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REACTIVITY AND CHARACTERIZATION OF THE RADICAL COPOLYMERIZATION OF ITACONIC ACID WITH SOME CONVENTIONAL MONOMERS

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ABSTRACT

Radical copolymerizations of itaconic acid (IA) with acrylamide (Am), *N*-vinyl pyrrolidone (NVP), ethyl methacrylate (EMA), and methyl methacrylate (MMA) were carried out in dioxane in the presence of azobisisobutyronitrile as the initiator at 65°C. The monomer reactivity ratios (r_1, r_2), Q, and e for IA with the four monomers were determined. The reactivity ratios show a tendency toward alternation, while the Q and e of IA indicate that it is an electron-accepting monomer. The polymers obtained were characterized by FT-IR, x-ray diffraction, intrinsic viscosity, and thermal stability measurements.

INTRODUCTION

Itaconic acid (IA) was isolated in 1836 from the pyrolysis of citric acid [1]. The effect of solvents on the behavior and the rate of polymerization were investigated on radical homopolymerization of itaconic acid in dioxane and ethanol at 60°C [2]. Many patents in the literature describe the use of poly-IA and its derivatives as protective and decorative coatings in synthetic fibers, as oil additives, and as rigid plastics. IA polymerizes in aqueous solution upon initiation with potassium persulfate. The effect of pH on the rate of polymerization was studied [3-5]. The copolymerizations of IA with styrene, acrylonitrile, and some esters were also investigated, and the monomer reactivity ratios were calculated [6-10]. The terpolymerizations of IA with acrylonitrile and different types of acrylates were carried out at 70°C by a free-radical mechanism [11-14]. The changes of conformation and supermolecular structure of the obtained polymer on swelling were revealed. The terpolymerizations of IA with *N*-vinylpyrrolidone (NVP) and methyl methacrylate (MMA) [15], and the copolymerization of IA with styrene or butylacrylate initiated by a redox system in the presence of nonionic emulsifier have also been studied [16, 17]. The thermal stabilities and the reactivity ratios of monomethyl itaconate and itaconic anhydride with MMA were investigated [18]. Characterization and physical properties of derivatives of poly(itaconic acid) (PIA) with different monomers such as acrylonitrile, styrene, and MMA were determined [19-22]. The aim of the present study was to determine the reactivity ratios of IA when copolymerized with various well-known systems like NVP, acrylamide (Am), and acrylate esters. The investigation will be extended to throw light on the thermal stabilities of the prepared copolymers.

EXPERIMENT

Materials

IA and Am (BDH) were used after recrystallization from distilled water, mp 160 and 84.8°C, respectively. NVP (Aldrich Chemical Co.) was distilled at 94°C/15 mmHg. Ethyl methacrylate (EMA) (Koch-Light) was first washed with 5% aqueous NaOH and then with distilled water until it was free of alkali, dried over $CaCl_2$, and distilled at 117.5°C. MMA (Koch-Light) was distilled at 100°C just before use. Azobisisobutyronitrile (AIBN) was recrystallized twice from methanol, mp 104°C. The other reagents and solvents were used after ordinary purification [23].

Copolymerization Procedure

Radical polymerization was carried out in Pyrex glass ampules charged with the monomer mixtures, dioxane, and the appropriate amount of the initiator (AIBN). The ampules were then cooled and sealed at normal pressure. The copolymerization was carried out in a water thermostat adjusted to 65 ± −0.1°C with periodic stirring for periods of time chosen to keep the conversion below 10%. The copolymerization reaction was then brought to a stop by opening the glass ampules and collecting the obtained polymers. The copolymers formed were insoluble in the reaction solvent except for the acrylate copolymers, for which it was necessary to precipitate the copolymers formed either in water or petroleum ether. The polymers, purified by reprecipitation to avoid the formation of homopolymers, were dried at 60°C in an air oven to constant weight.

Copolymer Analyses

The copolymer compositions were calculated for their nitrogen and/or carbon contents. The analyses were performed at the Central Micro-analytical Unit, Cairo University.

FT-IR Spectroscopy

FT-IR spectroscopy was measured using a Testscan Shimadzu 8000 FTIR spectrometer.

X-Ray Diffraction

The x-ray diffraction curves were obtained using a Phillips apparatus (pw 1390 channel control and pw 373 goniometer supply) with nickel-filtered CuKα radiation. The measurements were made on unoriented films.

Viscosity Measurements

The intrinsic viscosities of the obtained polymers were measured either in distilled water or in acetone at 30°C, using an Ubbelohde-type viscometer.

Thermal Stability Measurements

The thermogravimetric analyses (TGA) were carried out under nitrogen using a Shimadzu TGA-50H apparatus for the copolymers of IA with Am and NVP, and in air for the copolymers of IA with EMA and MMA.

