

Kinetics Studies on Copolymerization of Acrylonitrile Vinyl Acids by Solvent–Water Suspension Polymerization

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ABSTRACT: Polyacrylonitrile is an important polymer that is widely used in the manufacture of synthetic fibers, particularly for applications in apparel. Although a vast amount of literature is available on the polymerization process of acrylonitrile (AN) with other monomers, there are few reports of studies on polymerization in a mixed solvent of water with an organic solvent. It is conceivable that this method could combine the advantages of the solution and suspension polymerization methods. Synthesis of AN copolymers with two vinyl acids, methacrylic acid (MAA) and itaconic acid (IA), is carried out by solvent–water suspension polymerization. The polymerizations are performed with an equal ratio mixture of dimethylformamide as a solvent and water as a nonsolvent at 60°C using α,α -azobisisobutyronitrile as an initiator. The kinetics of polymerization are studied by plotting the conversion versus reaction time for different mole ratios of AN with vinyl acids. Copolymers are

characterized by FTIR and capillary viscometry. The results show that IA depresses the rate of polymerization more than MAA in this reaction medium, and this effect becomes more significant at higher vinyl acid mole ratios. High conversion in a short reaction time is obtainable for copolymers with a low vinyl acid mole fraction. However, for mole ratios of more than 93:7, the rate of the reaction is drastically reduced and low conversion (<60%) results, even after 8 h. The intrinsic viscosities of all cases are surprisingly high. Although they are reduced with increasing acidic comonomer mole fraction, this reduction is more significant for IA compared to MAA. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1284–1291, 2005

Key words: copolymerization; polyacrylonitrile; kinetics; FTIR

INTRODUCTION

Acrylonitrile (AN) based copolymers are widely used as plastics, rubbers, and synthetic fibers and in various composites. They are also the most common precursors for carbon and graphite fibers. PAN and its copolymers are prepared by free radical polymerization methods. It is well known that three general methods of free radical polymerization are used commercially, namely, solution, suspension, and emulsion methods. In commercial practice, solution and, in particular, suspension methods are the most commonly employed methods for acrylic fiber manufacture. The advantage of solution polymerization is that the polymer solution can be converted directly into the spinning dope for fiber production.^{1,2} Polymers prepared by this technique have lower molecular weights and fewer molecular defects as branching than aqueous suspension polymerization.³ Aqueous suspension polymerization has been extensively used to produce AN copolymers.⁴ Because the chain transfer constant of water is almost zero, higher molecular weight polymers are obtainable by aqueous suspension polymerization.⁵

AN copolymers obtained by these conventional techniques usually have a reduced viscosity of 2.0 or less, and the fibers that are obtained therefore usually have a strength of 5 g/den at most. This strength, although sufficient for the fibers used in textiles, is not enough for the fibers to be used for industrial applications.⁶ The tenacity of PAN fibers monotonically increases with the polymer molecular weight.^{7,8} It is conceivable that polymerization in the mixed medium of water with an organic solvent could combine the advantages of solution and aqueous suspension polymerizations and could produce PAN copolymers with high molecular weights and few molecular branching defects. Bajaj et al.⁹ copolymerized AN with vinyl acid comonomers including methacrylic acid (MAA), AA, and itaconic acid (IA) using the solution polymerization method. The maximum intrinsic viscosity for the produced copoly(AN/MAA) after an 8-h reaction at 60°C was about 1.2 dL g⁻¹. The conversion percentage of the reaction after 8 h was less than 50% in all cases. Other researchers reported similar results for the dimethylformamide (DMF) solution polymerization method.^{10–12}

Higher molecular defects are also reported when these copolymers are produced by the aqueous suspension technique.³ In contrast, by using an organic radical initiator, polymers free from metallic contamination can be obtained.

