Radical Polymerization and Copolymerization Behavior of N-Acryloyl N'-Cyanoacetohydrazide

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ABSTRACT: The radical polymerization and copolymerization of N-acryloyl N'-cyanoacetohydrazide (ACAH), were carried in dimethyl formamide in presence of azobisisobutyronitrile as initiator and kinetic studies on the polymerization behavior of ACAH, conducted. Complex formation of ACAH monomer and polymer (PACAH) with Cu(II) and Fe(II) cations was investigated and the stability constant determined. The rate of copolymerization of ACAH with some conventional monomers named vinyl acetate, methyl methacrylate, and acrylonitrile was measured as a function of mole fractions of comonomers. The reactivity ratios (r_1, r_2) for the various investigated copolymer systems with the Q and e values of ACAH monomer were determined. The thermal gravimetric analysis of prepared polymer and copolymers with acrylonitrile was done.
    KEY WORDS   Polymerization / Copolymerization / Reactivity Ratios /

Synthesis of new polymer ligands has great importance in both academic and applied points of view.[1-6] The polymer metal complex could have catalytic activities[1,5] and may offer an excellent model for metalloenzymes.[1]

N-Acryloylbenzhydrazide (ABH) has been synthesized and polymerized by Tazuke and Nakamura.[6] Polymerization was performed by both free radical and anionic mechanism of polymerization. The monomer reactivity ratios for radical copolymerization of ABH with styrene and acrylonitrile were investigated. The polymer formed a stable chelates with copper ions.

N-Acryloyl N'-cyanoacetohydrazide (ACAH) has been synthesized for the first time in our laboratory as a new water soluble chelating monomer.[3] This new monomer readily undergoes free radical polymerization in aqueous and non-aqueous media. The thermal behavior of poly(ACAH) and its copper and nickel complexes was also investigated. Until now no kinetic studies on its polymerization have been published. Consequently, it is of interest to evaluate the rate of polymerization of ACAH and factors affecting it. This work measured the copolymerization of this new monomer with some conventional monomers. Some characterization of the prepared poly(ACAH) and its copolymers including thermal behavior and complexation with some metal cations was done.

EXPERIMENTAL

Materials

ACAH was prepared as previously.[3] The structure was confirmed by ^{1}H NMR (Varian 200 MHz) and ^{13}C NMR (Bruker MSL, 300 MHz) (Figure 1a), as well as by FT-IR spectroscopy (8201 PC Shimadzu).

Vinyl acetate (VA) (Aldrich Chem.), methyl methacrylate (MMA) (Koch, Light), and acrylonitrile (AN) (BDH) were distilled just before use. $ZnCl_2$ (Prolabo, France) was dried at 120°C under vacuum. Azobisisobutyronitrile (AIBN) (E. Merck) was recrystallized twice from methanol (mp 104°C). Other solvents and reagents are all analytical grades and used as such.

Experimental Techniques

1. Polymerization and Copolymerization Processes

a) Determination of the Rate of Homo and Copolymerization   The rats of homopolymerization and copolymerization were measured dilatometrically using pyrex glass dilatometers with calibrated and graduated capillary tubes with bulb capacity of 3—5 ml, and fitted with ground joint. The monomer(s) with required amount of initiator (AIBN) were dissolved in dimethylformamide (DMF). Monomer concentration was determined in mole/liter. The reaction mixture was transferred to the dilatometer. The dilatometer was placed in a water thermostat adjusted to the required temperature (± 0.1°C). Change in volume (ΔV) was plotted *versus* time of polymerization. At the end of the polymerization, the dilatometer was removed from the water thermostat and quickly immersed in an ice-water–salt mixture to stop the radical polymerization reaction. The polymeric solution was withdrawn using a vacuum line, and precipitated in cold ethanol, filtered, washed several times with ethanol and finally dried in an air oven at 60°C until constant weight. The degree of conversion was then calculated gravimetrically. The structure of the polymer was confirmed by both ^{1}H NMR and ^{13}C NMR as shown in Figure 1b.

