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## Ultrasonic Degradation and Copolymerization of Poly(Vinyl Alcohol) with Acrylonitrile

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### ABSTRACT

The ultrasonic degradation of poly(vinyl alcohol) (PVA) in aqueous solution and copolymerization of PVA with acrylonitrile (AN) were studied. It is confirmed that the rate of degradation of PVA follows the kinetic equation suggested by Baramboim. Both water-soluble and water-insoluble copolymer can be obtained by changing the irradiation time or the amount of AN added to the aqueous solution of PVA. The structure of the copolymer was identified by IR, MS, PGC, and x-ray diffraction. The copolymer prepared is mainly a block one. By irradiating 2% PVA/AN (1/1.6, w/w) at  $20 \pm 1^\circ\text{C}$  and 21.5 kHz with 490 W for 28 min, the yield of water-soluble copolymer is 25.49%, the AN content in which is 13.98%. After 100 min, with the weight ratio between PVA and AN 1/4, the yield of the water-insoluble copolymer amounted to 296.01%, the AN content in which is 75.56%.

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\*Other participants in this work include Yanghua Liang, Zuyiao Tan, and Shiyu Zhao.

## INTRODUCTION

Poly(vinyl alcohol) (PVA) is a water-soluble polymer from which Vinyon fiber is made. The fiber has high strength and fairly good hygroscopicity, but its elasticity and dyeability are not very good. If a block or graft copolymer of acrylonitrile (AN) and PVA could be prepared, perhaps it would be endowed with wool quality and improved dyeability and dress quality. In petroleum and natural gas field exploitation, PVA may be used as a mud additive in well drilling operation. The thermostability, resistance to water loss, and rheologic properties may be better for a block or graft copolymer of AN-PVA.

The effects of solution concentration, reaction temperature, ultrasonic intensity, and irradiation time on the ultrasonic degradation of PVA in aqueous solution are studied in this paper. Favorable conditions for ultrasonic copolymerization of AN/PVA mixtures, the yield, the chemical composition, and structure of the resultant copolymer have been determined.

## EXPERIMENTAL

### Materials

**PVA.** To a 6% filtered aqueous solution of PVA (degree of polymerization, 1 700; degree of hydrolysis, 97%), absolute alcohol was added to precipitate the PVA. The precipitate was dissolved in water and reprecipitated with acetone, then dried to constant weight in vacuum at 50-60°C. The purified PVA possesses a molecular weight of  $1.430 \times 10^5$ , calculated according to  $[\eta] = 6.90 \times 10^{-4} \bar{M}_v^{0.61}$  (dL/g, water, 25°C) [1].

**AN.** Chemical pure, used after removal of inhibitor by distillation under nitrogen.

### Ultrasonic Reactor

The reactor was the same as reported in Ref. 2. The wave frequency was 21.5 kHz. The amplitude probe, which is made of stainless steel (1Cr18Ni9Ti), is conical, 120 mm long with an end diameter of 20 mm.

### Ultrasonic Degradation

Hydroquinone (free radical terminator) (1.0 mmol/L) was added to a 2% aqueous solution of PVA, and then the degradation reaction was carried out under different conditions.

### Ultrasonic Copolymerization of AN/PVA in Aqueous Solution

A PVA aqueous solution (2%) containing a certain amount of AN was irradiated for a certain period at  $20 \pm 1^\circ\text{C}$  with a sonic intensity corresponding to 490 W. Then the copolymer formed was isolated according to the schemes shown in Figs. 1a and 1b.

### Identification of the Copolymer

The AN-PVA copolymer was distinguished from a PAN/PVA mixture by solubility testing. The composition of the copolymer was determined by means of elementary analysis. The chemical and bulk structure of the copolymer were identified by IR, MS, PGC, and x-ray diffraction.