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As reported by Peebles,¹³ aqueous suspension polymerization has three loci of polymerization. Because of partial solubility in water, a two-phase liquid system exists in which one phase is monomer rich, whereas the other is monomer poor. Initiation and some propagation occur in the aqueous phase prior to the precipitation of the growing radicals. The second locus of polymerization takes place at the particle-solution interface, whereas the third locus of polymerization is interior polymerization through buried free radicals, which is controlled by the diffusion of monomer to the active sites.

Herma and Ulbricht¹⁴ studied the effect of hydrogen bonding on the reactivity of carboxylic acid comonomers in the copolymerization of AA or MAA with styrene or AN systems. They concluded that in proton-acceptor solvents, vinyl acid comonomers have lower reactivity ratios compared to copolymerizations in bulk or in water at pH 2.5. They explained this behavior as hydrogen bonding of the —COOH groups to the solvents.

Because of the combination of high melting point, high melt viscosity, poor thermal stability, poor hydroscopicity, and low dye uptake, AN homopolymers have few applications. By copolymerizing AN with other suitable monomers like acrylates, the deficiencies of PAN have been tempered and desirable properties have been achieved.^{9,15}

The influence of different vinyl comonomers on the kinetics of copolymerization and reactivity of monomers in different polymerization systems has been investigated. Karkinska et al.¹⁶ studied the kinetics of copolymerization of AN and methyl acrylate (MA) in an aqueous solution of sodium thiocyanate (NaSCN), and the rate constant was reported to be 3.6×10^{-3} dm³/mol s. The effect of the polymerization time on the yield of the AA/or IA-AN-MA copolymerization was investigated by Artemenko et al.¹⁷ Ge and Xang¹⁸ studied the mechanism and kinetics of radiation-induced copolymerization of AN, MA, and IA. They concluded that the copolymerization rate is proportional to the dose rate with 0.97 power and proportional to the monomer concentration with 0.72 power, and the apparent activation energy is 12.7 kJ/mol. Park et al.¹⁹ calculated the reactivity ratios of AN and methyl methacrylate (MMA) as $r_1 = 0.121$ and $r_2 = 2.30$, respectively, in a phase-transfer radical copolymerization system by tricaprilmethyl ammonium chloride in an Na₂S₂O₄ aqueous —CCl₄ organic two-phase system at 25°C under a nitrogen atmosphere. Group-transfer copolymerizations of AN/MMA, AN/ethyl methacrylate, and AN/butyl methacrylate were initiated by 1-methoxy-2-methyl-1-trimethylsilyloxy propane as an initiator and tetrabutyl ammonium dibenzoate as a catalyst in THF solution by Zou et al.²⁰ The reactivity ratios of the comonomers were calculated.

Ahn et al.²¹ showed that the addition of IA favors the stabilization of polymers by lowering the initiation temperature. It slows down the reaction rate and extends the temperature range within which the stabilization may be completed, whereas other nonacidic vinyl comonomers show different behavior on heat treatment of PAN fibers. A study on the heat treatment of AN/MA copolymers shows that the cyclization mechanism and fine structure of PAN fibers are significantly affected if the MA content is more than 3%. With increasing MA content, the exothermic onset and peak in the thermogram was found to shift toward higher temperatures, whereas the aromaticity index decreased. In addition, MA does not activate cyclization but instead interferes with it.^{22,23}

In this article we studied the effects of two acidic comonomers (MAA and IA) on the kinetics of the polymerization of AN with a solvent-water suspension polymerization method.

EXPERIMENTAL

Materials

AN (Fluka) was purified from the inhibitor by washing with 5% NaOH, 3% *ortho*-phosphoric acid, and triply distilled water and distilling under reduced pressure. MAA (Merck) was purified by distillation under a vacuum at 77°C/12 mmHg, and IA (Merck) was recrystallized twice from water. α,α' -Azobisisobutyronitrile (AIBN, Polyscience) was purified by recrystallization from methanol, and DMF (Merck) was dried over calcium oxide and distilled at 153°C.