b) Copolymerization Procedure   Glass vials were charged with the required amounts of the two monomers together with the required amount of initiator and DMF as solvent. The vials were then closed with rubber septum through which passed two needles, one for bubbling purified nitrogen to eliminate dissolved oxygen and a second to equilibrate the pressure. The copolymerization was performed at 60 ± 0.1°C in a water thermostat with periodical shaking for a definite time in such a way to keep always the conversion below 10%. At that time, the copolymerization reaction was brought to a stop by cooling the vials in an ice-water–salt mixture followed by pouring the contents into a large amount of cold
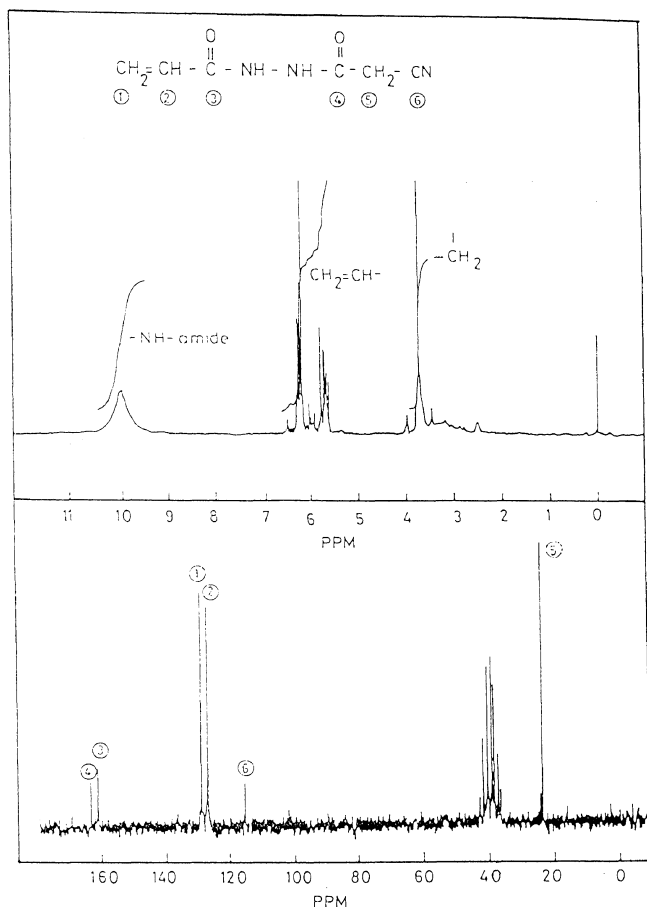
Figure 1a. ^1H and ^{13}C NMR spectra of ACAH in DMSO.
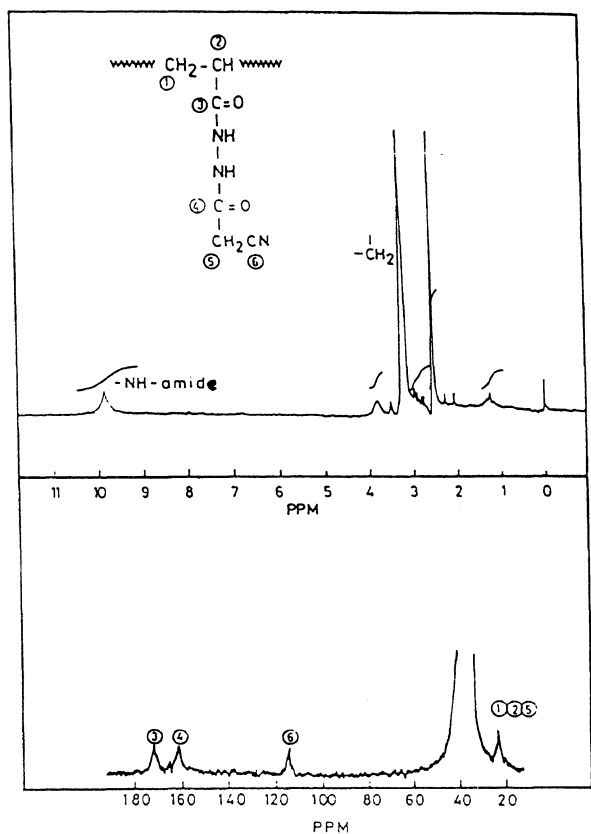