## RESULTS AND DISCUSSION

### Ultrasonic Degradation of PVA

Baramboim [3] suggested that the kinetics of polymer degradation under stress may be expressed as

$$-\frac{d[(\bar{M}_t - \bar{M}_\infty)/\bar{M}_\infty]}{dt} = K \left( \frac{\bar{M}_t - \bar{M}_\infty}{\bar{M}_\infty} \right),$$

where  $\bar{M}_t$  and  $\bar{M}_\infty$  are the viscosity-average molecular weights at irradiation time  $t$  and its limiting value, respectively. The experimental data were treated by a curve-fitting method, and  $\bar{M}_\infty$  and  $K$  were evaluated with the aid of a computer. It can be seen from the data in Table 1 that the degradation increases with increasing sonic intensity, but with decreasing solution concentration and temperature.

Figures 2-4 show that the molecular weight decreases very rapidly in the early stage of irradiation, the curves gradually trending toward a limiting value with time. The kinetic curves fitted the experimental data well.

### Ultrasonic Copolymerization of AN and PVA

The data in Table 2 show that, as the irradiation time becomes longer, the yield of copolymer increases owing to the increased amount

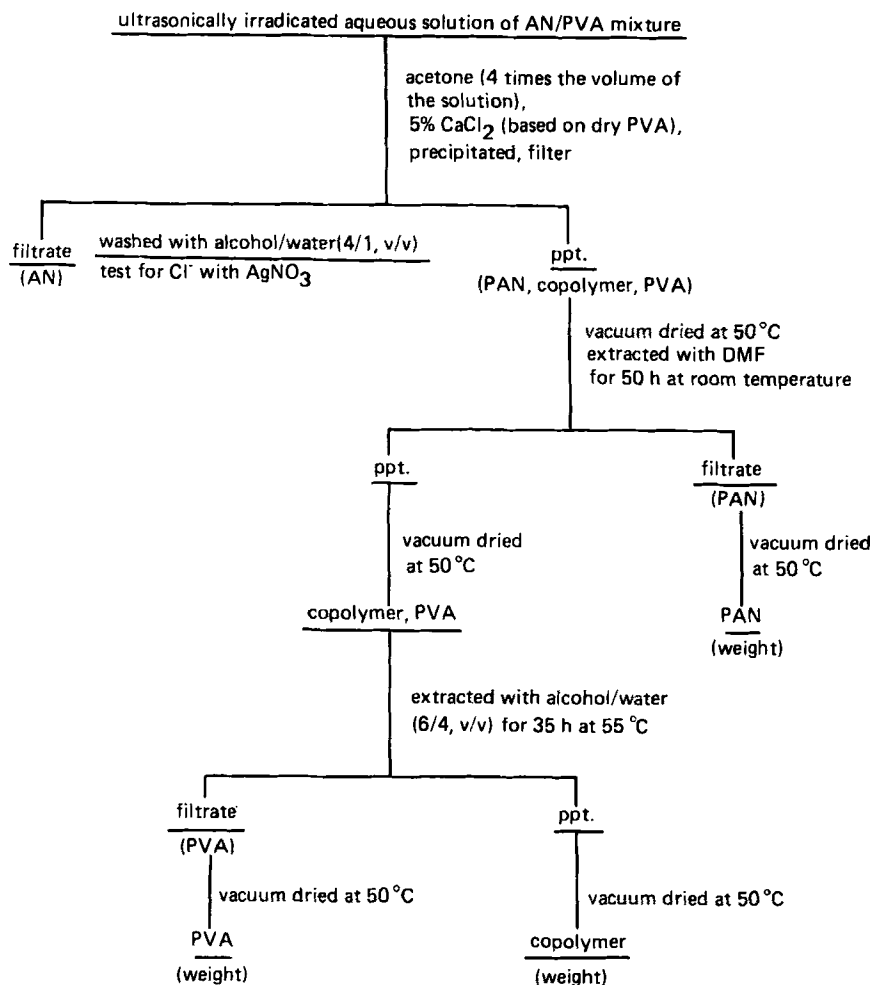


FIG. 1a. Separation scheme of PAN, PVA, and AN-PVA copolymer (for water-soluble copolymer).