Polymerization

Copolymerizations of AN with MAA and IA were carried out in a 500-mL four-necked reactor with a motor-driven glass stirrer and a condenser. A mixture of water with DMF (50:50 wt %) was added into the reactor, the flask and contents were heated to 600°C, and the AN with acid comonomer mixture was fed into the reactor. The system was deaerated by sparging with nitrogen for 15 min, and AIBN dissolved in DMF was injected. The mole fraction of the acid comonomers was varied from 0.01 to 0.07, and the solvent to monomer ratio was kept at 3. The polymerization was carried out at four different times for each composition. The resulting polymers were recovered by filtration, washed repeatedly with water, and dried at 50–550°C to constant weight. The conversion was determined gravimetrically.

pH measurements

For each composition, the pH of the system was measured using a Metrohm 691 pH meter before initializing the reaction.

TABLE I
Polymerization of AN with MAA

Code	Comonomer feed (mol fraction)	Polymerization time (min)	Conversion (%)	Intrinsic viscosity (dL/g)	M_v
PAN100	0.0	30	70.35	5.88	742,400
PMA-1	0.01	45	29.30	2.37	202,700
PMA-2		60	43.73	2.38	203,900
PMA-3		100	68.34	2.45	212,600
PMA-4		120	82.97	2.72	246,800
PMB-1	0.03	120	71.1	1.00	59,100
PMB-2		240	79.9	1.83	140,000
PMB-3		360	83.06	1.86	143,400
PMB-4		480	86.6	1.97	155,700
PMC-1	0.05	120	32.07	0.74	38,400
PMC-2		240	47.37	0.96	55,700
PMC-3		360	54.71	1.00	59,100
PMC-4		480	59.05	1.17	73,900
PMD-1	0.07	120	25.93	0.64	31,200
PMD-2		240	40.81	0.77	40,700
PMD-3		360	48.07	0.98	57,400
PMD-4		480	55.82	1.08	66,000

Intrinsic viscosity measurements

The intrinsic viscosities $[\eta]$ of the copolymers were measured in DMF using a Ubbelohde viscometer in a constant temperature bath at 300°C. Flow time agreement was within 0.2 s.

The molecular weights of the synthesized copolymers were calculated using the following equation²⁴:

$$[\eta] = 4.57 \times 10^{-4} M_v^{0.7}$$

for DMF at 30°C, where M_v is the volume-average molecular weight. The results are reported in Tables I and II.

FTIR

The FTIR spectra of the copolymers were obtained with a Nicolet Nexus 670 FTIR spectrophotometer using KBr pellets.

RESULTS AND DISCUSSION

The polymerization of AN-MAA or IA in a solvent mixture of water-DMF and initiated by AIBN showed the characteristics of heterogeneous polymerization. The reaction system, although homogeneous before initiating the polymerization, became heterogeneous

TABLE II
Polymerization of AN with IA

Code	Monomer feed (mol fraction)	Polymerization time	Conversion (%)	Intrinsic viscosity (dL/g)	M_v
PIA-1	0.01	45	43.84	2.47	215,000
PIA-2		60	58.72	2.51	220,000
PIA-3		100	77.56	2.68	241,600
PIA-4		120	87.07	2.89	269,100
PIB-1	0.03	120	58.35	0.86	47,600
PIB-2		240	63.97	1.13	70,900
PIB-3		360	78.93	1.41	96,500
PIB-4		480	87.01	1.79	135,800
PIC-1	0.05	120	16.23	0.63	30,500
PIC-2		240	18.57	0.89	50,000
PIC-3		360	31.42	0.97	56,000
PIC-4		480	44.91	1.09	66,800
PID-1	0.07	120	9.22	0.59	27,800
PID-2		240	12.16	0.68	34,100
PID-3		360	21.58	0.89	50,000
PID-4		480	31.06	0.99	58,300