Figure 1b. ^1H and ^{13}C NMR spectra of PACAH in DMSO.
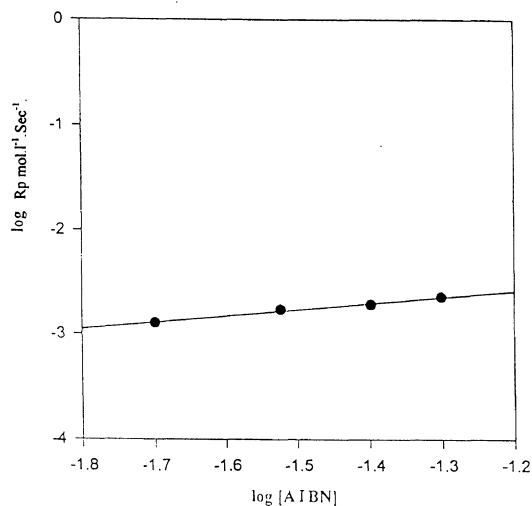

Figure 2. Effects of initiator concentration on the rate of polymerization of ACAH at 60°C, $[M] = 1.0 \, mol \, l^{-1}$.

ethanol. The copolymers were purified by reprecipitation in cold ethanol and allowed to dry under high vacuum at room temperature.

c) Copolymerization Analysis The copolymer composition was calculated on the basis of the nitrogen content of the copolymers, at the Central Micro Analytical Unit in Cairo University.

2. Preparation of Monomer and Polymer Metal Complexes

Copper and iron complexes of ACAH monomer and its corresponding polymer were prepared by mixing the monomer or the polymer with copper acetate or ferrous sulfate in various molar ratios ranging from zero to 100% dissolved in H_2O or DMF.

The stability constants of the prepared complexes were determined by the continuous variation method.[7] The UV-Vis spectra of the complexes was recorded (the spectra of the complexes were measured at wave length equal 271.9 mu and 210.1 mu in DMF and H_2O, respectively) using Perkin-Elmer, Lambda 3 spectrophotometer equipped with a thermostated cell. The temperature was adjusted at $20 \pm 0.1°C$.

3. Viscosity Measurements

Viscosity measurements were carried out using an Ubbelohde suspended level dilution viscometer. DMF was used as solvent with a flow time of 133 seconds at 30°C.

4. Thermal Analysis

Thermal gravimetric analysis (TGA) was conducted using Shimadzu DSC 50.

RESULTS AND DISCUSSION

The dependence of the rate of polymerization of ACAH monomer on the initiator concentration is illustrated in Figure 2. The polymerization reactions were performed in DMF at 60°C at a constant monomer concentration of $1.0 \, mol \, l^{-1}$. A straight line was obtained when log of the initial rate of polymerization was plotted *versus* log initiator concentration. The slope of the line a kinetic orders (n) with respect to initiator, which is equal to 0.41, indicating termination to occur mainly bimolecularly.
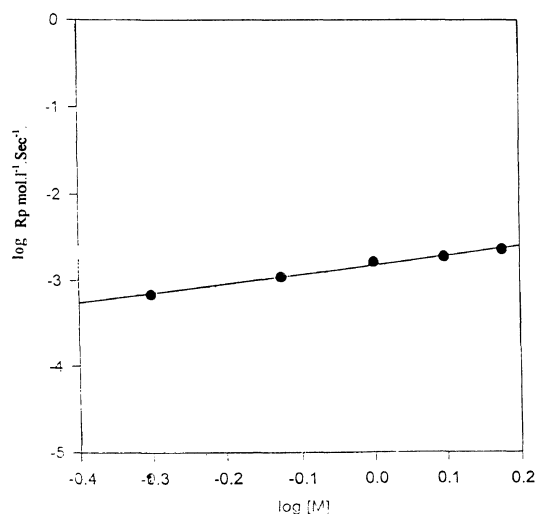
Figure 3. Effects of monomer concentration on the rate of polymerization of ACAH in DMF at 60°C, [AIBN] = 0.03 mol l⁻¹.
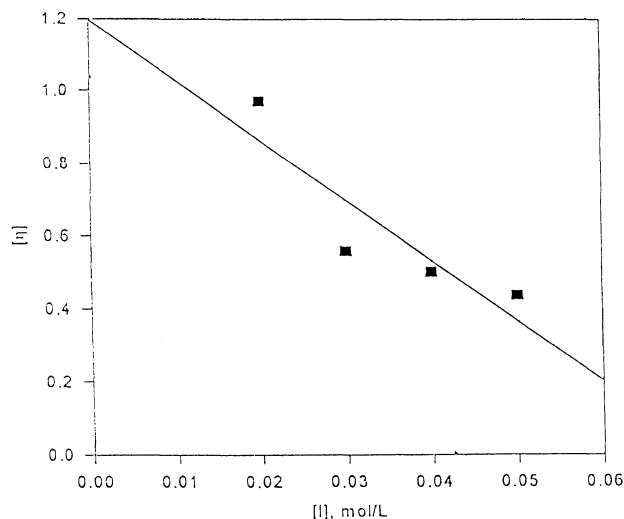

