

KINETIC PARAMETERS OBTAINED FROM TG AND DTG CURVES OF ACRYLAMIDE–MALEIC ANHYDRIDE COPOLYMERS

R. Vîlcu, F. Irinei, J. Ionescu-Bujor, M. Olteanu and I. Demetrescu

PHYSICAL CHEMISTRY DEPARTMENT, BD. REPUBLICII 13, BUCHAREST, ROMANIA

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The thermal behaviour of acrylamide–maleic anhydride copolymers was studied by thermogravimetric (TG and DTG) analysis. The obtained data permitted the calculation of activation energies and reaction orders of the decomposition steps by the Coats–Redfern and Freeman–Carroll methods.

Thermal analysis shows four distinct peaks in the case of polyacrylamide and AA:MA (7:1) copolymer and only three for AA:MA (1:1) copolymer.

In AA:MA (1:1) copolymers intermolecular imidization occurs only and thermal degradation is influenced more by the anhydride groups which are equal in number with the amide ones.

The effects of the monomer ratio and of the solvent in which the copolymer was prepared upon the physico-chemical properties of the copolymer are well known as important factors (e.g. [1]).

In this paper we have made a comparative study of the thermal degradation of a new acrylamide–maleic anhydride (AA–MA) copolymer [2], which was prepared in three different solvents (benzene, dioxane and methyl ethyl ketone) at several monomer ratios.

Experimental

Materials

Solvents: p.a. grade benzene, dioxane and methyl ethyl ketone. Acrylamide (AA): recrystallized from benzene, melting point = 85°. Maleic anhydride (MA), melting point = 56°. 2,2'-Azobisisobutyronitrile, purum.

The copolymerization of acrylamide with maleic anhydride was carried out in the presence of 2,2'-azobisisobutyronitrile as initiator at 65°.

Acrylamide polymerization in benzene was performed under the same conditions. The copolymer composition [3] was determined by means of the Kjeldahl method and by potentiometric titration of the acidic groups. The reactivity ratios indicate an

alternating structure for the 1:1 AA:MA copolymer, and a random structure for the 6–7:1 AA:MA copolymers.

Molecular weight was determined by means of light scattering (\bar{M}_g) and viscosimetry (\bar{M}_v) [4, 5] in 0.6 *N* NaNO₃ solution at 25°. In the case of polyacrylamide $\bar{M}_v = 1.35 \times 10^6$ and in the case of the copolymers the molecular weight is between 1.25×10^4 and 11×10^4 . Random copolymers have higher molecular weights.

Apparatus and procedure

A TGS 2 Perkin–Elmer thermobalance was used. Thermal decomposition of the copolymers was carried out in an inert medium (argon) at constant heating rates (5, 10 and 20 deg/min). The sample size was 5–7 mg.

Infrared spectra were recorded using a UR-10 Karl Zeiss (Jena) spectrophotometer, within the range 400–4000 cm⁻¹, on pellets containing 0.3 KBr and 0.002 g copolymer.

Results and discussion

TG and DTG curves for polyacrylamide and AA:MA copolymers are presented in Figs 1–7; the samples were heated at a rate of 20 deg/min.

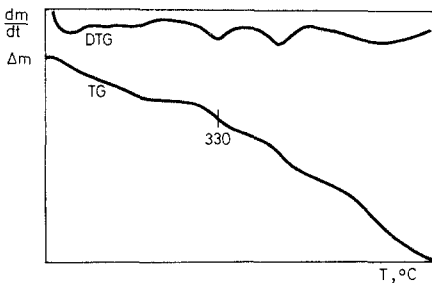


Fig. 1 TG and DTG curves of polyacrylamide ($\bar{M}_v = 1.35 \cdot 10^6$)