RESULTS AND DISCUSSION

Copolymerizations of IA with different monomers (Am, NVP, EMA, and MMA) were carried out in dioxane at 65°C using azobisisobutyronitrile (AIBN, 5×10^{-3} mol/L) as initiator. The composition of the monomer feed mixtures and that of the copolymers for the four investigated systems are compiled in Tables 1-4, and the monomer-copolymer composition curves are presented in Fig. 1.

TABLE 1. Copolymerization Data for the IA-NVP System

No.	Monomer IA, mol%	N, wt%	Copolymer composition, mol%	[η]
1	10	10.68	13.39	–
2	20	9.27	23.54	–
3	30	8.14	31.93	0.099
4	40	7.18	39.25	0.082
5	50	6.31	46.03	0.070
6	60	5.45	52.88	0.051
7	70	4.54	60.29	0.030
8	80	3.48	69.14	–
9	90	2.09	81.13	–

TABLE 2. Copolymerization Data for the IA-Am System

No.	Monomer IA, mol%	N, wt%	Copolymer composition, mol%	[η]
1	10	16.89	8.38	–
2	20	14.42	16.71	0.214
3	30	12.23	24.06	0.194
4	40	10.25	33.53	0.179
5	50	8.42	42.29	0.159
6	60	6.69	51.54	–
7	70	5.04	61.40	0.123
8	80	3.40	72.39	–
9	90	1.74	84.95	–

The data in the tables were analyzed by the Fineman-Ross [24] method where r_1 and r_2 represent the slope and the intercept of Eq. (1) respectively. In the Kelen-Tüdös equation [25], the least-squares method was used throughout the calculations for the determination of the slopes and intercepts. Averaged values were used to construct theoretical composition curves. The fit with the experimental points was rather good. Kelen-Tüdös plots for the four systems are presented in Fig. 2. The intercept of the line at $\zeta = 1$ is equal to r_1 and that at $\zeta = 0$ is equal to r_1/α [26] from Eq. (2).

$$X(Y - 1)/Y = X^2/Yr_1 - r_2 \tag{1}$$

$$\eta = G/(F + \alpha), \qquad \xi = F/(F + \alpha) \tag{2}$$

and α is an arbitrary constant [$\alpha = (F_{\max}F_{\min})^{0.5}$].

TABLE 3. Copolymerization Data for the IA-EMA System

No.	Monomer, mol%	C, wt%	Copolymer composition, mol%	[η]
1	10	59.11	21.50	–
2	20	57.27	31.60	0.00778
3	30	56.21	37.60	–
4	40	55.50	41.70	–
5	50	54.97	44.80	0.006
6	60	54.52	47.40	–
7	70	54.09	49.90	–
8	80	53.56	53.10	0.004
9	90	52.58	59.10	–

TABLE 4. Copolymerization Data for the IA–MMA System

No.	Monomer, mol%	C, wt%	Copolymer composition, mol%	[η]
1	10	59. 9	4.50	–
2	20	58.35	9.40	0.0050
3	30	57.48	14.60	–
4	40	56.56	20.20	0.0040
5	50	55.58	26.50	0.0042
6	60	54.51	33.50	–
7	70	53.30	41.90	–
8	80	51.85	52.40	0.003
9	90	49.86	67.70	–

$$G = \frac{X(Y-1)}{Y}, \qquad F = \frac{X^2}{Y}$$

where $X = [M_1]/[M_2]$, $Y = d[M_1]/d[M_2]$, and $[M_1]$ and $d[M_1]$ are the composition of IA in the monomer and copolymer, respectively.

Table 5 summarizes the values of r_1 and r_2, and Q and e values of IA in every case. Two values are usually obtained for each e parameter. The positive value was used for compiling the table. It was chosen because the two carboxyl groups of IA

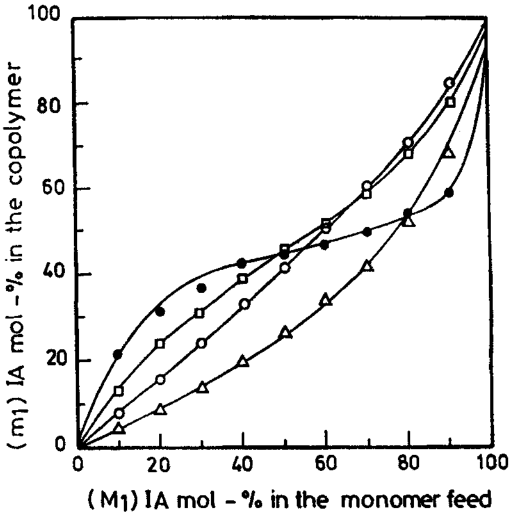


FIG. 1. The comonomer–copolymer composition curves for copolymerization of IA (M_1) in dioxane at 65°C. AIBN = 5 × 10^{-2} mol·L^{-1} with (△) MMA, (○) Am, (□) NVP, (●) EMA.

