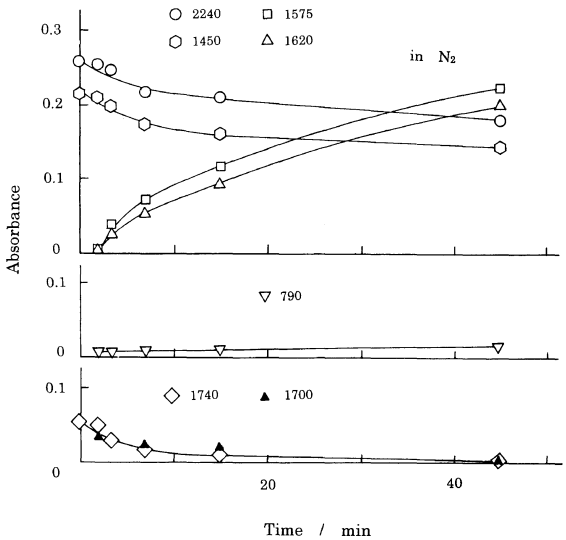

Figure 13. Early time region of intensity changes of main IR bands during stabilization under N_2 at 230°C.

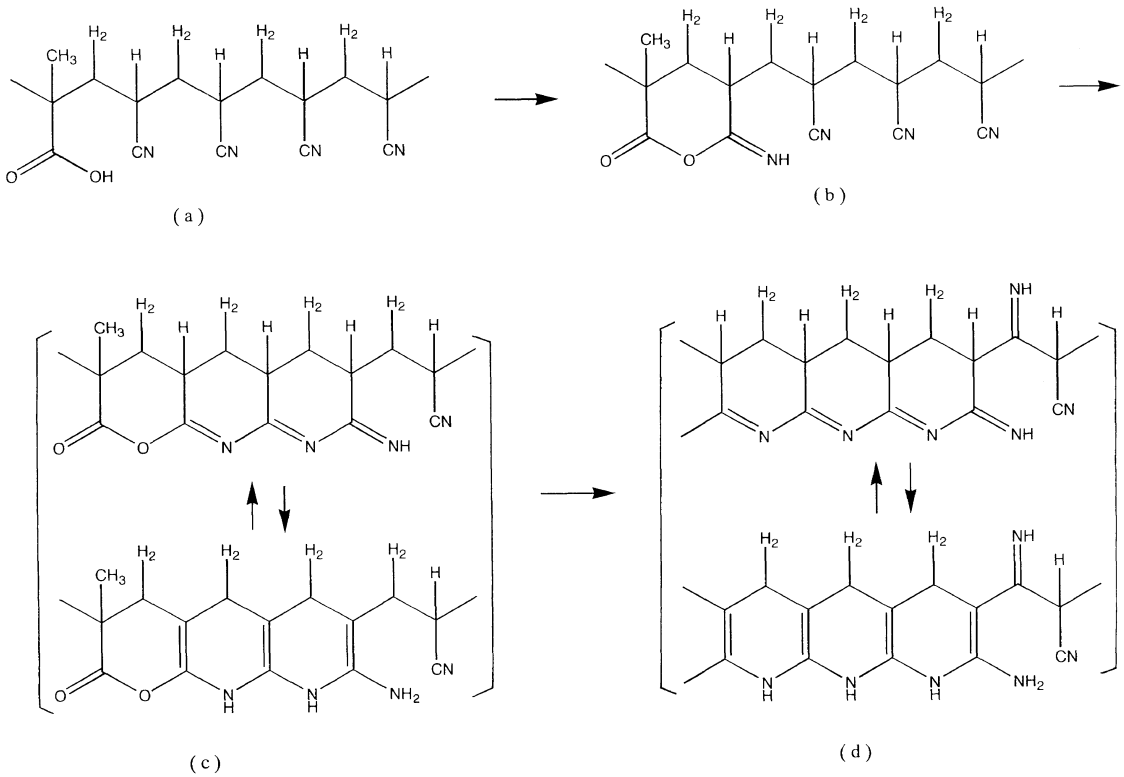

Figure 14. Structural changes during stabilization under N_2 flow at 230°C.

