

Thermal Stability of Copolymer Acrylamide–Maleic Anhydride

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Synopsis

The thermal degradation of copolymer acrylamide–maleic anhydride prepared in various solvents (benzene, dioxane, methylethyl ketone) and different monomer ratios was investigated. The techniques of thermogravimetry (TG and DTG) and differential scanning calorimetry (DSC) were used. The IR spectra of degraded copolymers are discussed.

INTRODUCTION

There are numerous studies devoted to the copolymers degradation behavior. Physical properties of copolymers are not necessarily the mean of the properties of the constituents, so that the stability or degradation properties are often unexpected.¹ The thermal degradation of polyacrylamide (PAA) and of copolymer acrylamide maleic anhydride (AA–AM), prepared in various solvents [benzene, dioxane methylethyl ketone (MEC)] and different monomer ratios was investigated.

The thermal decomposition of copolymer (AA–AM) was studied by thermogravimetry² (nonisothermal conditions, constant heating rate) and by DSC. The reaction order and activation energy were computed by means of the Freeman–Carrol³ and Coats–Redfern⁴ methods, using a modified FORTRAN program.⁵

The results concerning copolymers synthesis, molecular weight, composition, spectral characterization and some potential industrial applications are given elsewhere.^{6–8}

EXPERIMENTAL

Materials. Solvents p.a. reagent grade benzene, dioxane and methylethyl ketone (MEC). Acrylamide (AA) recrystallized from benzene (melting point = 85°C). Maleic anhydride (AM) (melting point = 56°C); 2-2'-azobisisobutyronitrile purum.

The copolymerization of acrylamide with maleic anhydride was carried out in the presence of 2-2'-azobisisobutyronitril as an initiator at 65°C in benzene, dioxane, and MEC. Acrylamide polymerization was done in the same conditions in benzene.

The monomer ratios in copolymers were obtained by nitrogen and carboxylic groups analysis, using Kjeldhal and potentiometric titration methods, respectively. The monomer ratios, average viscosimetric molecular weight (\bar{M}_v) and the constants α , K (from the Mark–Houwink equation) for (AA : AM) copolymers are given in Table I.⁹

TABLE I
The Monomer Ratios AA : AM in Copolymer and the Average Viscosimetric
Molecular Weight (\bar{M}_v)

No.	Sample	Monomer ratio	Solvent	$[\eta]$ (dL/g)	$K \times 10^5$	a	\bar{M}_v
1	PAA	—	Benzene	0.62	5.57	0.66	1.35×10^6
2	AA : AM	1 : 1	Benzene	0.108	10.5	0.66	3.66×10^4
3	AA : AM	1 : 1	Dioxane	0.083	10.5	0.66	2.50×10^4
4	AA : AM	1 : 1	MEC	0.050	4.84	0.66	2.7×10^4
5	AA : AM	7 : 1	Benzene	0.087	5.57	0.66	6.9×10^4
6	AA : AM	6.3 : 1	Dioxane	0.115	5.57	0.66	10.5×10^4
7	AA : AM	6 : 1	MEC	0.138	5.23	0.66	15.28×10^4

The intrinsic viscosity $[\eta]$ in NaNO_3 solutions 0.6N at 25°C was determined using an Ubbelohde viscosimeter (type 0.1). From the experimental data concerning monomer ratio in copolymer and knowing the fact that AM generally does not polymerize under our working conditions (but copolymerizes with various vinylic monomers) it is possible to consider that the copolymer AA : AM (1 : 1) has an alternating structure.

APPARATUS AND PROCEDURE

The Perkin-Elmer TGS.2 thermobalance and the DSC 2 calorimeter were used. Thermal decomposition was carried out in argon flow, at a constant heating rate (20°C/min). Infrared spectra were recorded using a UR-10 Karl Zeiss-Jena spectrophotometer within the 400–5000 cm^{-1} range on pellets with 0.3 g KBr and 0.002 g copolymer.