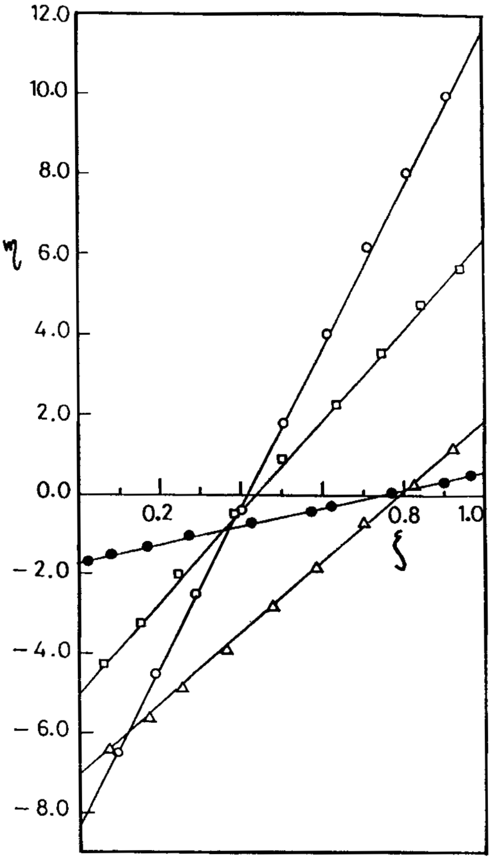


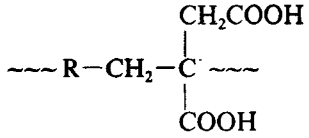
FIG. 2. Kelen–Tüdös plot for IA and (□) NVP, (○) Am, (●) EMA, (△) MMA.

TABLE 5. Reactivity Ratios and *Q*–*e* Parameters for IA [M_1] and Other Monomers [M_2]

	K–T		F–R		Parameters	
M_2	r_1	r_2	r_1	r_2	Q_1	e_1
Am	0.574	1.17	0.599	1.184	2.14	1.89
NVP	0.407	0.64	0.398	0.64	0.057	0.070
EMP	0.054	0.298	0.054	0.298	3.90	2.38
MMA	0.181	2.272	0.180	2.272	0.84	1.33

withdraw electrons from the double bond, rendering it relatively positively charged. The reactivity ratios of IA and other monomers show a tendency toward alternation. The alternation takes place in the following order: EMA > NVP > Am > MMA.

The structure of the obtained copolymer may be



$$\sim\sim\sim R-CH_2-\overset{\overset{\displaystyle CH_2COOH}{|}}{\underset{\underset{\displaystyle COOH}{|}}{C}}\sim\sim\sim$$

where R = NVP, Am, MMA, or EMA.

The calculated values of *Q* and *e* of IA indicate that it is an electron-accepting conjugative monomer.

Characterization of the Copolymers

The FT-IR spectra of the various investigated copolymers are presented in Fig. 3(a-d). The absence of the absorption band at 1640 cm^{-1}, characteristic of the carbon—carbon double bond, in the four investigated systems clearly indicates that a true copolymer is formed in all cases since homopolymer formation should be minimal due to reprecipitation of the copolymers. In Fig. 3(a) the absorption bands at 1652 cm^{-1} illustrate the carbonyl group and the N—H stretching vibration of the Am copolymer, respectively. In Fig. 3(b) the carbonyl group at 1457 cm^{-1} and the C—N stretching vibrating band at 1292.2 cm^{-1} indicate the presence of NVP in the copolymer. On the other hand, the bands that at 2579.6 and 2575.8 cm^{-1} in Fig. 3(b) are assigned to OH stretching (bonding) of the carboxylic group of IA. In Figs. 3(c) and 3(d) the bands that appear at 1728 cm^{-1} are assigned to the C=O group of the vinyl ester of both EMA and MMA, respectively, whereas the bands that appear at 3564.2 and 3544.9 cm^{-1} are assigned to intermolecular H-bonding between the carboxylic groups of IA. The bands that appear in the 2943-2960 cm^{-1} range in all FT-IR spectra indicate the aliphatic C—H stretching vibration.

The x-ray diffractions of the copolymers of itaconic acid with the aforementioned comonomers clearly reveal a decrease in the degree of crystallinity, and an amorphous halo pattern takes place, Fig. 4(a-d). This is quite reasonable because the presence of any of the four comonomers (Am, NVP, EMA, MMA) in the copolymer of IA will be at the expense of the degree of crystallinity of the latter. Moreover, the degree of crystallinity will be inversely proportional to the molar ratio of any of the four monomers in the copolymer feed with IA. On the other hand, the x-ray diffraction curves throw light on the structure and the morphology of the obtained copolymers. The data indicate that the crystallinity of the obtained copolymers increases in the order NVP > Am > MMA > EMA.