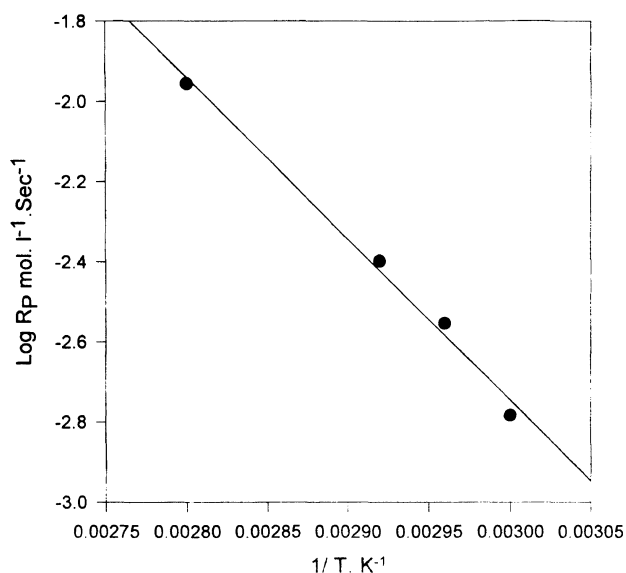**Figure 5.** Dependence of the intrinsic viscosity of PACAH on the initiator concentration.

Figure 4. Effects of temperature on the rate of polymerization of ACAH in DMF. [M] = 1 mol l⁻¹, [AIBN] = 0.03 mol l⁻¹.

Figure 6. Dependence of the intrinsic viscosity of PACAH on the monomer concentration.

Figure 3 illustrates the dependence of the rate of polymerization of ACAH as a function of monomer concentration. The amount of initiator was kept constant at $0.03 \, mol \, l^{-1}$, and the temperature was fixed at 60°C. The log–log plots of the rate of polymerization *versus* monomer concentration give straight lines, the slopes of which give the order of the reaction (m) equal to 1.1 by applying the following equation

$$R_p = K[M]^m \cdot [I]^n \qquad (1)$$

where K is the overall polymerization rate constant $(K = K_p(K_d/K_t)^{1/2})$ K_p is the rate constant of propagation step, K_t is the rate constant of termination, and K_d is the rate constant of initiator decomposition. m (1.1) was a little higher than the usual order of magnitude which is 1.0 characteristic for free radical polymerization. This may be attributed to steric and solvent effect.

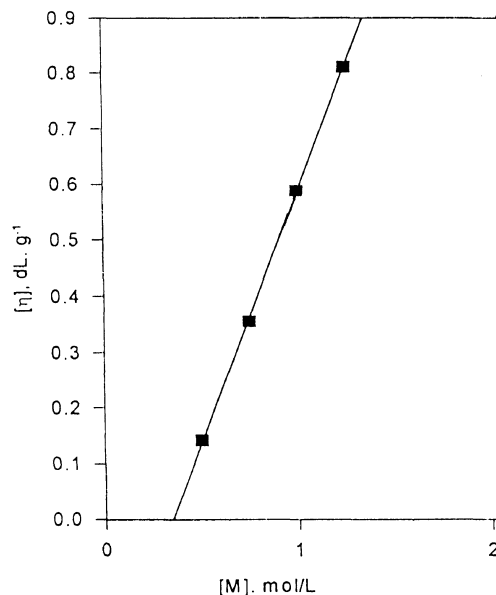The effect of temperature on the polymerization of ACAH is represented in Figure 4. The activation energy

(ΔE) which is a composite of $E_p + 1/2 \, E_d - 1/2 \, E_t$ (where E_p refers to the energy of propagation, E_d to initiator decomposition, and E_t to termination) was found to be $19.3 \, kcal \, mol^{-1}$, which is normal for a free radical polymerization.

The dependence of the intrinsic viscosity [η] on monomer and initiator concentrations are represented in Figures 5 and 6, respectively. Viscosity measurements were carried out in dimethyl formamide at 30°C. [η] increased with monomer concentration and decreased with increase in initiator concentration.