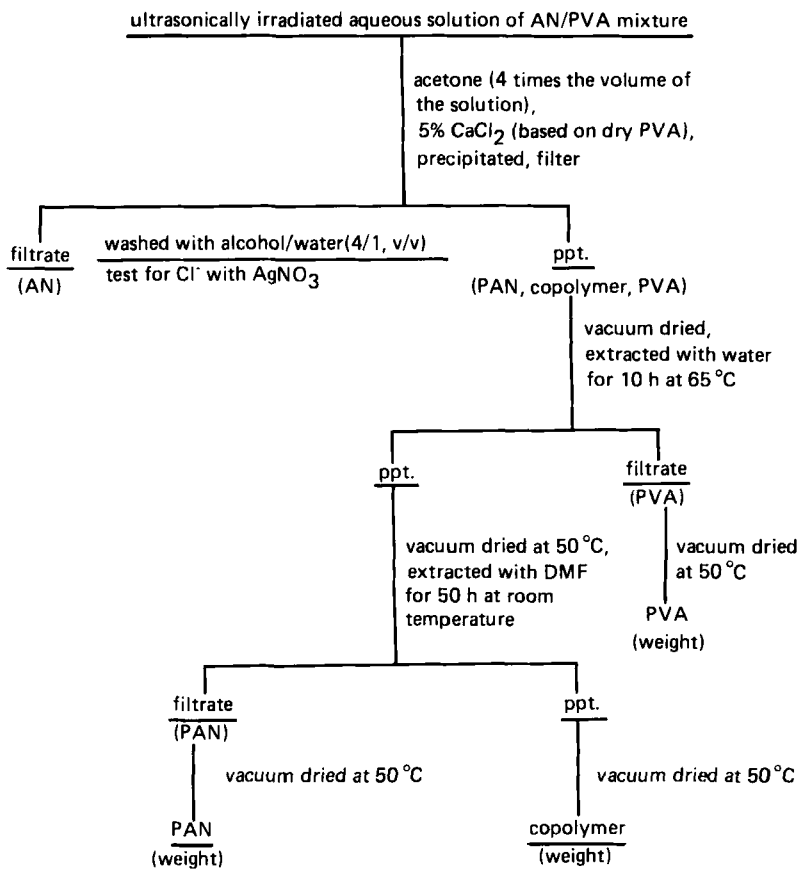


FIG. 1b. Separation scheme of PAN, PVA, and AN-PVA copolymer (for water-insoluble copolymer).

TABLE 1. Kinetic Parameters of Degradation of PVA ( $\bar{M}_{\eta_0} = 1.43 \times 10^5$ ) in Aqueous Solution under Different Conditions

	Sonic intensity, W (2%, 18°C)			Solution concentration, % (490 W, 18°C)			Temperature, °C
	170	370	490	1	2	3	
$\bar{M}_{\infty} \times 10^{-5}$	0.795	0.694	0.649	0.573	0.649	0.683	0.649
K, min <sup>-1</sup>	0.0143	0.0200	0.0371	0.0384	0.0371	0.0164	0.0371
							18
							37

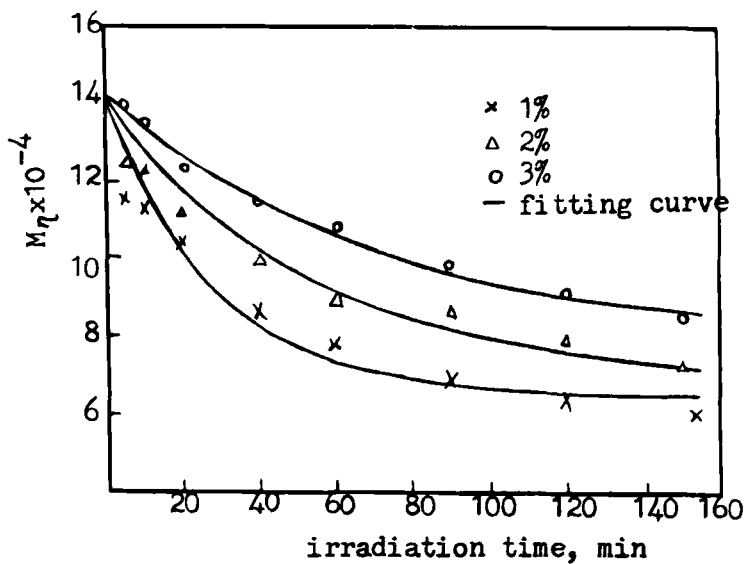


FIG. 2. Ultrasonic degradation of PVA in aqueous solution at different concentrations.