Intrinsic viscosity measurements of copolymers of IA with NVP and Am were performed in distilled water; those with ethyl and methyl methacrylate were performed in acetone. All intrinsic viscosity measurements were made at 30 ± 0.1°C. Figure 5 indicates that $[\eta]$ increases with a decrease in the molar ratio of IA in the four investigated systems.

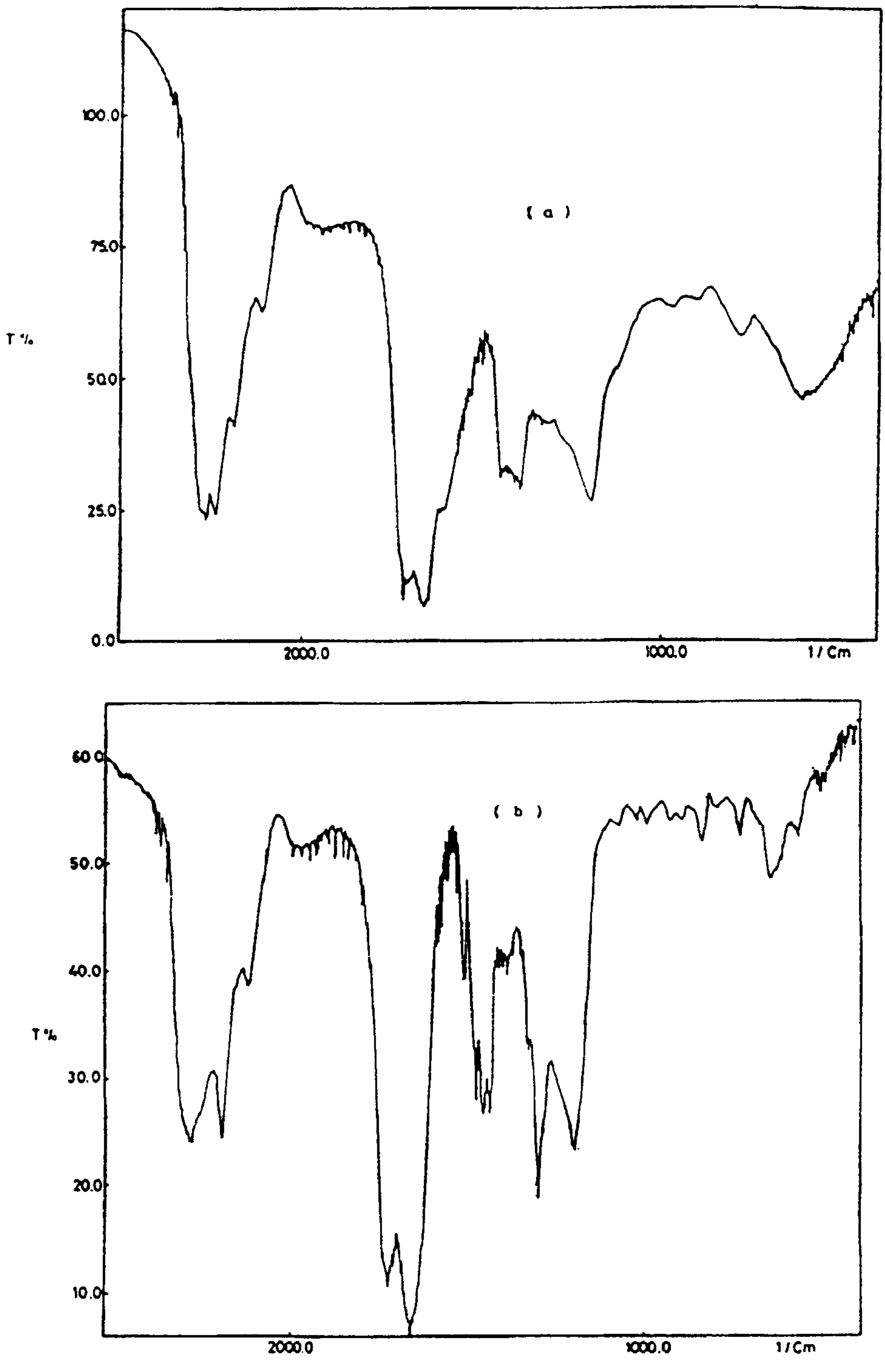


FIG. 3. FT-IR spectra of the copolymer of IA with (a) Am, (b) NVP, (c) EMA, (d) MMA.