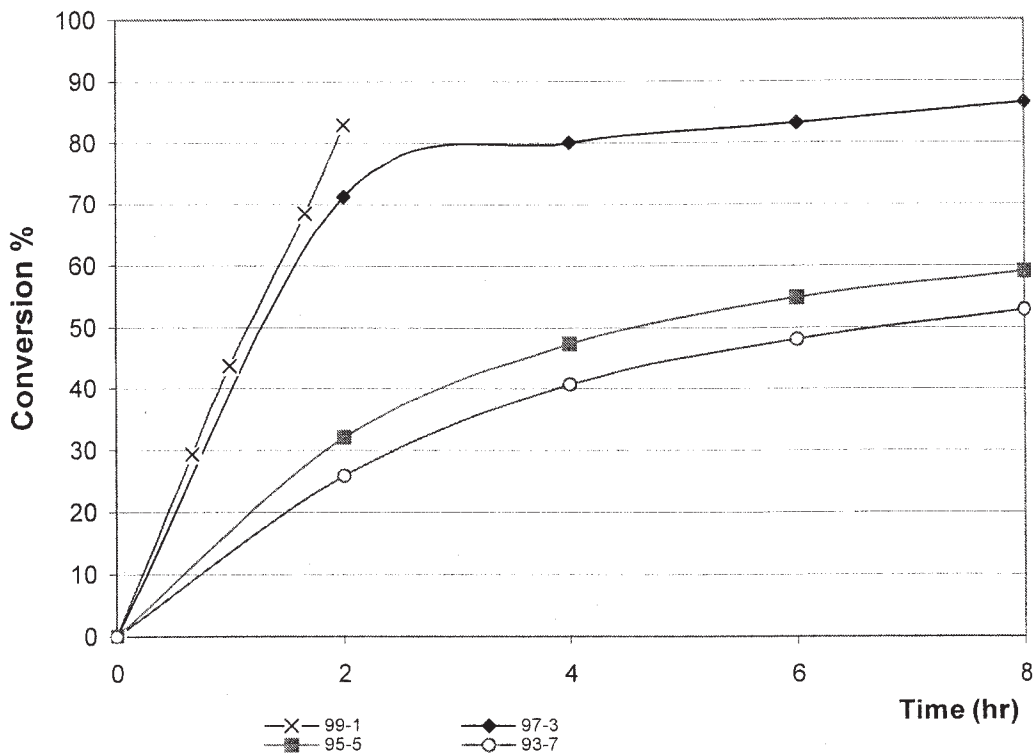


Figure 1 The time versus conversion of the copolymerization of AN with MAA.

as soon as the reaction was started by adding an initiator, because of the insolubility of the polymer in the solvent mixture. However, it is important to note the influences of the acid comonomer and its mole fraction on the physical state of the system after starting the reaction and on the rate of polymerization. The

results of the copolymerization and the comonomer content in the feed (M_2) are given in Tables I and II.

In homo- and copolymerization with a small amount of acid, the rate of reaction is high and high conversion is obtainable in a short reaction time. The medium viscosity becomes very high and polymer

