

# Thermoanalytical Study of Acrylonitrile—Vinylidene Chloride Copolymers

<sup>a</sup>Š. FLORIÁN and <sup>b</sup>M. BERT

<sup>a</sup>Polymer Institute, Slovak Academy of Sciences,  
CS-842 36 Bratislava

<sup>b</sup>Laboratoire des Matériaux Organiques, Centre National de la Recherche Scientifique,  
Vernaison, France

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Thermal degradation of emulsion statistical copolymers of acrylonitrile and vinylidene chloride and/or terpolymers with glycidyl methacrylate or glycidyl acrylate was carried out in the temperature range from 25 to 450 °C in nitrogen and was studied by conductometry and by gas chromatography. We have found that epoxy groups of the third component of terpolymers favourably affect the beginning of dehydrochlorination because they bind the first amounts of the releasing hydrogen chloride. With decreasing molecular mass of a sample, the rate of the HCl abstraction considerably increases. With samples of the lowest molecular masses, almost complete dehydrochlorination occurs.

The thermal stability of copolymers of acrylonitrile and vinylidene chloride of various chemical compositions has already been studied [1, 2] and these copolymers have found their application in technical practice, in the production of incombustible fibres. There are some drawbacks, however, which hinder their wider application. It is mainly the release of hydrogen chloride during processing, which causes corrosion of the equipment, the insufficient hydrophilicity of copolymers and excessive softening at higher temperatures leading to fibre sticking.

Much effort has been made to remove these shortcomings either by introducing suitable additives into polymer *via* its grafting or by terpolymerization with another monomer, *e.g.* with acrylamide. In this paper we present results from the study of the acrylonitrile—vinylidene chloride (AN—VDC) modified by glycidyl methacrylate (GMA) or glycidyl acrylate (GA). The aim of the modification is an increase of the thermal stability of a copolymer. But mainly by using glycidyl acrylate, better internal plasticization of a polymer has been achieved.

The authors in [3] described a favourable effect of glycidyl groups on thermal stability of a polymer containing bound chlorine. In paper [4] a remarkable effect of the distribution of monomer units in a terpolymer macromolecule on its properties was reported, as well as on some kinetic anomalies of terpolymerization as a function of a solvent used and the chromatographic method specially adapted for a complex study of the reaction system was described.

## EXPERIMENTAL

Acrylic monomers were at first purified by shak-

ing with a 10 % NaOH solution, then with distilled water, and dried over CaCl<sub>2</sub>. Monomers were deprived of residual additives *via* vacuum distillation before use. The chemicals used were of anal. grade.

AN—VDC copolymers and AN—VDC—GA or AN—VDC—GMA terpolymers were prepared by emulsion polymerization at 150 °C in redox system (sodium sulfite—potassium sulfate) in a polymerization reactor in a nitrogen atmosphere under constant stirring. Since at the actual degree of conversion remarkable changes occur in the composition of terpolymers (Fig. 1) because of different values of the copolymerization parameters, the polymerization equipment was adjusted according to [5] so as to keep the monomer composition in the reaction constant throughout polymerization; this is a condition for the preparation of terpolymers of low compositional heterogeneity. Fig. 2 shows the scheme of

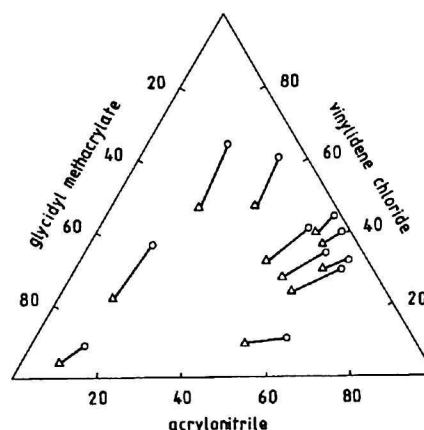


Fig. 1. Ternary diagram of the reaction mixture. o Monomer feed composition; Δ terpolymer composition.