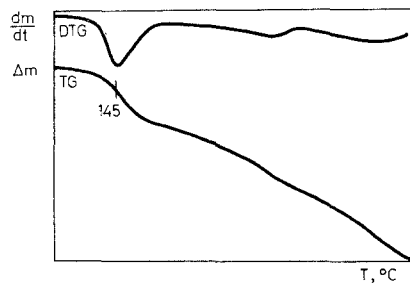


Fig. 2 TG and DTG curves of copolymer AA:MA (1:1) in benzene

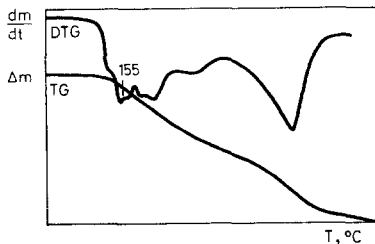


Fig. 3 TG and DTG curves of copolymer AA:MA (1:1) in dioxane

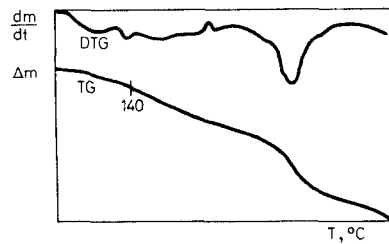


Fig. 4 TG and DTG curves of copolymer AA:MA (1:1) in methyl ethyl ketone

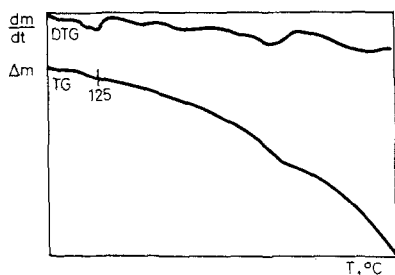


Fig. 5 TG and DTG curves of copolymer AA: MA (7: 1) in benzene

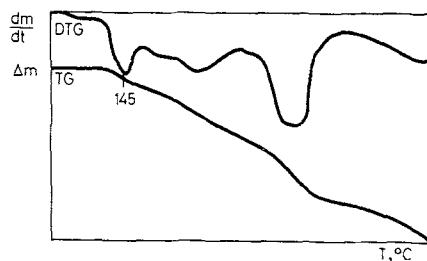


Fig. 6 TG and DTG curves of copolymer AA: MA (6.3: 1) in dioxane

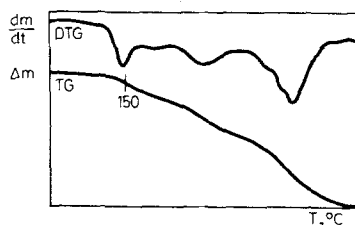


Fig. 7 TG and DTG curves of copolymer AA: MA (6: 1) in methyl ethyl ketone

Table 1 lists the characteristic temperatures of the decomposition steps and the corresponding weight losses.

Table 2 shows kinetic parameters, activation energies and reaction orders, calculated for the decomposition steps by the differential Freeman–Carroll method [6] and by the integral Coats–Redfern [7] method, using a modified Fortran programme [8].

It must be pointed out that in the case of the thermal degradation of polymers the calculated kinetic parameters depend on the experimental conditions (heating rate, sample weight, etc.). The kinetic parameters of degradation were evaluated from the experimental data at a heating rate of 20 deg/min, for in this case the separation of the decomposition steps is more pronounced than under other conditions.

As can be seen in Figs 1–7, both polyacrylamide and copolymers with a high content of this monomer (Figs 1, 5, 6 and 7) give four distinct peaks (DTG curves), while the random copolymers (Figs 2–4) give only three peaks.

The first thermal decomposition stage is due to water loss (from the polymer matrix); the weight loss in this step is 5–8% for the copolymers, and 11.5% for polyacrylamide. The activation energy $E = 60$ kJ/mol and the value of 1 for n (the order of reaction) are characteristic for such processes [9].

The second decomposition stage may be connected with the beginning of reactions involving the side-groups: imidization with NH_3 and elimination and decarboxylation

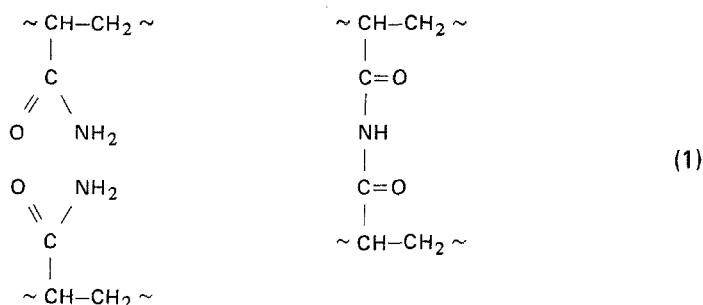
Table 1 Characteristic temperatures and weight loss of copolymers (AA : MA) (heating rate 20 deg/min)