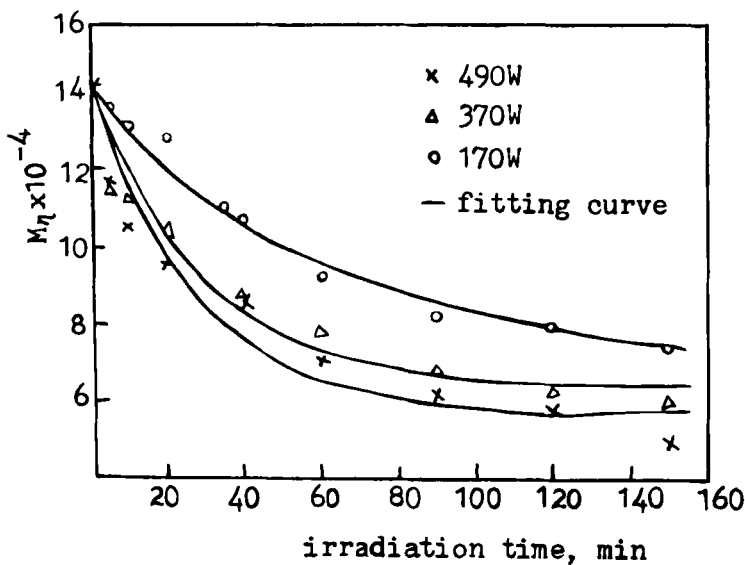


FIG. 3. Ultrasonic degradation of PVA in aqueous solution at different sonic intensities.



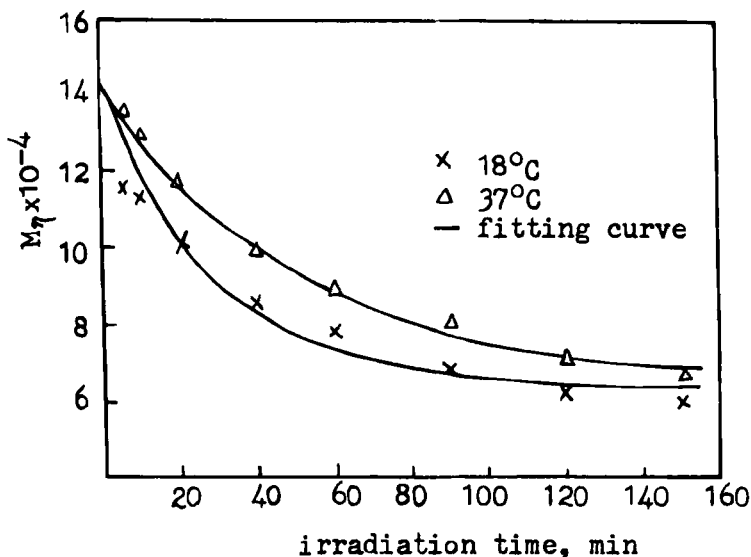


FIG. 4. Ultrasonic degradation of PVA in aqueous solution at different temperatures.

of AN copolymerized with PVA. The yield and AN content of the copolymer reach to a maximum at 100 min. If the irradiation time is extended further, the yield of copolymer decreases because of the diminishing amount of AN present in the reaction system and because of chain scission of the copolymer formed.

Table 3 shows the dependence of the transmissivity of AN/PVA aqueous solution on irradiation time, measured with a Model 751 ultraviolet-visible light spectrophotometer. The transmissivity is nearly unchanged because only a very small amount of copolymer is formed and the copolymer is water soluble for an irradiation time of less than 30 min. After 30 min the copolymer formed is water insoluble and the transmissivity declines very rapidly. The copolymer yield and the AN content of the copolymer reach a maximum at 100 min (Table 2), where the transmissivity is, therefore, at its lowest. After 100 min the transmissivity rises again because of the scission reaction of the copolymer.