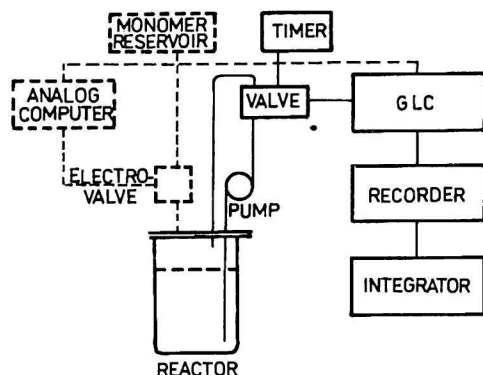


Fig. 2. Scheme of the polymerization apparatus.

the apparatus used for polymerization. The monomer composition in a reactor was determined in regular intervals by a gas-liquid chromatograph, deviations were evaluated by a computer and the monomer, the loss of which had already been recorded was added into the reactor by an electrovalve.

After the completion of the polymerization the terpolymer samples were several times washed with distilled water, dried *in vacuo* to constant mass and then characterized osmotically and by elemental analysis (Table 1). The polymer samples of AN-VDC, AN-VDC-GMA, and AN-VDC-GA were then fractionated from a solution in a mixture

of DMF and acetone gradually adding *n*-hexane as a precipitant. The isolated vacuum-dried fractions were characterized viscometrically in DMF at 25 °C and osmotically in propylene carbonate at 37 °C (Table 2). On the basis of the low compositional heterogeneity of copolymers secured by the method of their preparation as well as a rather narrow and regular molecular-mass distribution of individual fractions obtained by GPC ( $\bar{M}_m/\bar{M}_N = 1.20-1.38$ ) we were able to determine Mark-Houwink constants [6] for the relation between the limiting viscosity number and the viscosity average molecular mass

$$\begin{aligned} \text{AN-VDC} & \quad [\eta] = 1.37 \times 10^{-3} \bar{M}_v^{0.673} \\ \text{AN-VDC-GMA} & \quad [\eta] = 2.137 \times 10^{-3} \bar{M}_v^{0.629} \\ \text{AN-VDC-GA} & \quad [\eta] = 1.787 \times 10^{-3} \bar{M}_v^{0.630} \end{aligned}$$

The selected fractions were later subjected to the thermal decomposition.

The equipment used for the thermal degradation study and constructed according to [7] was described earlier [8]. The thermobalance was connected with the equipment for dosing ions, which can be precipitated with silver nitrate, with a differential conductometer described elsewhere [2, 9] and with gas chromatograph, analyzing a mixture of the volatile products of thermal degradation.

Table 1. Preparation of AN-VDC Copolymer and Its Terpolymers with GMA and GA

Polymer sample	Initial monomer composition			Terpolymer composition*				$\bar{M}_N \cdot 10^{-4}$
	$\bar{x}(\text{VDC})$	$\bar{x}(\text{AN})$	$\bar{x}(\text{GMA or GA})$	$\bar{x}(\text{VDC})$	$\bar{x}(\text{AN})$	$\bar{x}(\text{GMA or GA})$	$w(\text{Cl})$	
	%	%	%	%	%	%	%	
AN-VDC	23	77	0	24.8	75.2	0		5.61
AN-VDC-GMA	24	75.5	0.5	27.2	72.8		29.5	2.96
				24.3	74.2	2.2	26.5	
AN-VDC-GA	25.5	74	0.5	26.0	72.4	1.6		7.50
				25.2	72.9	1.5	27.4	

\*The second values of terpolymer composition were calculated from the copolymerization parameters.

Table 2. Characterization of Fractions of Copolymer Samples

Fraction	AN-VDC				AN-VDC-GMA (2.2 mole % GMA)				AN-VDC-GA (1.6 mole % GA)			
	$[\eta]$ $\text{cm}^3 \text{g}^{-1}$	$\bar{M}_v \cdot 10^{-5}$	$\bar{x}(\text{AN})$ %	$\bar{x}(\text{VDC})$ %	$[\eta]$ $\text{cm}^3 \text{g}^{-1}$	$\bar{M}_v \cdot 10^{-4}$	$\bar{x}(\text{AN})$ %	$\bar{x}(\text{VDC})$ %	$[\eta]$ $\text{cm}^3 \text{g}^{-1}$	$\bar{M}_v \cdot 10^{-5}$	$\bar{x}(\text{AN})$ %	$\bar{x}(\text{VDC})$ %
1	564	2.32	76	24	229	6.56	82	16	652	4.50		
2	554	2.26			219	6.11	82	16	623	4.18		
3	533	2.13	78	22	207	5.58	82	16	516	3.10	76	22
4	517	2.04			208	5.62			494	2.90		
5	501	1.95	67	33	201	5.32	81	16	478	2.75		
6	412	1.46			191	4.90			468	2.66		
7	395	1.37	70	30	168	3.99	76	22	448	2.48	73	22
8	373	1.26			136	2.85			423	2.27		
9	242	0.661	65	35	129	2.61	73	25	352	1.69		
10	83	0.134	59	41	61	0.70			324	1.48	74	25
11									207	0.73	68	30
12									76	0.149	67	31
13									67	0.122		