Complexation Behavior of the Prepared Monomer and Polymer

The structure of the prepared monomer with its function side group warrant its investigation as chelating monomer.
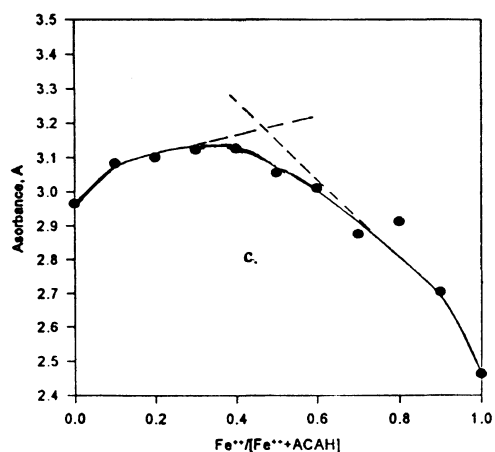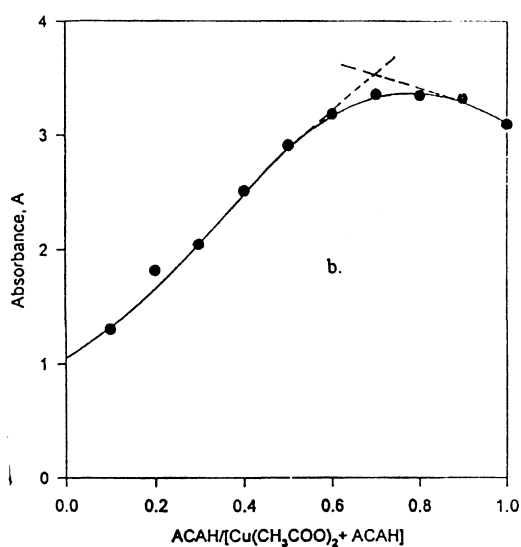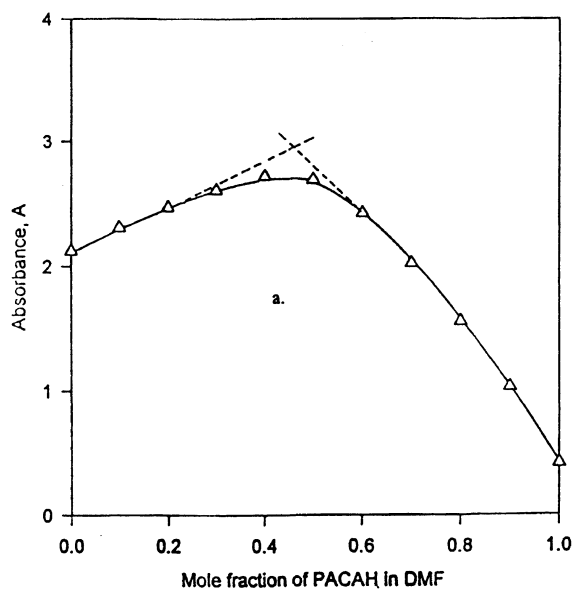
$$CH_2 = \underset{|}{CH}$$
$$CONHNHCOCH_2CN$$

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Figure 7. Complexation of ACAH with: a, Cu(II) acetate in DMF; b, Cu(II) acetate in H_2O; c, $FeSO_4$ in DMF.

Table I. Complexation data for ACAH and polymer

Compound	Metal ion	Solvent	K^a	Type of comp.
ACHA	Cu^{2+}	H_2O	3.2×10^{-6}	2 : 1
ACAH	Cu^{2+}	DMF	1.7×10^{-6}	1 : 1
PACAH	Cu^{2+}	DMF	4.1×10^{-6}	1 : 1
ACAH	Fe^{2+}	DMF	5.3×10^{-7}	1 : 1
PACAH	Fe^{2+}	DMF	—	—

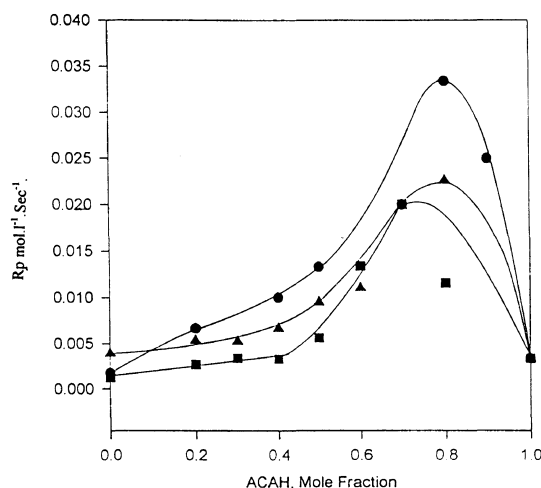[a] Dissociation constant equal to $1/K_{stab}$.