Nr.	Probe	Range I		Weight loss, %	Range II		Weight loss, %	Range III		Weight loss, %
		Temperature, °C a	Temperature, °C b		Temperature, °C a	Temperature, °C b		Temperature, °C a	Temperature, °C b	
1.	Polyacrylamide	50	85	11.5	135	190	4.5	230	325	17
2.	AA : MA (1 : 1) in benzene	50	80	5	120	170	17.5	230	270	8.5
3.	AA : MA (1 : 1) in dioxane	50	90	8	140	190	9	230	270	10
4.	AA : MA (1 : 1) methyl ethyl ketone	50	80	7.5	140	170	16.5	230	270	8
5.	AA : MA (7 : 1) in benzene	50	95	6	130	220	4	230	265	11.5
6.	AA : MA (6.3 : 1) in dioxane	50	80	6.5	120	155	14	230	275	9.5
7.	AA : MA (6 : 1) in methyl ethyl ketone	50	125	6.5	170	187	9.5	230	270	11.5

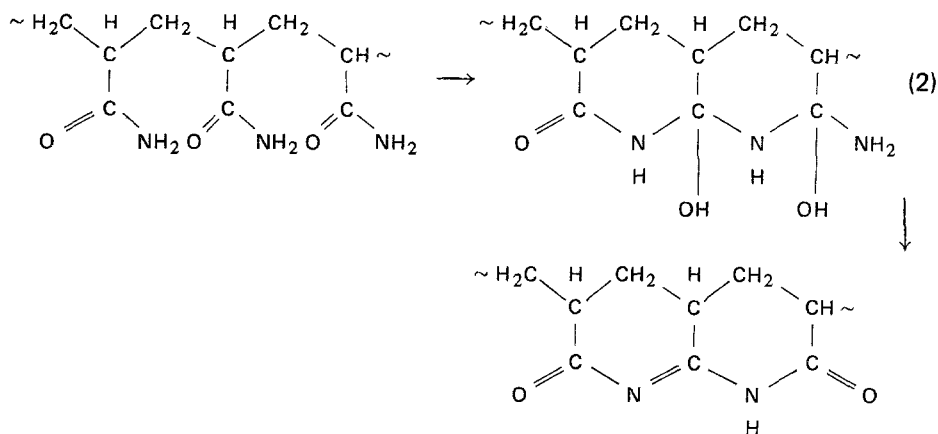
a = initial temperature, b = temperature of maximum weight loss.

of maleic anhydride. The literature data [10] indicate a first-order reaction for both formation of the imide functional group and evolution of ammonia, with an apparent activation energy of 40–60 kJ/mol in the temperature range 175–300°. The data from this paper for a polyacrylamide with $\bar{M}_V = 1.35 \times 10^6$ in the temperature range 135–230° are $E = 77$ kJ/mol and $n = 1$. The acrylamide-rich copolymers have almost the same kinetic parameters. 1:1 AA:MA copolymer has an activation energy close to this value, but the reaction order is higher.

In the case of alternating copolymers, the formation of the imide functional group occurs only as an intermolecular reaction, according to the following reaction:



In the case of polyacrylamide and random copolymers, the formation of imide takes place both intermolecularly and intramolecularly, via cyclization:



In random copolymers, imidization occurs at the same time with anhydride group reactions.

In the third range, at 230–320° for copolymers and 230–370° for polyacrylamide, the reactions of side-groups still continue, together with some main chain scissions. In this stage polyacrylamide has a high activation energy (149 kJ/mol!).

The 6:1 AA:MA copolymer, prepared in methyl ethyl ketone (MEK) as solvent, displays a higher tendency to alternation in comparison to copolymers prepared in

Table 2 Kinetic parameters of the thermal degradation of copolymers AA:MA) (heating rate 20 deg/min)

Nr.	Probe	Range I		Range II		Range III	
		<i>n</i>	<i>E</i> , kJ/mole	<i>n</i>	<i>E</i> , kJ/mole	<i>n</i>	<i>E</i> , kJ/mole
1.	Polyacrylamide	1	65±3	1	77±2	2	149±6
2.	Copolymer AA:MA (1:1) benzene	1	57±2	1.4	42±2	—	—
3.	Copolymer AA:MA (1:1) dioxane	1	65±2	2	71±3	—	—
4.	Copolymer AA:MA (1:1) methyl ethyl ketone	1	44±2	2	68±3	—	—
5.	Copolymer AA:MA (7:1) benzene	1	71±3	0.8	79±4	1	136±4
6.	Copolymer AA:MA (6.3:1) dioxane	1	69±3	1	55±2	1	82±3
7.	Copolymer AA:MA (6:1) methyl ethyl ketone	0.2	19±1	1	52±3	0.4	36±1

benzene or dioxane. This tendency is justified by the small value for the product of the reactivity ratios (0.027). The AA:MA copolymer in MEK might undergo some imidization on synthesis (up to 30% insoluble substance). This copolymer displays much smaller activation energies and a fractional reaction order in all decomposition steps. All studied samples have a peak (DTG curve) with maximum at 420°, associated with an activation energy of ~ 160 kJ/mol and a weight loss of ~ 30%. This thermal decomposition stage is connected with the random scission of the main chain characteristic for such vinyl polymers [11].