RESULTS AND DISCUSSION

TG, DTG, and DSC concerning copolymers AA : AM (1 : 1) and AA : AM (7 : 1) in benzene are presented in Figures 1 and 2. Polyacrylamide, copolymers AA : AM (6.3 : 1) in dioxane and AA : AM (6 : 1) in MEC show similar curves as in Figure 1. Copolymers AA : AM (1 : 1) in dioxane and MEC show similar curves as in Figure 2.

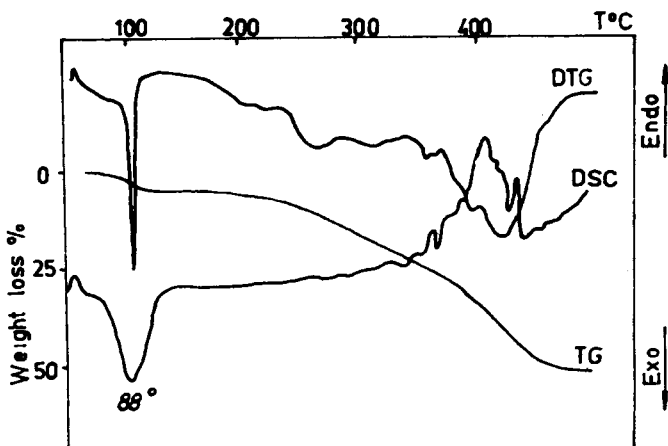


Fig. 1. TG, DTG, and DSC curves of copolymer AA : AM (7 : 1) in benzene.

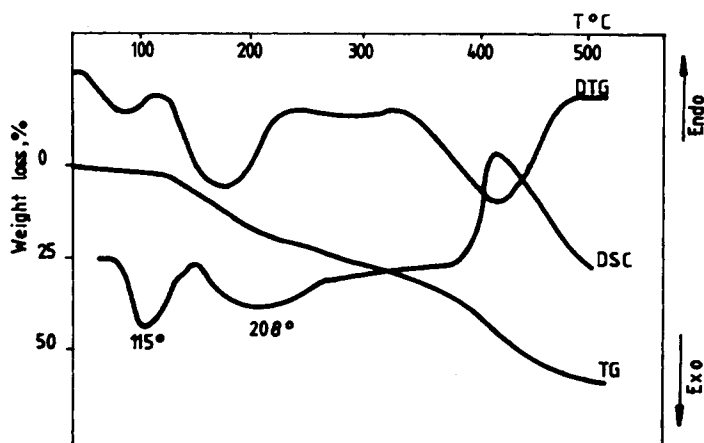


Fig. 2. TG, DTG, and DSC curves of copolymer AA : AM (1 : 1) in benzene.

In Table II the characteristic temperatures of decomposition stages, the corresponding weight loss, and kinetic parameters are listed. Activation energies (E) and reaction orders (n) were calculated by the differential Freeman-Carroll method and the integral Coats-Redfern method using a modified FORTRAN program. ΔH data from DSC are presented in Table III.

Thermal analysis DTG curves show four peaks in the case of polyacrylamide and the copolymer AA : AM (6-7 : 1) corresponding to the following temperature stages: 50-120°C (stage I); 120-230°C (stage II); 230-330°C (stage III); 330-500°C (stage IV) (Fig. 2 and Table II).

For AA : AM (1 : 1) copolymer DTG curves show only three peaks: the peak corresponding to the decomposition stage (230-330°C) is not present (Fig. 1 and Table II). Experimental data (DSC) indicate in the case of polyacrylamide and copolymer AA : AM (6-7 : 1) an exothermic peak and an endothermic one.

The shape of the endothermic peak (Fig. 1) does not allow the calculation of the ΔH for the copolymers AA : AM (6-7 : 1) (Table III) in spite of the fact that their properties are closer to polyacrylamide than to copolymers AA : AM (1 : 1). Copolymers AA : AM (1 : 1) show two exothermic peaks and an endothermic one.

All seven studied polymers present high hygroscopicity. First thermal decomposition stage is due to water loss from polymer; weight loss in this zone is between 5 and 8% for copolymers and of 11.5% for polyacrylamide. The activation energy $E = 60$ kJ/mol and the value 1 for n (the order of reaction) are characteristic for such processes.¹⁰ An exception is the case of copolymer AA : AM (6 : 1) in MEC. In the second and third stages the reactions are mainly the same. The second decomposition stage can be connected with the beginning of the reactions of the lateral groups to the main chain: imidization with NH_3 elimination and decarboxylation of maleic anhydride.