Polymer samples were pyrolyzed in the thermo-balance over the temperature range from 25 to 450 °C with constant temperature increase (2 °C min<sup>-1</sup>) in a stream of nitrogen. The aliquot fraction of degradation products was injected in certain time intervals into a chromatographic column packed with Porapak Q and heated to 130 °C. At the end the gas passed through a cuvette of the differential conductometric equipment filled with a silver nitrate solution in 0.1 M-HNO<sub>3</sub>. A decrease in the concentration of silver ions was directly proportional to the amounts of HCl and HCN added in degradation gas products. The released HCN was determined chromatographically on the basis of the calibration by an ethanol solution of HCN. The abstracted hydrogen chloride was then established as a difference between the argentometrically determined amount of a mixture of HCl and HCN and the HCN determined by chromatography.

Absorption measurements in the UV sphere were carried out in a silica cell (thickness 10 mm), measurements of IR spectra in KBr tablets (the approximate content of polymer 1 vol. %). Homogenization of KBr with polymer was carried out in pulverizer at 70 °C.

## RESULTS AND DISCUSSION

With regard to the high sensitivity of conductometry we were able to follow the very beginnings of the polymer sample degradation, which is also important from the point of view of the safety of their industrial processing. Fig. 3 shows that even a small amount of GMA or GA in a polymer increases remarkably the temperature limit of the hydrogen chlo-

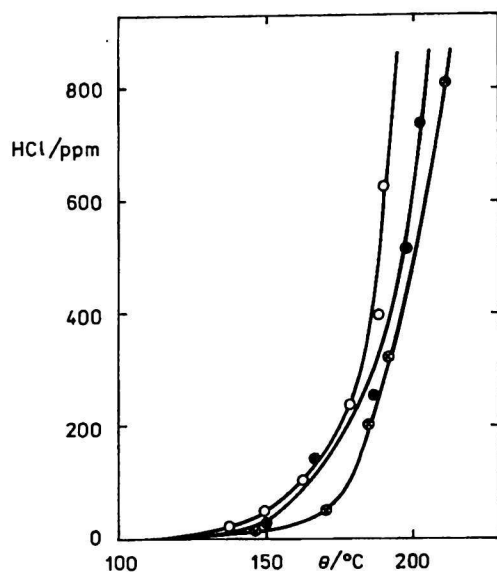
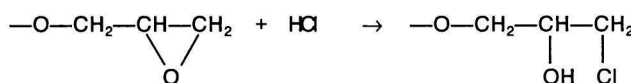


Fig. 3. Relative amount of abstracted HCl at the beginning of pyrolysis of AN—VDC copolymer (○), AN—VDC—GMA (●) and AN—VDC—GA (⊗) terpolymers.

ride abstraction by 10—15 °C. This increase can be explained by addition of the first amounts of hydrogen chloride released to epoxy groups as has been proved by IR spectroscopy; a comparison of the spectra of the polymer after the degradation and before showed that the bands of the epoxy group at  $\tilde{\nu} = 850$  and  $910$  cm<sup>-1</sup> almost vanished and an increase of intensity of the OH group band at  $3400$  cm<sup>-1</sup> was observed.



Moreover, at higher temperatures, a new absorption band appeared in the region around  $1770$  cm<sup>-1</sup> corresponding to intramolecular lactonization between two units. The effect of the higher content of the epoxy groups of the AN—VDC—GMA terpolymer on its thermal stability is eliminated by its lower molecular mass as compared with AN—VDC—GA terpolymer.