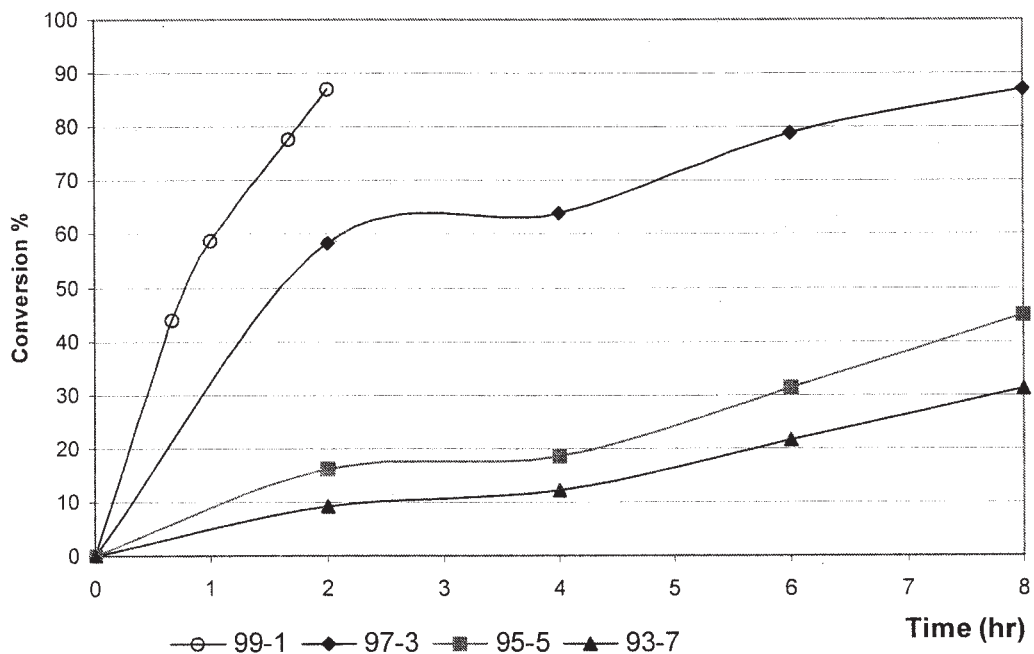


Figure 2 The time versus conversion of the copolymerization of AN with IA.

TABLE III
Initial pH of Copolymerization System Before Adding Initiator

Code	PAN100	PMA-4	PMB-1	PMC-1	PMD-1	PIA-4	PIB-1	PIC-1	PID-1
pH	6.33	4.47	4.16	4.01	3.87	3.74	3.42	3.33	3.17
Conversion	70.35	82.97	71.10	32.07	25.93	87.07	58.35	16.23	9.22

rapidly precipitates in a dense form. In the more viscous medium, the chain mobility is reduced, with the result that chain end radicals have a lower probability of being in position to effect termination. Because the small monomer molecules can still diffuse to the active chain ends even as the termination rate decreases, there is a marked increase in the polymerization rate.

Another interesting observation is the change in the pattern of the time versus conversion percentage graph. Acid comonomers depress the rate of polymerization and this effect becomes more significant at higher vinyl acid mole ratios and more obvious in the case of IA (Figs. 1, 2). As can be seen from Figures 1 and 2, the rate of reaction is reduced when increasing the time of reaction. This trend may be attributed to the decrease of the initiator efficiency with increasing conversion because of recombination of primary radicals. Several studies were carried out on the decrease of AIBN efficiency with increasing conversion in different polymerization methods.^{25,26} This reduction is more rapid at higher monomer conversion. The decomposition of AIBN can be described as a two-step reaction. In the first step a cyanopropyl radical and a diazenyl radical are produced from an AIBN molecule. Then, a cyanopropyl radical and nitrogen are

produced from a diazenyl radical in the second step (β scission). Takenada et al.²⁶ named these two steps cage-A and cage-B. If initiation of the polymerization takes place before the production of a cage-B situation, the initiator efficiency must be unity because recombination between cyanopropyl radicals and diazenyl radicals gives only AIBN molecules and no by-products. However, if initiation occurs after the establishment of the cage-B state, by-products are produced along with initiator, causing a decrease in the initiator efficiency. The likelihood of one primary radical meeting another in the presence of monomer is very low, because the radical concentration is much less than the monomer concentration. Thus, the effect of the initiator efficiency reduction will be dominant after consumption of a good extent of monomers. Whereas the rate of the solvent-water suspension polymerization method is high (especially for comonomer contents of <3%), a large number of monomers would be polymerized after a 2-h reaction, causing a significant reduction of the slope of the mentioned curves. Similar observations on the pattern of the conversion percentage versus time curves were observed and reported by Bajaj et al.²⁷