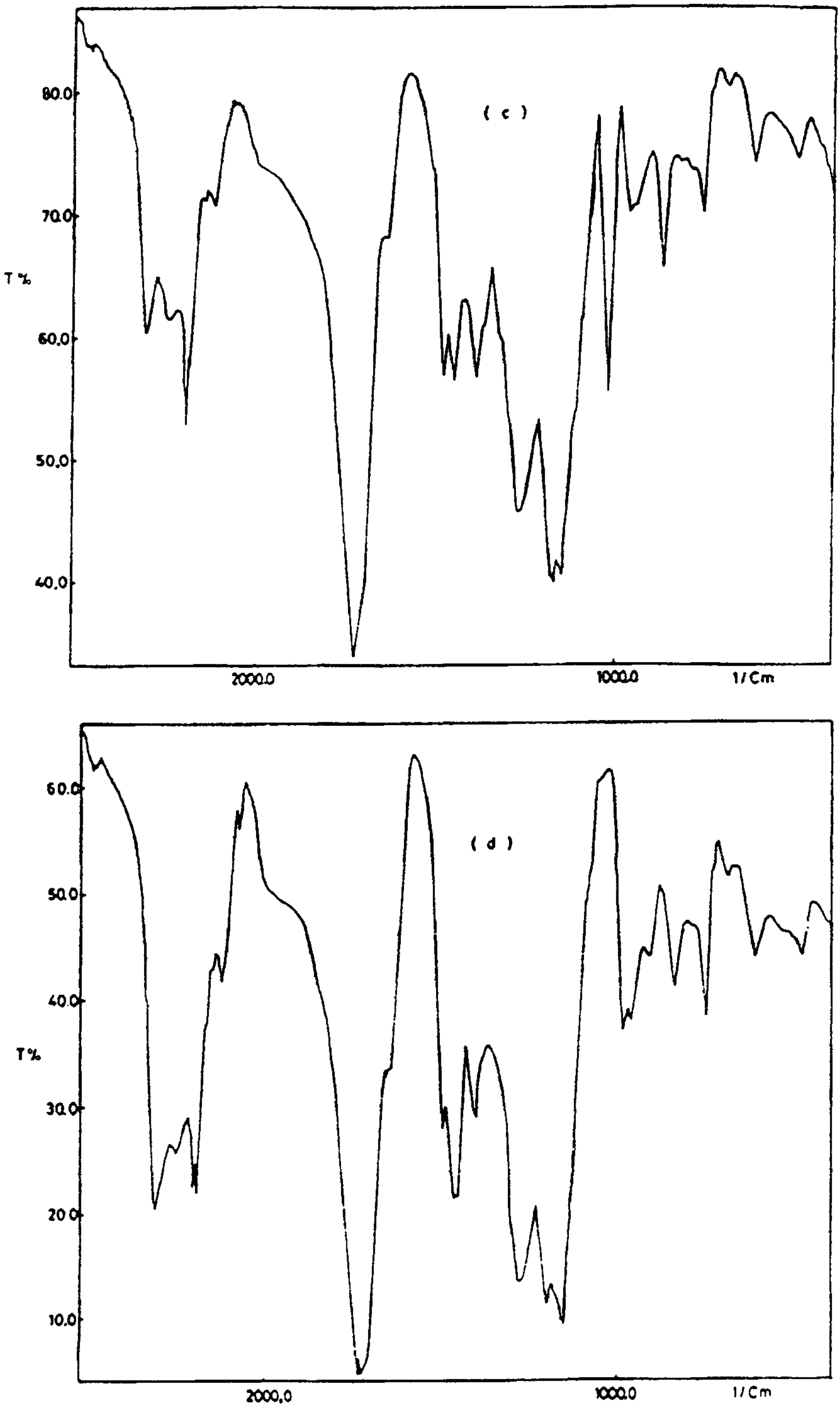


FIG. 3 (continued).