Table 4 shows that the copolymer changes to water insoluble from water soluble as the time of irradiation is lengthened and the amount of AN added is increased. Thus, both water-soluble and water insoluble copolymer can be obtained by regulating the concentration of AN and the irradiation time. If irradiation is stopped as soon as the reaction solution appears turbid, the copolymer obtained is water soluble.

TABLE 2. Dependence of Yield and Composition of Copolymer on Irradiation Time<sup>a</sup>

Irradiation time, min	Sample weight, g						AN content of copolymer, %
	Before copolymerization		After copolymerization		Yield, % <sup>b</sup>		
	PVA	AN	Copolymer	PVA			
30	1.001	4.002	0.4875	0.6221	48.8	22.5	
40	1.001	4.002	1.1205	0.6304	112.0	67.0	
50	1.001	4.002	1.5818		158.2		
70	1.001	4.002	2.0953	0.4247	209.5	72.5	
100	1.001	4.002	2.9604	0.2764	296.0	75.6	
150	1.001	4.002	2.6871	0.3042	268.7	74.1	

<sup>a</sup>PVA/AN (1/4, w/w), concentration 2%, 490 W, 20 ± 1 °C.

<sup>b</sup>Copolymer yield, % =  $\frac{\text{copolymer weight}}{\text{PVA added}} \times 100\%$ .

TABLE 3. Dependence of Transmissivity of AN/PVA in Aqueous Solution on Irradiation Time<sup>a</sup>

Irradiation time, min	0	30	40	50	70	100	150
Transmissivity, %	99.0	97.4	91.2	82.9	69.5	41.1	62.6

<sup>a</sup>PVA/AN (1/1.6, w/w), concentration 2%, 490 W, 20 ± 1°C.

TABLE 4. Dependence of Water Solubility of Copolymer on Irradiation Time and Amount of AN Added<sup>a</sup>

AN added, g	Irradiation time, min	Water Solubility of copolymer
1.2006	30 (reaction solution appears turbid)	Soluble
	50	Insoluble
1.6008	28 (reaction solution appears turbid)	Soluble
	35	Swell
	50	Insoluble
2.0010	26 (reaction solution appears turbid)	Soluble
	50	Insoluble
4.0020	22 (reaction solution appears turbid)	Soluble
	30	Swell
	40	Insoluble

<sup>a</sup>PVA/AN (1/1.2-1/4, w/w), concentration 2%, 490 W, 20 ± 1°C.

TABLE 5. Elemental Analysis of Copolymer

Element	H	C	N
Content, %	6.16	19.39	63.10

By irradiating 2% PVA/AN (1/1.6, w/w) at  $20 \pm 1^\circ\text{C}$  and 21.5 kHz with 490 W for 28 min, the yield of the water-soluble copolymer is 25.49% and its AN content is 13.98%.

### Analysis and Identification of the Copolymer

#### Elemental Analysis

Table 5 lists the hydrogen, carbon, and nitrogen content in the copolymer obtained by irradiating for 100 min, determined with a MOD-1106 elemental analyzer. The calculated AN content in the copolymer is 73.41%, fairly close to the 75.56% (Table 2) obtained by material balance.

#### Solubility Test

As shown in Table 6, the copolymer obtained by ultrasonic irradiation is entirely insoluble in both DMF and water. In contrast, the homopolymer mixture exhibits considerable loss of weight, indicating that the reaction product is a copolymer rather than a mixture of PVA and PAN.

#### Pyrolysis Gas Chromatography

The relative areas (characterizing the relative yield of fragments pyrolyzed) of the fragment peaks in the PGC spectra of PVA, PAN, AN-PVA (75.56/24.44, w/w) copolymer, and the PAN/PVA mixture of the same composition listed in Table 7 were measured with a GC-1C chromatograph and processed by normalization. Although the copolymer has the same peaks as that of the mixture, the yield of its fragments is much different, demonstrating that the copolymer exhibits different pyrolysis behavior at high temperature due to its group boundary effect. For example, for a retention time of 36-37 s, the relative yield of the copolymer is 0.46, whereas the relative yield of the mixture is 1.80; the latter is 3.91 times higher than the former. The same is true of the other fragment peaks. This suggests an appreciable difference in the structure of the copolymer and the mixture, further confirming that the AN-PVA is a copolymer rather than a mixture of PAN and PVA.