Figure 8. Rate of copolymerization of ACAH with: ▲, AN; ■, VA; ●, MMA, in DMF at 65°C; [AIBN] = 0.03 moll^{-1}; total monomer concentration, 1 moll^{-1}.

variation method. Complexation of ACAH and PACAH with Cu(II) and Fe(II) are shown in Figure 7. The dissociation constants of different complexes are compiled in Table I. PACAH did not give a maximum when reacted with Fe^{2+} cations, and consequently no stability constant calculation was possible. Stability constant was high indicating strong and stable complexes between the monomer or its polymer with different cations. From these data, one may conclude that the investigated monomers could be used for ion exchange resins or modification of natural polymers.

Copolymerization Behavior of N-Acryloyl N'-Cyanoaceto-hydrazide

The copolymerization behavior of ACAH with three conventional monomers namely VA, MMA, and AN was investigated. The copolymerization reactions were carried out in DMF at 65°C. The rate of copolymerization of the investigated systems was measured dilatometrically. The time of copolymerization reactions was adjusted in such a way to keep always conversion below 10%. Figure 8 represents the variation of the copolymerization rates as a function of monomer composition (*i.e.*, the mole fraction of the two comonomers). The absence of any maxima around the 0.5 mol fraction which indicates the absence of strong association between ACAH and conventional investigated monomers.

The compositions of the monomers feed mixtures and that of the copolymers for the investigated systems including the effect of Lewis acid ($ZnCl_2$) are compiled in Table II. The monomer–copolymer composition

ACAH and PACAH showed a strong chelation. Cu(II) and Fe(II) cations were used for this investigation. The stability constant or the dissociation constant of the formed complexes was estimated by the continuous

Table II. Copolymerization data for ACAH (M_1) and monomers

Monomer composition ACAH (M_1) mol%	a) VA			b) MMA			c) MMA ($ZnCl_2$)		
	N%	Copolymer composition ACAH (M_1)		N%	Copolymer composition ACAH (M_1)		N%	Copolymer composition ACAH (M_1)	
		wt%	mol%		wt%	mol%		wt%	mol%
10	8.57	31.22	20.37	2.64	9.61	6.50	3.99	14.53	12.65
20	12.57	45.79	32.19	5.05	18.41	12.85	7.61	27.67	22.73
30	15.06	54.88	40.61	7.28	26.55	19.11	10.89	39.60	31.24
40	16.93	61.66	47.48	9.39	34.22	25.37	13.88	50.50	38.84
50	18.50	67.41	53.76	11.41	41.58	31.75	16.63	60.47	46.02
60	19.98	72.81	60.08	13.42	48.88	38.46	19.15	69.65	53.25
70	21.49	78.30	66.98	15.81	56.50	45.91	21.48	78.12	61.08
80	23.14	84.32	75.14	17.89	65.81	55.02	23.63	58.96	70.29
90	25.07	91.32	85.14	21.12	79.93	68.55	25.63	93.23	82.26
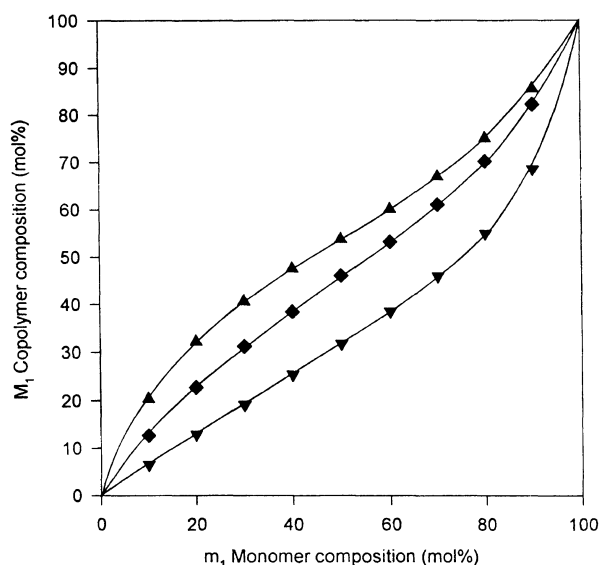
Figure 9. Monomer–copolymer composition curves for copolymerization of ACAH (M_1) in DMF at 65°C with: ▲, VA; ■, MMA; ▼, MMA (in presence of $ZnCl_2$).