The course of the more intense HCl abstraction at higher temperatures is evident from the results of potentiometric measurements shown in Figs. 4—6.

For individual polymer samples, both the rate and the final degree of HCl abstraction depend on their molecular mass; the dehydrochlorination being the smallest for AN—VDC copolymer and the strongest for AN—VDC—GMA. A two-step mechanism of dehydrochlorination expected for AN—VDC copolymers — gradual intra- and intermolecular HCl abstraction in the presence of acrylonitrile units in the second step [10] —

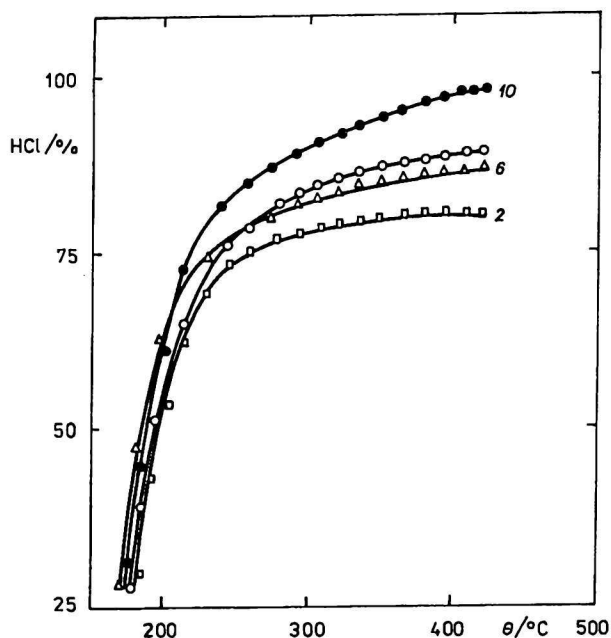


Fig. 4. Relative amount of abstracted HCl of AN—VDC copolymer (○) and its fractions as a function of degradation temperature.

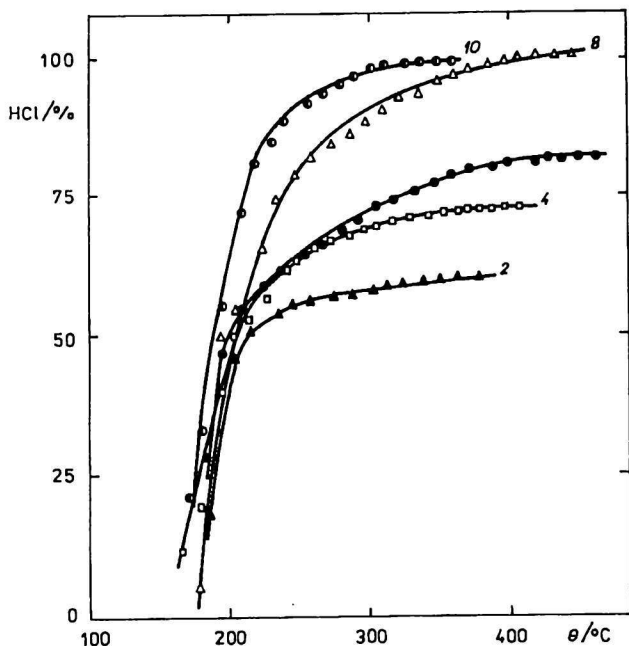


Fig. 5. Relative amount of abstracted HCl of AN-VDC-GMA terpolymer (●) and its fractions as a function of degradation temperature.