#### Mass Spectrographic Analysis

Figure 5 shows the mass spectra of PVA, PAN, and AN-PVA (75.56/24.44, w/w) copolymer measured with a MAT mass-spectrometer. The mass spectrum of AN-PVA is nearly the superposition of the mass spectra of PAN and PVA. Usually, block copolymer has less effect on the mass spectrum than graft copolymer, and the spectrum is more similar to that of homopolymers.

TABLE 6. Solubility Behavior of PVA, PAN, AN-PVA (46.52/53.48, w/w) Copolymer and PAN/PVA (50.08/49.92, w/w) Mixture at Room Temperature

		Sample						
		Mixture			Copolymer			
Solvent	PVA	PAN	Before extraction, g	After extraction, g	Weight change, %	Before extraction, g	After extraction, g	Weight change, %
DMF	insol	sol	0.2854	0.1442	49.47	0.1935	0.1933	-0.10
Water	sol	insol	0.2986	0.1615	45.91	0.2520	0.2521	+0.04

TABLE 7. Relative Areas of Fragment Peaks in PGC<sup>a</sup>

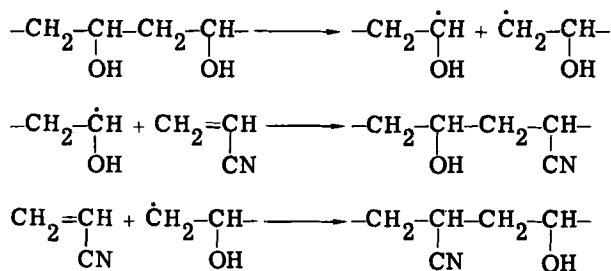
Sample	Time, s					
	36-37	45-46	55-58	66-72	83-84	142
Copolymer	0.46	0.13	1	0.13	0.57	
Mixture	1.80	0.34	1	0.45	1.37	
PVA	6.76	1.86	1	0.32	4.75	0.91
PAN			1	1.83		

<sup>a</sup>JHP-2 Ci pyrolyzer; silicone oil column; column temperature 120°C; pyrolysis temperature 518°C.

### IR Analysis

Figure 6 shows the IR spectra of PVA, PAN, and AN-PVA (75.56/24.44) copolymer measured with a PE-580B IR spectrophotometer. The peaks at 3 340 and 2 942-2 910  $\text{cm}^{-1}$  are due to the strong stretching vibration band of -OH and -CH groups in PVA [4], and that at 2 240-2 225  $\text{cm}^{-1}$  is due to the strong stretching vibration band of the -CN group in PAN [5]. The AN-PVA copolymer possesses all the peaks possessed by the homopolymers PVA and PAN. Comparison of the absorption intensity of -OH and -CH groups in AN-PVA copolymer with that in PVA reveals no obvious differences, i.e., neither the hydrogen at the hydroxyl (-OH) nor the hydrogen at the tertiary carbon (-CH) is replaced, excluding the possibility that AN grafts at -OH or -CH. Consequently, the product AN-PVA is mainly a block copolymer.

Fujiwara [6] suggested that, under ultrasonic irradiation, the bond in PVA molecules would split homolytically, so that the course of copolymerization may be