At a temperature of around 500°, all studied copolymers and polyacrylamide display a weight loss = 60%, the total loss being completed at 650°.

This behaviour is supported by the IR spectral data. The spectrum of the 1:1 AA:MA copolymer heated at 170° presents characteristic absorptions of the imide group ($\nu_{C=O}$ in the imide group at 1750 cm^{-1} and a new band at 1790 cm^{-1}). The changes in the IR spectrum (notably a small peak at 1645 cm^{-1}) could possibly indicate the formation of C=C bonds as a result of the disproportionation reaction.

Bands appear at 1790, 1720, 1380 and 1125 cm^{-1} in the spectrum of the 6–7:1 AA:MA copolymers heated at 170°. The last two bands are characteristic of cyclic imide.

The AA:MA copolymers reveal C=O and NH absorption at different values than those for the monomer. The shifts are much higher in more polar solvent (solvent of copolymer synthesis). For the copolymer prepared in MEK (dielectric constant

$D = 18$) the shifts are $\Delta(\text{NH})_1 = 55 \text{ cm}^{-1}$ and $\Delta(\text{NH})_2 = 35 \text{ cm}^{-1}$. The shifts for the absorption of the C=O and NH bonds were calculated using as reference the value for acrylamide in infinitely diluted CCl_4 solution (literature data [1] indicate $\Delta(\text{NH})_1 = 15 \text{ cm}^{-1}$ and $\Delta(\text{NH})_2 = 10 \text{ cm}^{-1}$) in benzene as an inert solvent. In the case of C=O absorption the shift is in the same direction, but is much smaller and it was not taken into account.

Conclusions

Thermal analysis (TG and DTG curves) shows four distinct peaks in the case of polyacrylamide and the random copolymers and only three for the 1:1 AA:MA copolymer.

In the 1:1 AA:MA copolymer, only intermolecular imidization occurs and during thermal degradation this is influenced by the anhydride groups, which are equal in number with the amide groups.

This fact is reflected in the n values ($n < 1$) and in the disappearance of the peak in the 230–320° temperature range of the DTG curve. The thermal decomposition in the temperature range 230–320° of the copolymers with high acrylamide contents is affected by the molecular weight; that the same time, the activation energy decreases with decrease in the molecular weight (\bar{M}_v). Above 320°, thermal decomposition occurs identically in all studied copolymers and in polyacrylamide as well.

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Zusammenfassung – Das thermische Verhalten von Acrylamid–Maleinsäureanhydrid-Kopolymeren wurde durch thermogravimetrische Analyse (TG und DTG) untersucht. Aus den erhaltenen Daten wurden die Aktivierungsenergien und Reaktionsordnungen der Zersetzungsschritte nach den Methoden von Coats–Redfern und Freeman–Carroll berechnet. Durch thermische Analyse können im Falle von Polyacrylamid und AA:MA (7:1)-Kopolymeren 4 Peaks und bei AA:MA (1:1)-Kopolymeren nur 3 Peaks unterschieden werden. Bei AA:MA (1:1)-Kopolymeren verläuft nur eine intermolekulare Imidisierung und der thermische Abbau wird mehr durch die in gleicher Zahl wie die Amidgruppen vorliegenden Anhydridgruppen beeinflusst.

Резюме — Методом ТГ и ДТГ изучено термическое поведение сополимеров акриламид (АА) — малеиновый ангидрид (МА). На основе полученных данных, используя методы Коутса—Рэдферна и Фримена—Кэрролла, были вычислены энергии активации и порядок реакционных стадий разложения. В случае полиакриламида и сополимера АА:МА (соотношение компонент 7:1) термический анализ показал четыре отдельных пика, тогда как для сополимера АА:МА состава 1:1 — только три пика. В сополимерах АА:МА состава 1:1 происходит только межмолекулярная имидизация, а термическое разложение в большей степени обусловлено ангидридными группами, равными по числу амидным.