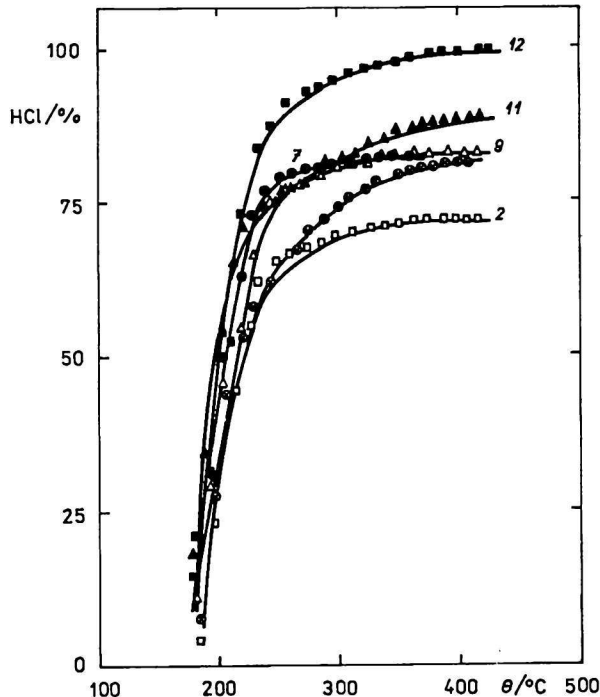
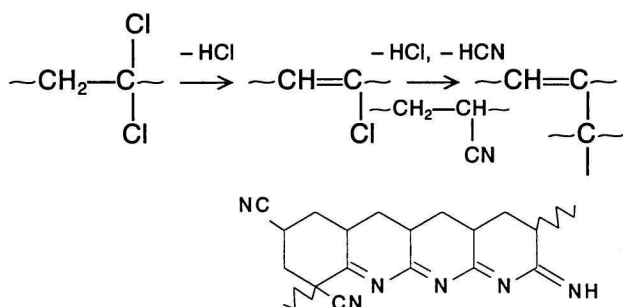


Fig. 6. Relative amount of abstracted HCl of AN-VDC-GA terpolymer (⊗) and its fractions as a function of degradation temperature.



lease of NH<sub>3</sub>, we can assume that the mechanism of HCN abstraction proceeds also via oligomerization of nitrile groups according to the scheme [11]

cannot explain the dependences mentioned above. The effect of the microstructure of polymer which changes with the order of the fraction probably appears here. The amount of the detected HCl released can also be influenced by the sequence of individual components in terpolymer. For instance, the three vinylidene chloride components following one after the other, give mainly trichlorobenzene to the detriment of the HCl abstraction. With AN-VDC-GMA, however, the strongest dehydrochlorination can be explained by its low molecular mass, when compared with other copolymer samples.

As seen in Fig. 7 a more intensive abstraction of HCN of the copolymers described occurs at the temperatures higher than 300 °C. Since HCN abstraction is accompanied with the re-

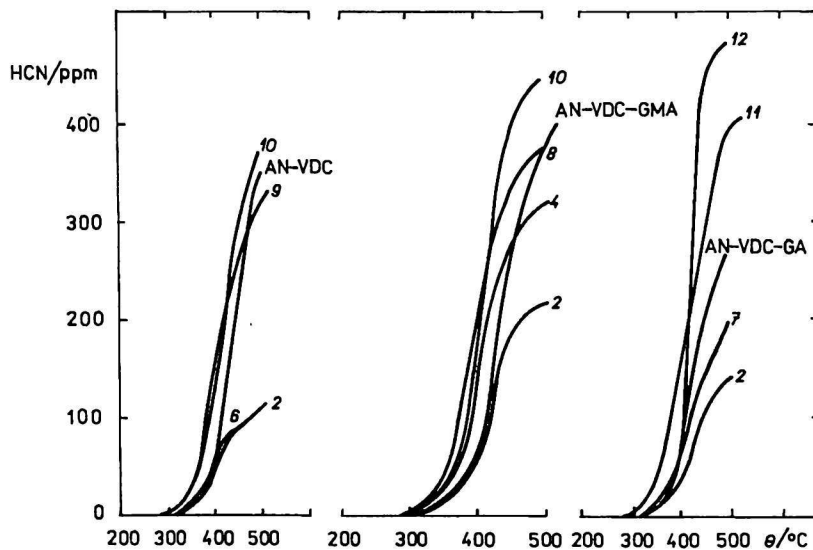


Fig. 7. Relative amount of abstracted HCN of AN-VDC copolymer, AN-VDC-GMA and AN-VDC-GA terpolymers and their fractions as a function of degradation temperature.