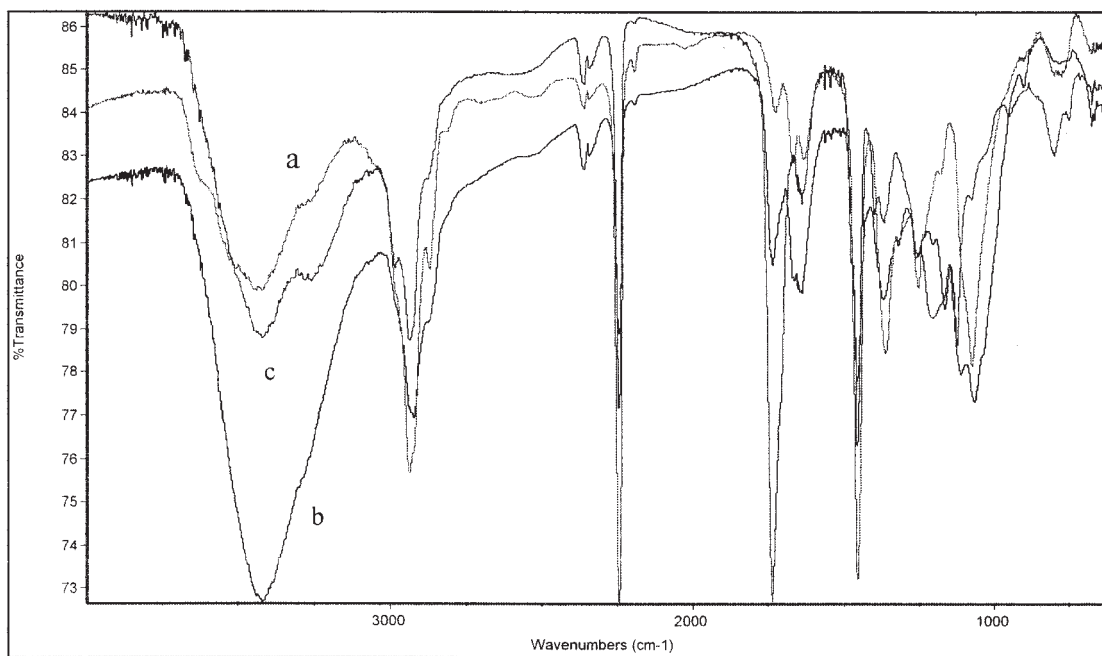


Figure 3 IR spectra of PAN (spectrum a) and AN-MAA copolymers 99-1 (spectrum b) and 95-5 (spectrum c); polymerization time = 30 min.

TABLE IV
ODR values of PAN and AN-MAA copolymers

sample	AN mole ratio in feed	—CN peak (cm^{-1})	C=O peak (cm^{-1})	ODR
a	100	2243	1720	0.071
b	99	2243	1732	0.78
c	95	2242	1733	1.33

It can be seen from Figure 1 that at a 2-h reaction time, the conversion percentage of copolymerization decreases with increasing mole fraction of acidic comonomer from 1 to 7%. At 2-h reaction the conversion percentage falls sharply from almost 83 to 26% for copolymers with 1 and 7% acidic comonomer contents in the feed, respectively.

For a copolymer of AN-MAA up to 2 h the slope of the graph is very high. This slope is reduced when the comonomer content in the feed decreases and at about a 2-h reaction, a sharp deviation can be seen, after which the rate of increasing the conversion percentage is drastically reduced. For example, in samples with 2% MAA, with a 2-h reaction time, 71% conversion was obtained whereas after 8 h the conversion percentage increased to 87% only. In the sample with 7% MAA the conversion with a 2-h reaction was 26%, which increased to 53% after 8 h.

Similar observations are made with copolymers of AN-IA. Because of the lower reactivity of IA, lower conversion is obtained after 8 h of reaction.