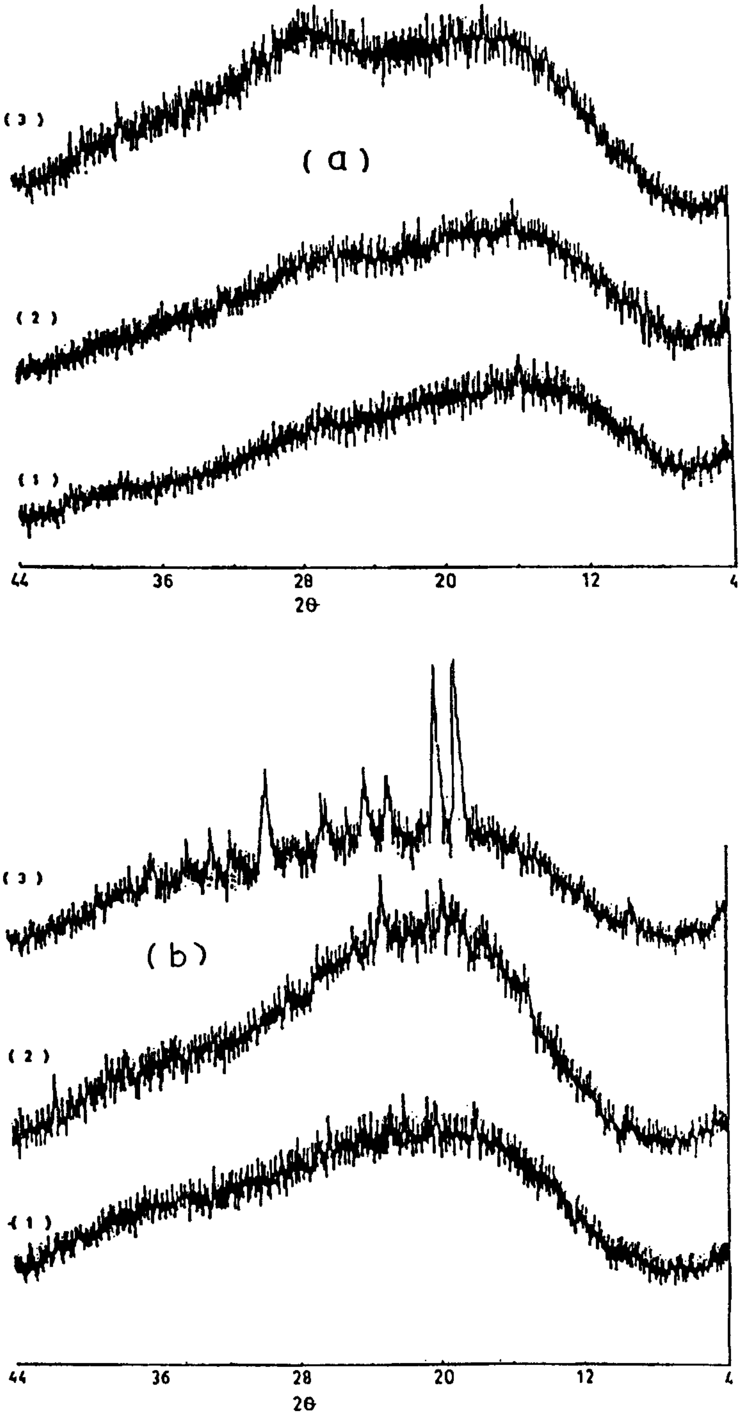


FIG. 4. *X*-ray diffraction of the copolymers. (a) P(IA:NVP) with 1) 31.93:68.07, 2) 46.03:53.97, 3) 60.29:39.71 (mol%). (b) P(IA:AM) with 1) 24.06:75.94, 2) 42.29:57.71, 3) 61.40:38.60 (mol%). (c) P(IA:MMA) with 1) 0.00:100, 2) 26.50:73.50, 3) 41.90:58.10 (mol%). (d) P(IA:EMA) with 1) 44.80:55.20, 2) 50.00:50.00 (mol%).