Literature data¹¹ indicate that a first order reaction is taking place for both formation of the imide functional group and evolution of NH_3 with an apparent activation energy of 40-60 kJ/mol within the range 175-300°C. Our data for a polyacrylamide with $\bar{M}_p = 1.35 \times 10^6$ are $E = 77$ kJ/mol and $n = 1$. The acrylamide-rich copolymers have almost the same kinetic param-

TABLE II
The Decomposition Stages (Characteristic Temperature, Weight Loss, and the Kinetic Parameters) of the Copolymers AA:AM and of PAA

Sample	Stage I (50–120°C)				Stage II (120–230°C)				Stage III (230–330°C)				Stage IV (330–500°C)						
	Temp (°C)		Weight loss (%)	<i>n</i>	Temp (°C)		Weight loss (%)	<i>n</i>	Temp (°C)		Weight loss (%)	<i>n</i>	Temp (°C)		Weight loss (%)	<i>E</i> (kJ/mol)			
	<i>a</i>	<i>b</i>			<i>a</i>	<i>b</i>			<i>a</i>	<i>b</i>			<i>a</i>	<i>b</i>					
PAA	50	85	11.5	1	65	135	190	4.5	1	77	230	325	17	2	149	330	420	30	160
AA:AM(1:1) benzene	50	80	5	1	57	120	170	17.5	1.4	42	230	270	8.5	—	—	330	420	30	160
AA:AM(1:1) dioxane	50	90	8	1	65	140	190	9	2	71	230	270	10	—	—	330	420	30	160
AA:AM(1:1) MEC	50	80	7.5	1	44	140	170	16.5	2	68	230	270	8	—	—	330	420	30	160
AA:AM(7:1) benzene	50	95	6	1	71	130	220	4	0.8	79	230	265	11.5	1	136	330	420	30	160
AA:AM(6.3:1) dioxane	50	80	6.5	1	69	120	155	14	1	55	230	275	8.5	1	82	230	420	30	160
AA:AM(6:1) MEC	50	125	6	0.2	19	170	187	9.5	0.9	52	230	270	11.5	0.4	36	330	420	30	160

^a Initial temperature.

^b Temperature of maximum weight loss.

TABLE III
 ΔH Data from DSC Curves

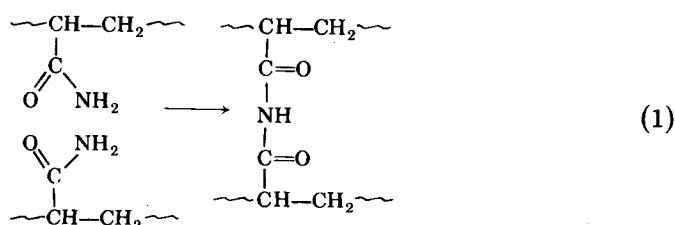
Sample	Peak DSC	ΔH (kJ/kg)	Peak DSC	ΔH (kJ/kg)
PAA	129°C (exo)	(-136.2)	313°C (endo)	+584.7
Benzene 1:1	115°C (exo)	(-142.9)	208°C (exo)	-145.04
Dioxane 1:1	130°C (exo)	(-247.4)	200°C (exo)	-86.94
MEC 1:1	120°C (exo)	(-283.8)	200°C (exo)	-91.96
Benzene 7:1	88°C (exo)	(-476.5)	—	—
Dioxane 7:1	107°C (exo)	(-429.2)	—	—
MEC 6:1	67°C (exo)	(-397.1)	—	—

ters. Copolymers AA:AM (1:1) have activation energies not far from this value, but the reactions orders are higher.