This may be explained by the fact that in aqueous-solvent suspension polymerization, oligomeric radicals may be formed in the aqueous phase at the initial stages of polymerization, which precipitate out after attaining a certain critical molecular weight and then act as primary particles. Depending on the stability of the monomers, the propagation then occurs in the water phase, the DMF phase, or at the interface of the solvent-water mixture. Thus, the solubility of the acidic comonomer in water and the partition coefficient between the aqueous and organic phase greatly affects the rate of copolymerization. Because IA is more hydrophilic, it remains in the macroradical-poor aqueous phase whereas MAA, which is more hydrophobic, stays in an organic, growing chain-rich phase and becomes buried in the growing particle core.

Table III shows the effect of the initial pH of the reaction mixture for different compositions of AN-MAA (MMA codes are PMA-4, PMB-1, PMC-1) or IA on the polymer conversion percentage after a 2-h reaction time. Although the acid comonomers under study (MAA and IA) are weak acids, and therefore their degree of dissociation and formation of carboxylate anions largely depend on their concentration, it can be seen from Table III that in each composition the pH of IA systems are less than the MAA one. Hence,

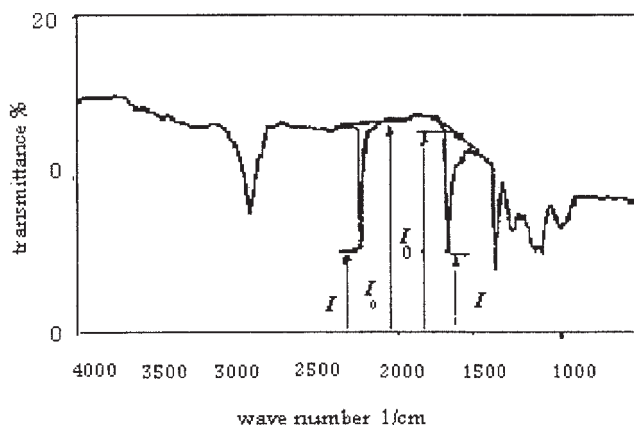


Figure 4 The determination of I and I_0 for the ODR relationship.²⁸

the lower polymer conversions in AN-IA copolymerizations could be attributed to the higher dissociation of IA than MAA. It seems that the dissociation of the acid comonomer can depress the yield of copolymerization via affecting the double bond of the monomer and mesomeric stabilization of its radical.

Figure 3 illustrates the IR spectra of PAN with two AN-MAA copolymers. In the case of PAN, the absorption band at 530 cm^{-1} is assigned to C—CN. Although there is some confusion in the assignment of this band, the band at 1075 cm^{-1} is assigned to the CH mode. However, the band at 1075 cm^{-1} is mixed with some other mode and the vibrational energy is not localized in the CH bending motion. The band at 1230 cm^{-1} is due to the twisting mode of the methylene (CH_2) group coupled with the methine group. The 1250 cm^{-1} band is assigned to the bending mode of the methine (CH) group coupled with the rocking mode of the methylene groups. The bands appearing at $1220\text{--}1270$, $1345\text{--}1375$, and $1440\text{--}1465 \text{ cm}^{-1}$ are assigned to C—H vibrations of different modes. Bands at 1640 and 1735 cm^{-1} are assigned to the hydrolysis

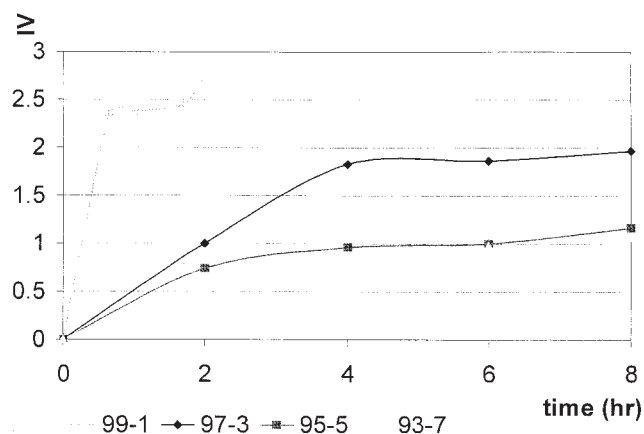


Figure 5 The intrinsic viscosities of AN-MAA copolymers.