Table III. Reactivity of copolymerization of ACAH (M_1) and monomers

Monomer	F-R		K-K		NLLS	
M_2	r_1	r_2	r_1	r_2	r_1	r_2
VA	0.572	0.352	0.572	0.348	0.579	0.350
MMA	0.183	1.830	0.172	1.519	0.172	1.510
MMA (in presence of $ZnCl_2$)	0.443	0.693	0.444	0.693	0.511	0.740

curves for the three systems using theoretical curves and experimental points are represented in Figure 9. The reactivity of the investigated systems has been calculated by Fineman–Ross,[8] Kelen–Tüdos,[9] and non-linear least squares.[10,11] All the data are compiled in Table III. The addition of Lewis acid in the polymerization or copolymerization system improves the reactivity of functional monomers.[12,13] The effect of $ZnCl_2$ on the reactivity of ACAH when copolymerization with MMA was investigated. Considerable improvement of $ZnCl_2$ (only 1%) where r_1 increased from 0.172 to 0.511, since $ZnCl_2$ associates with ACAH monomer through its carbonyl group, thus increasing electron accepting
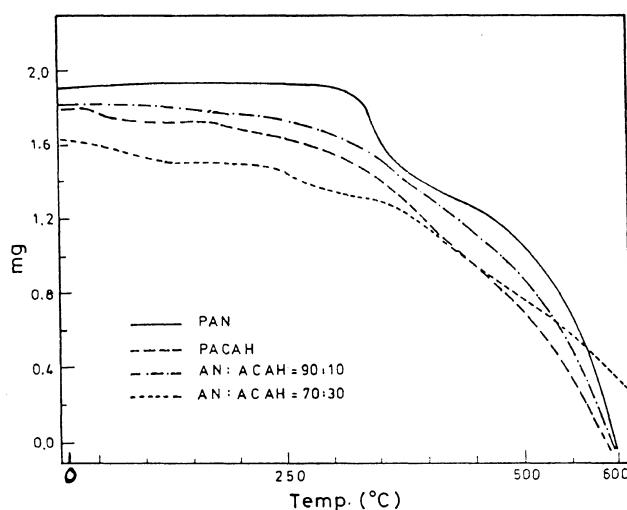
Figure 10. Thermogravimetric analysis in nitrogen atmosphere of PACAH, PAN, and copolymers.

ability. On colliding with the second monomer, the Lewis acid is liberated again.

Though we could measure the rate of copolymerization of ACAH/AN system, it was impossible for us to obtain meaningful values of AN with ACAH, and consequently, we could not construct a copolymerization curve for this copolymerization system and we did not determine reactivity of this system.

From the data of reactivity (Table III), it seems that ACAH has no tendency for alternation with different comonomers, but the empirical parameters Q and e for this new monomer were calculated. Positive e for ACAH was chosen, because a negative value could not be taken based on the chemical structure of the monomer which has electron attracting groups ($-C=O$ and $-C\equiv N$). The average Q_{ACAH} was 0.45 and e_{ACAH} 1.14.

Thermal Behavior of Poly(ACAH) and Copolymers with AN

The thermal stability of polyacrylonitrile (PAN) and copolymers has attracted attention,[14–17] and therefore, it was of interest to investigate the effects of some units of ACAH on the back bone of the industrially important PAN. Figure 10 illustrates TGA data of PACAH, PAN, and their copolymers. Analysis was performed under nitrogen at a heating rate of 10°C min^{-1}. Poor thermal

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stability of PACAH as compared with PAN was noted. The initial decomposition temperature for PACAH is around 232°C and the weight loss was 11.2% and 82—87% at 250°C and 600°C, respectively, the results show decrease of the thermal stability of the copolymers with the increase in the percent of ACAH in the copolymer. This acceleration of decomposition may be due to the inhibiting effect of ACAH on the nitrile oligomerization of PAN. It can be concluded that ACAH units initiate and accelerate the thermal degradation of ACAH/AN copolymers.

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