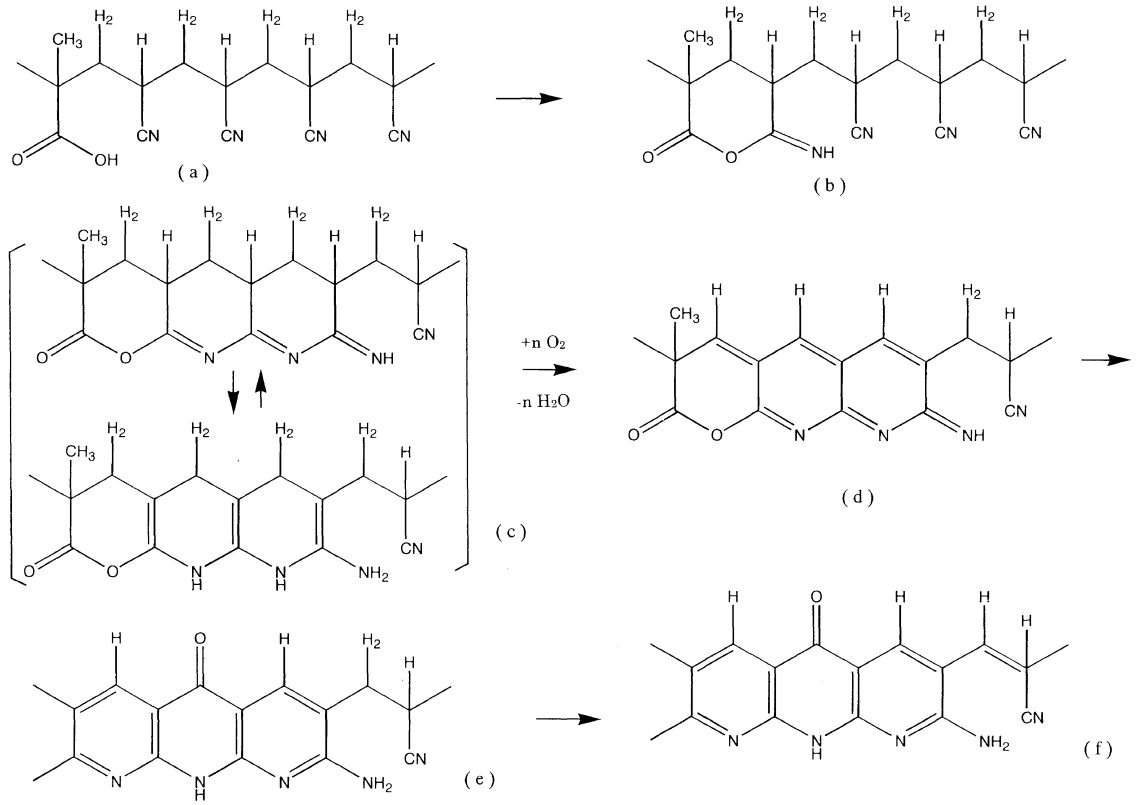

Figure 15. Structural changes during stabilization under O_2 and air at 230°C.

structure formation during stabilization under the three atmospheres may be described as follows.

In O_2, the exothermic peak of the isothermal DSC thermogram appears a little later and also the 1700 cm^{-1} reacted MAA band becomes stronger a little later than in N_2 gas, so the reaction of MAA with adjacent nitrile group occurs later than in N_2. The reason why stabilization occurs a little later in O_2 than in N_2 is not clear. The cyclization proceeds and a cyclic structure exists as a tautomeric structure as shown in the Figure 15(c), and immediately, as the result of dehydrogenation caused by oxygen, a conjugated structure is formed and

oxygen is introduced into the molecule and remaining nitrile becomes α,β-unsaturated nitrile. This reaction is shown in Figure 15.

In air, structure formation during stabilization is almost the same as under O_2 gas. But the tautomeric structure, Figure 15(c), exists a little longer than in O_2 and also the conjugated structure (d) is formed a little later than in O_2. Perhaps this is the reason why the exothermic peak of the isothermal DSC thermogram under air flow has a shoulder at a shorter time.

In the case under N_2 gas flow, the 1700 cm^{-1} band becomes stronger a little earlier than the other two cases, so the initiation reaction of MAA is a little faster than in the other cases, but the reason is not clear. The 1620 and 1575 cm^{-1} bands continue to be observed, and also the 1450 cm^{-1} $\delta(CH_2)$ band remains for 1000 min stabilization. Dehydrogenation occurs only a little, so the formation of the conjugated structure cannot occur, and the tautomeric structure, Figure 14(c), continues for 1000 min stabilization. At last the remaining nitrile group becomes β-iminonitrile as shown in Figure 14(d). Structural changes in N_2 atmosphere are shown in Figure 14. Because the triad tacticity of the used polymer is low, $mm=0.27$, the average length of isotactic sequence is thought to be short, and when dehydrogenation does not occur as in Figure 14(c) or (d), successive rings may be only two or three.

The 3360, 3200, 2920, 2850, 1255, 1145, and 750 cm^{-1} bands, assigned to $\nu(NH_2)$, $\nu(NH)$, $\nu(CH_2)$, $\nu(CH)$, $t(CH_2)$, $\gamma(CN)+\gamma(NH)$, and $\gamma(CH_2)$, respectively by referring to Table II, can be explained by structure (d) in Figure 14.

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