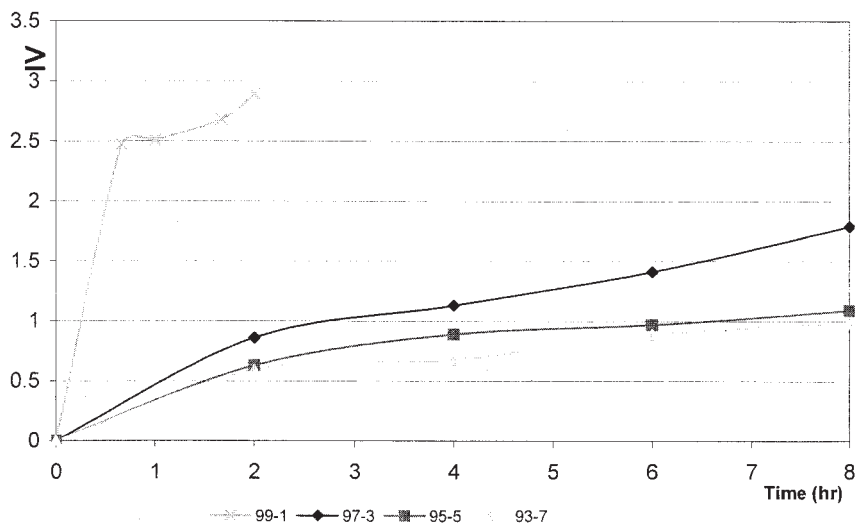


Figure 6 The intrinsic viscosities of AN-MAA copolymers.

of the AN unit during the polymerization process. The strong band at 2240 cm^{-1} is assigned to $-\text{CN}$.

In the IR spectra of the copolymer, the strong band at 1730 cm^{-1} is attributable to the carboxyl stretching vibration of the carboxylic acid group.

Table IV shows that by increasing the acid monomer content in the feed, the $-\text{CN}$ band shifts to a lower wavenumber. The carboxyl group band shifts to higher wavenumbers.

The optical density ratio (ODR) values of the copolymers were measured by the following relationship:

$$\frac{\log\left(\frac{I_0}{I}\right)_{\text{C=O}}}{\log\left(\frac{I_0}{I}\right)_{\text{C=N}}} = y$$

where I and I_0 were determined as shown in Figure 4. The results are tabulated in Table IV.

With the introduction of acidic comonomers, the ODR increases. The ODR was used to calculate the composition of the copolymer using the equation proposed by Pandey et al.²⁸ However, for feed ratios of $<7\%$, the results obtained for the composition were near the values calculated from the CHN analysis, but above this ratio the results did not match.

Homopolymerization of AN by the solvent-water suspension polymerization method produces a high molecular weight polymer in a short period of time. The intrinsic viscosity of this polymer (PAN100) is 5.88. Incorporation of acidic comonomers reduces the molecular weight of the copolymers. As can be seen from Figures 5 and 6, at a 2-h reaction time and with increasing mole fractions of acidic comonomers, the intrinsic viscosity decreases. However, when increas-

ing the reaction time, the intrinsic viscosity increases at a lower rate.

This influence is more significant for IA, particularly with mole ratios of $>1\%$. Although for PI-7-8 an intrinsic viscosity of nearly 1 is obtainable, this is still sufficient for fiber formation.

It is concluded that higher conversion percentages and higher molecular weight copolymers of AN with MAA or IA (more than that obtained from solution polymerization) at shorter period of time are obtainable (see Tables I, II). For copolymers with acidic monomer mole fractions of $\leq 3\%$ (suitable carbon fiber precursors), conversions $>85\%$ and high intrinsic viscosities are easily obtainable by the solvent-water suspension polymerization method in a short period of time.

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