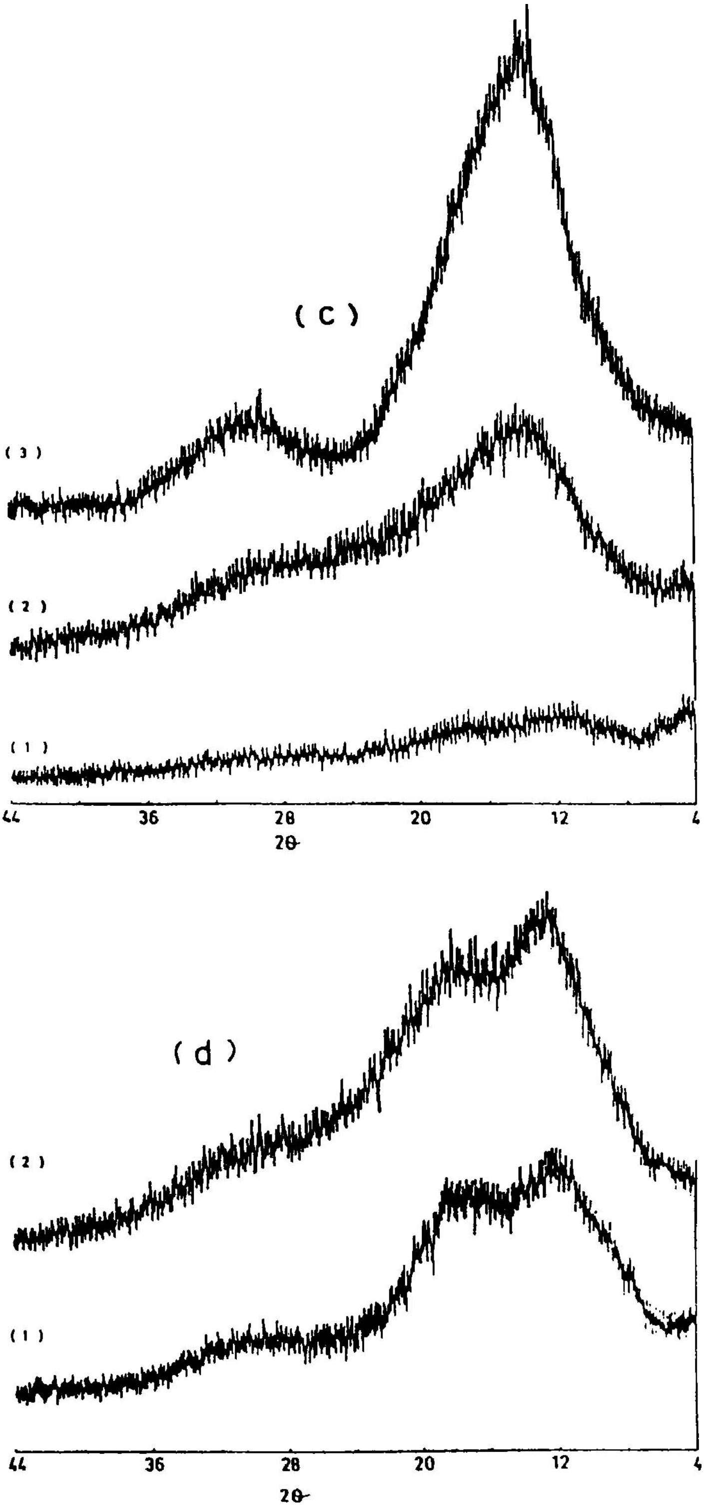


FIG. 4 (continued).

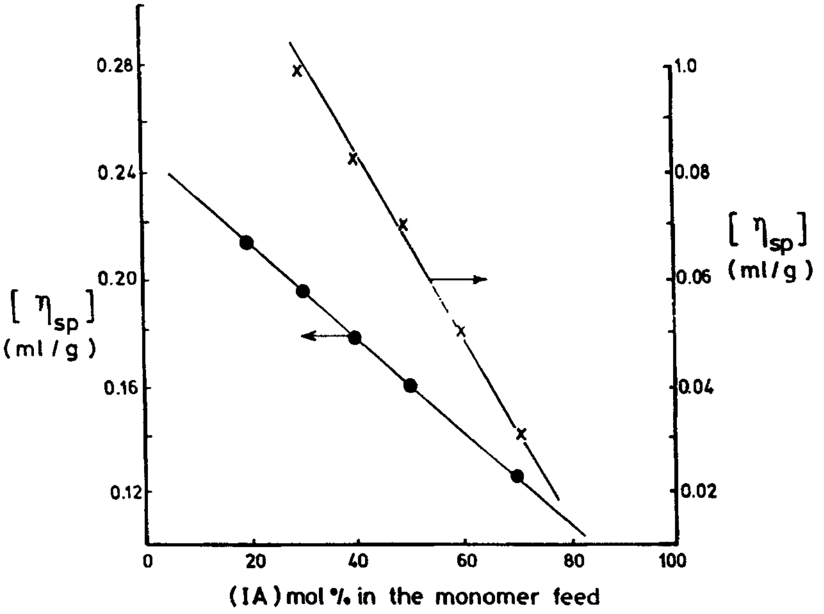


FIG. 5. The intrinsic viscosity-monomer composition relationships for IA with (●) Am, (×) NVP.

Thermal Analysis

As is known from the literature [5], IA homopolymer partially decarboxylates on heating, even under mild conditions, since it loses about 0.25-0.3 mol of CO_2 per monomer unit at 100°C. It was therefore interesting to investigate the thermal stability of the prepared copolymers. The TGA curves of these copolymers are presented in Fig. 6(a-c). Thermogravimetric measurements of itaconic acid-acrylamide and vinylpyrrolidone copolymers were conducted in nitrogen gas while those with methyl methacrylate were measured in air.

The initial temperature (T_{init}) and the final decomposition temperature (T_{fin}) are summarized in Table 6, together with the residual copolymer percentage at 500°C.

The TGA presented reveal the high thermal stability of IA copolymer with NVP as compared with the other copolymers. The copolymer of IA with MMA undergoes a remarkable weight loss (about 5%) at 75°C; this may be attributed to the presence of residual solvent in the system. Generally, the thermal stability of the IA/MMA copolymer system was lower than that of all the others; this may be explained by the fact that the molecular weight of this copolymer is not high [22]. From the data obtained, it is clear that the increase in the molar ratio of IA in the copolymers increases the thermal decomposition of the obtained copolymer. This may be due to the ease of thermal decomposition of the carboxylic group with the subsequent evolution of CO_2 gas. From the results of thermal analyses, one can conclude that a real improvement in the thermal stability of PIA could be achieved through its copolymerization with other monomers. In this respect, further studies are needed.