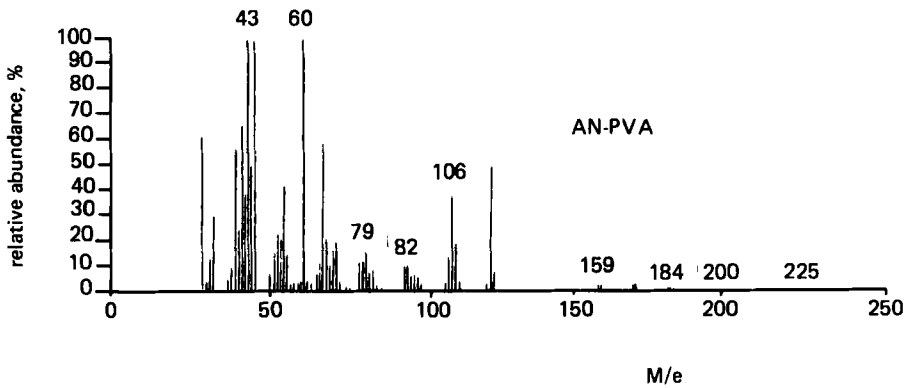
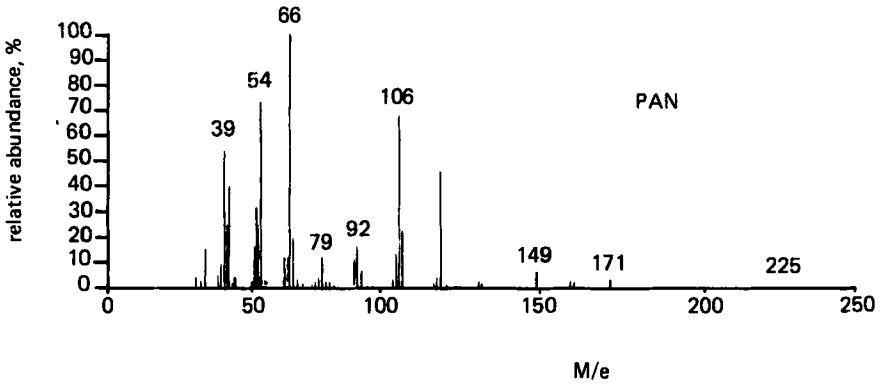
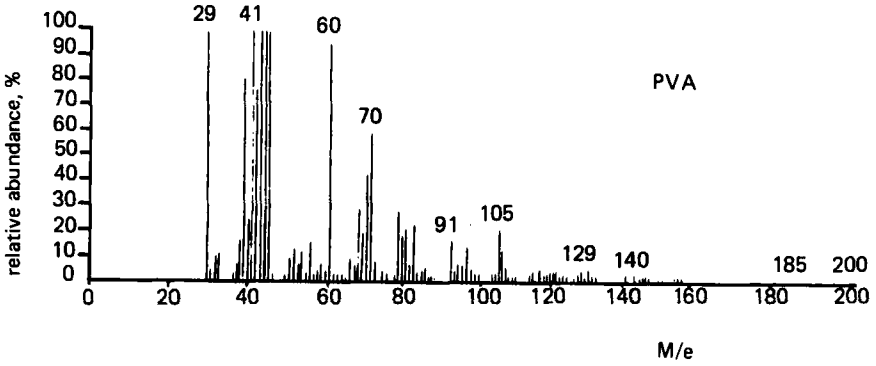


FIG. 5. Mass spectra of PVA, PAN, and AN-PVA copolymer.