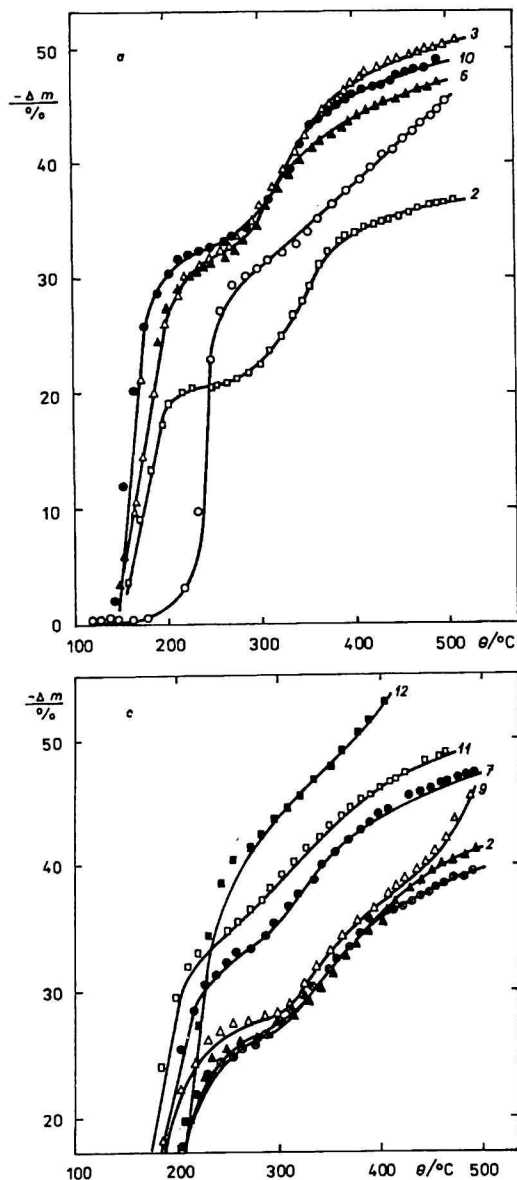
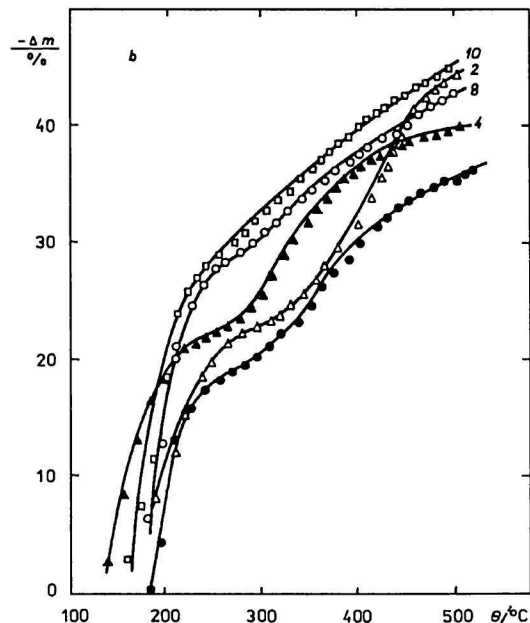


Fig. 8. Mass losses of a) AN—VDC copolymer (○), b) AN—VDC—GMA (●), and c) AN—VDC—GA (⊗) terpolymers and their fractions as a function of degradation temperature.

This mechanism is also confirmed by a slight increase of absorption in the UV region at  $\lambda = 336$  nm for degraded polymer, the band belonging to the structure shown above. This can also account for a remarkably lower formation of HCN in the case of the AN—VDC—GMA terpolymer, where the possibility of the formation of oligomeric nitrile structures is rather limited. Generally one can say that the more intense formation of HCN takes place under similar conditions with the fractions in which increased dehydrochlorination occurs. A study of the distribution of the sequences of monomer units in a macromolecular chain of these copolymers might bring better explanation.

Figs. 8 show the percentage mass loss of the polymer samples during degradation being mostly



caused by abstracted hydrogen chloride, participating by 50–70 % in the overall reduction of volume at 400 °C. The lowest fractions of copolymers are completely dehydrochlorinated at this temperature (see Figs. 4–6). The abstraction of HCN and  $\text{NH}_3$  is only slightly reflected on the mass loss of the samples. A typical two-step mechanism of abstraction of the low terpolymer fractions changes to gradual abstraction with one marked break.

Finally we can assume that the presence of GMA or GA units in AN—VDC copolymer has positive results from the point of view of thermal stability at the beginning of polymer degradation only. Further course of degradation is not influenced by their presence any more.

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