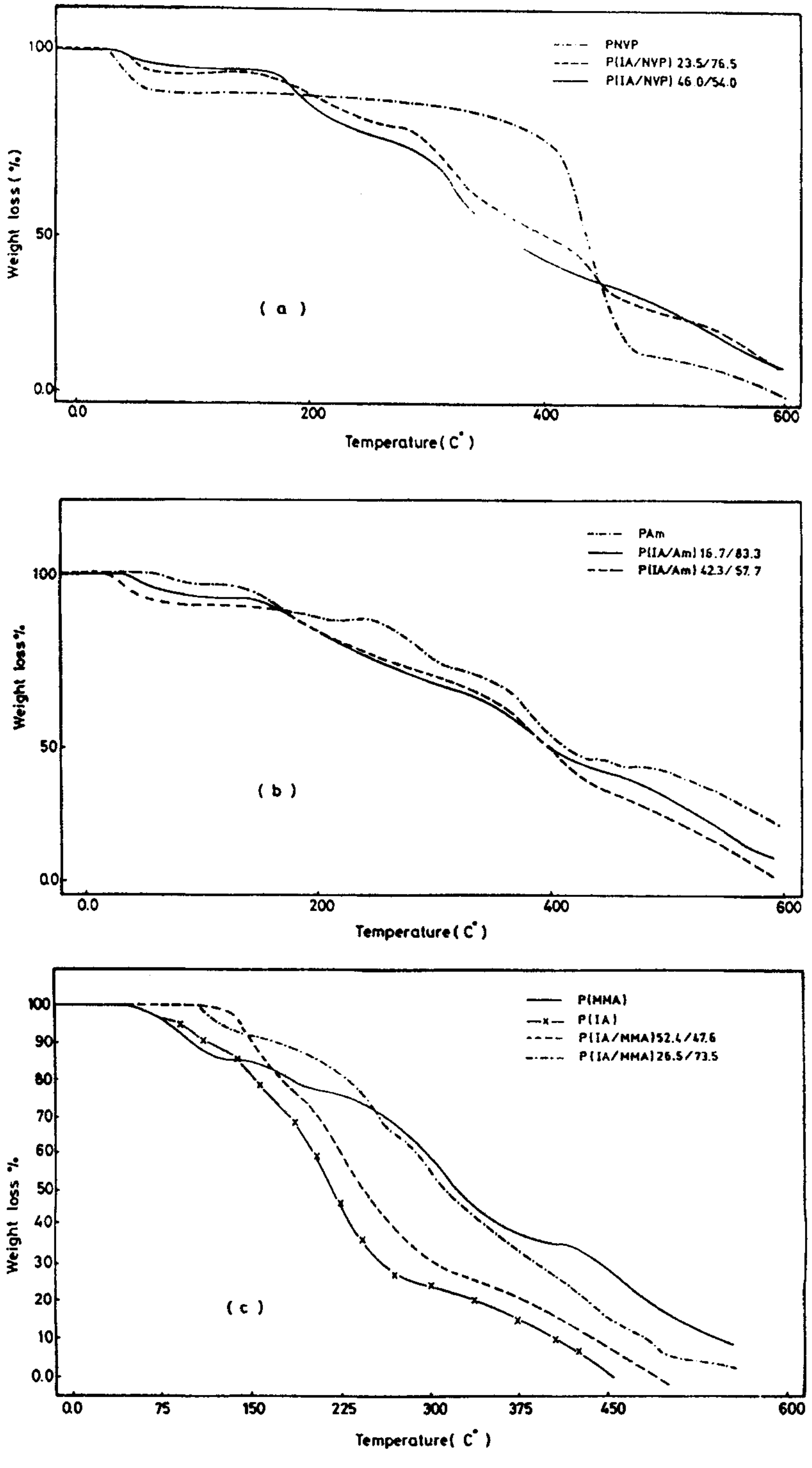


FIG. 6. TGA curves for IA with (a) NVP, (b) Am in a N_2 stream with a heating rate of 10°/min, (c) MMA in air with a heating rate of 10°/min.

TABLE 6. Thermogravimetric Analysis of IA Copolymers

Polymer	mol%	T_{init}, °C	Residual at 500°C, %	T_{fin}, °C
PIA	–	140	10.0	450
PAm	–	242.9	50.0	600
PNVP	–	300	22.0	600
PMMA	–	120	35.5	555
P(IA/Am)	16.71/83.29	150	30.0	600
P(IA/Am)	42.29/57.71	140	25.0	600
P(IA/NVP)	23.54/76.46	173.1	41.0	600
P(IA/NVP)	46.03/53.97	200	28.0	600
P(IA/MMA)	31.90/68.10	130	25.7 (400°C)	555
P(IA/EMA)	58.82/41.18	75	19.3 (400°C)	495

CONCLUSION

The reactivity ratios (r_1, r_2), Q, and e of the copolymerization of itaconic acid with four different monomers show a tendency toward alternation, and IA is an electron-accepting conjugative monomer. The presence of IA in the copolymer increases the crystallinity of the copolymers obtained. Also, the viscosity measurements and the thermal stabilities of the copolymers increase with a decrease of the molar ratio of IA in the copolymer composition.

Therefore, the copolymerization of itaconic acid with different monomers may improve the physical properties and thermal stability of PIA.

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