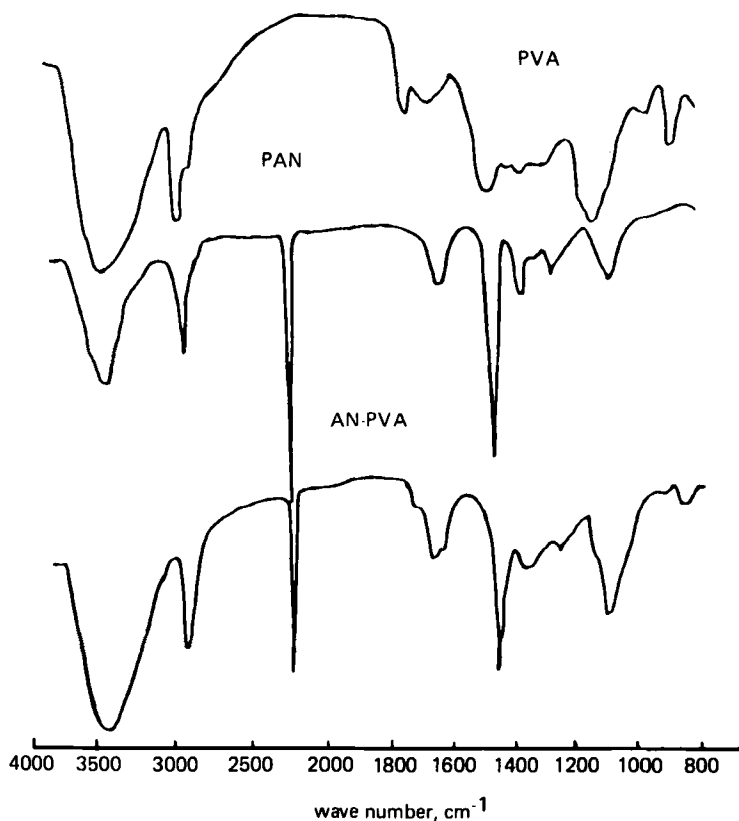


FIG. 6. IR spectra of PVA, PAN, and AN-PVA copolymer.

### X-ray Diffraction

Figure 7 shows the x-ray diffraction spectra of PVA, PAN, and AN-PVA (75.56/24.44) block copolymer measured with a Model 3015 x-ray diffraction fluorescence spectrometer. Both PVA and PAN are crystalline polymers. For PVA the characteristic peaks appear at the scanning angles ( $2\theta$ ) 10-14° and 18-22°; for PAN at 15-19°. All these peaks appear for the copolymer, only their positions are shifted slightly, indicating that the copolymer obtained is still a crystalline polymer.

### CONCLUSIONS

1. The rate of ultrasonic degradation of PVA in 1-3% aqueous solution at 18-37 ± 1°C and 21.5 kHz with sonic intensity corresponding to



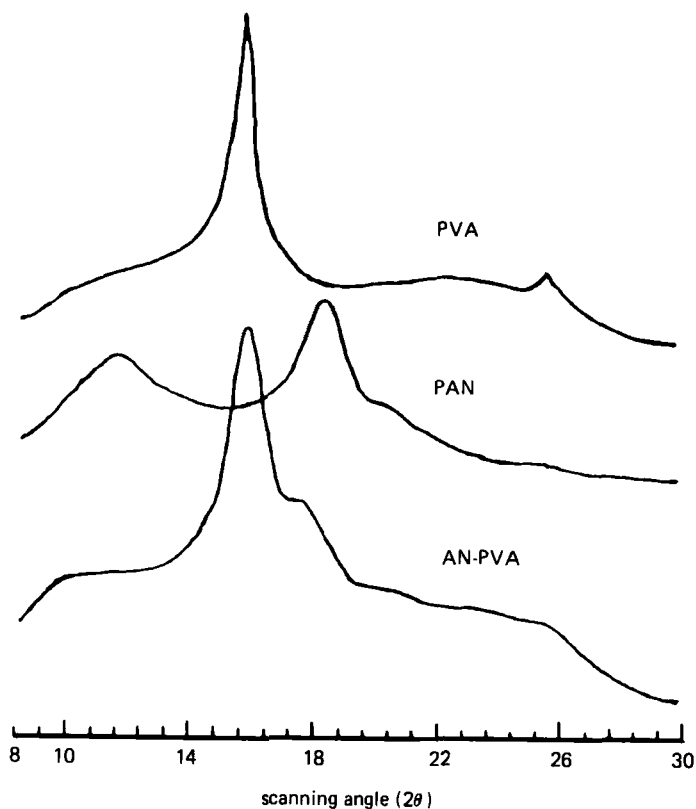


FIG. 7. X-ray diffraction spectra of PVA, PAN, and AN-PVA copolymer.

170-490 W follows the mechanodegradation kinetic equation suggested by Baramboim.

2. AN-PVA copolymer can be prepared by ultrasonic irradiation. Both water-soluble and water-insoluble copolymer can be obtained by regulating the irradiation time or the concentration of AN in solution.

3. By irradiating a 2% PVA/AN (1/4, w/w) mixture for 28 min at  $20 \pm 1^\circ\text{C}$  and 21.5 kHz with 490 W, the yield of water-soluble copolymer is 25.5% and the AN content of the copolymer is 14.0%. If irradiation is prolonged to 100 min, the product is water insoluble, the yield amounts to 296%, and the AN content in the copolymer is 75.6%.

4. It is confirmed by IR and MS that the copolymer prepared by ultrasonic irradiation is a block copolymer.

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