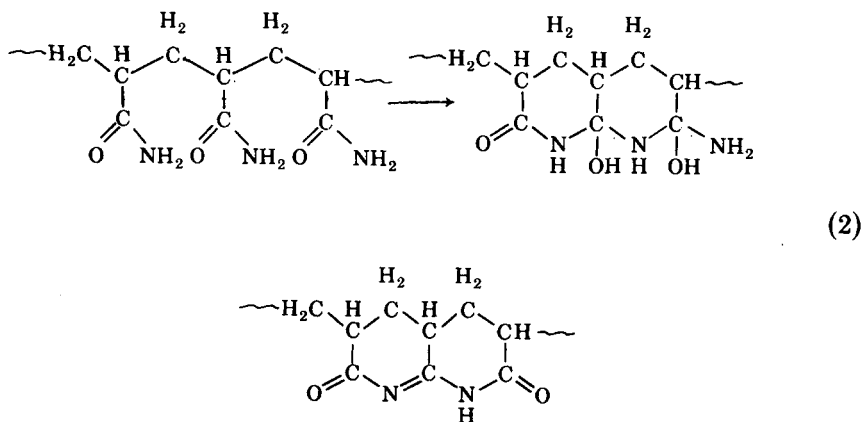
The copolymer AA:AM (6:1) in MEC presents activation energies much smaller and fractional reaction orders in all decomposition stages; this copolymer might present some imidization by synthesis (up to 40% insoluble substance).

The behavior of copolymers is supported by IR spectral data; thus the spectrum of the copolymer AA:AM (1:1) heated at 170°C presents the characteristic absorption of imide group ($\nu_{C=O}$) in imide group at 1720 cm^{-1} and a new band at 1790 cm^{-1} . Bands at 1790, 1720, 1380, and 1125 cm^{-1} appear in the spectrum of the heated copolymer AA:AM (6-7:1); the last two bands are characteristic of cyclic imide. At a higher temperature all these bands are more pronounced; that might suggest that in the same time with other processes (decarboxylation anhydride group) the imidization is taking place, too. In order to check the changes in molecular weight with the temperature increase, the polymers have been heated at 130 and 300°C. For example, the results obtained for PAA and copolymer AA:AM (1:1) in benzene are as follows: The samples heated 15 min at 130°C do not present modifications in M_v values. At 300°C the polymers present a soluble and an insoluble part. \bar{M}_v of soluble part of PAA is 5.44×10^5 and the initial M_v for PAA is 1.35×10^6 ; for copolymer AA:AM (1:1) in benzene M_v at 300°C is 0.82×10^4 and the initial M_v 3.66×10^4 .

Taking into account DTG, spectral analysis, and changes in molecular weight with the temperature increase, intramolecular and intermolecular imidization and decarboxylation of maleic anhydride might be considered as main processes in the second and third decomposition stages. In the case of copolymers (1:1), formation of imide functional group occurs only as intermolecular reactions, according to the following scheme:



In the case of PAA and copolymers (7-6 : 1) it is possible that the formation of imide takes place also intramolecularly, via cyclization:



During the stage IV (330–500°C), at about 420°C all studied samples have the maximum of the peak associated with an activation energy of 160 kJ/mol and a weight loss of 30%; the insoluble part appearing in the previous stage diminishes much as compared to the soluble part. From viscosity data for the soluble part of polymers it results that their molecular weight strongly decreases in this domain, which was attributed to the beginning of the degradation with random scission of the main molecular chain. This stage of thermal degradation was related to the random scission of the main chain characteristic for vinyl polymers.¹ At a temperature around 500°C, all studied copolymers and polyacrylamide have a weight loss of 60%, a total loss being achieved at 650°C.

CONCLUSION

1. Thermal analysis of DTG curves shows four peaks in the case of PAA and the copolymer AA : AM (6-7 : 1), corresponding to four temperature stages. For copolymer AA : AM (1 : 1) DTG curves show only three peaks.

2. Experimental data (DSC) indicate in case of PAA and the copolymers AA : AM (6-7 : 1) an exothermic peak and an endothermic one; the copolymers AA : AM (1 : 1) present two exothermic peaks and an endothermic one.

3. The degradation processes are mainly: water loss, imidization with NH₃ elimination, decarboxylation of maleic anhydride, and over 420°C random scission of the main chain.

4. At a temperature around 500°C, all studied copolymers and PAA have a weight loss of 60%, the total loss being completed at 650°C.

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