

CHARACTERIZATION OF SOME ACRYLIC ANION-EXCHANGERS BY PYROLYSIS-GAS CHROMATOGRAPHY

C. N. Cașcaval, G. Mocanu and A. Carpov

"PETRU PONI" INSTITUTE OF MACROMOLECULAR CHEMISTRY,
ALEEA GR. GHICA VODA NR. 41A, IASI 6600, ROMANIA

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Pyrolysis-gas chromatography was used in the study of the thermal behaviour of some acrylic anion-exchangers for identification of the thermal decomposition products and their percentage estimation. The acrylic anion-exchangers were prepared by aminolysis of cross-linked acrylic ester copolymer with difunctional amines. The pyrolysis-gas chromatography studies, coupled with data obtained by thermogravimetry, showed that the acrylic anion-exchangers first lose the water easily absorbed from the air, and the decomposition starts at temperatures above 100°. The great number of decomposition products identified in the pyrograms on the thermal degradation of acrylic anion-exchangers indicated a complex degradation mechanism, with important variations in the contents of the evolved amine compounds.

Pyrolysis-gas chromatography (Py-GC) has already been used for the characterization of various types of ion-exchange resins via the identification and analysis of the thermal decomposition products. Thus, Parris [1, 2] has obtained information about the capacity and the cross-linking of some ion-exchange resins. The relative amount of styrene produced on the pyrolysis of cross-linked polystyrene resin was found to be inversely related to its exchange capacity, while the relative amount of xylene was shown to depend on the cross-linking.

Important studies on the use of the Py-GC technique to characterize ion-exchange resins were performed by Blasius et al. [3-6]. By following the content: of styrene and divinylbenzene copolymers, as well as of some strong acid cation-exchangers (e.g. divinylbenzene, ethylvinylbenzene and α -methylstyrene) in the main pyrolysis products, they showed that it was possible to determine the cross-linking degree by Py-GC [3, 4]. In addition, with the aid of capillary columns and various detectors [5, 6] information was obtained concerning the polymeric matrix, the nature of the functional groups and of the anion, the substitution position of the anchor group on the matrix, and the stereospecific substitution.

Infrared spectrophotometry has also been used in the quantitative analysis of ion-exchange resins [7].

In connection with the characterization of ion-exchange resins, the literature contains few data on acrylic anion-exchangers. A limited number of data were obtained

by using the following instrumental techniques: infrared spectrophotometry [8, 9], potentiometric titration [10] and Py-GC-mass spectrometry [11, 12].

The present paper reports data obtained by Py-GC on the thermal behaviour of various acrylic anion-exchangers. The Py-GC results are supplemented with data obtained by thermogravimetry (TG).

Experimental

The acrylic anion-exchangers were synthesized by aminolysis of a cross-linked acrylic ester copolymer with difunctional amines. The content of comonomers in the ternary copolymers was assumed to be equal to the initial amount of monomer [13], while the amine content was evaluated from the amount of nitrogen, obtained by elementary analysis of the copolymers [14].

The samples listed in Table 1 have both untransformed copolymers and functional groups attached by amide bonds on the macromolecular chain.

Table 1 The composition of the aminated acrylic anion exchangers

Sample	Chemical composition, %					Amine	N ₂ content, %
	Divinyl-benzene	Methyl-methacrylate	Methyl-acrylate	Ethyl-acrylate	Acrylo-nitrile		
A-411	10	35	—	50	5	Triethylene-tetramine	18.2
A-318	10	35	—	50	5	Diethylene-triamine	16.8
A-41	10	—	85	—	5	Ethylene-diamine	9.35
A-44	10	—	85	—	5	Hydrazine	10.12
A-40	10	—	85	—	5	p-Fenylene-diamine	10.7

The polymer samples were weighed in small platinum boats (0.7 mg) and were pyrolysed at 490° with a filament-type pyrolysis unit described elsewhere [15]. The separation and analysis of the pyrolysis products was carried out with a Siemens L-400 gas chromatograph provided with a flame ionization detector, under the following operating conditions: the chromatographic column (2 X 3 mm i.d.) was packed with Chromosorb W (60–80 mesh) coated with 15% free fatty acid phase (FFAP); the column temperature was first programmed from 60 to 180° at a rate of 11.5 degree/min, and it was then operated isothermally at 180°; argon was used as a carrier gas at a flow rate of 30 ml/min. This column was used to separate the liquid hydrocarbon products.

The gaseous hydrocarbon products and also the amines and liquid acrylic compounds were analysed on a chromatographic column (3 X 3 mm i.d.) packed with Porapak Q. This phase was preliminary treated with 5% by weight KOH. In addition, the SE-30 silicon phase coated on Chromosorb W was used for the identification of amine compounds with high boiling points which could result on pyrolysis of the acrylic anion-exchangers.

The pyrolysis products were identified by using the relative retention times of various reference substances and taking into consideration the result of Blasius et al. [3-6] and Oheme et al. [11] on the thermal degradation products of various ion-exchangers.

Some additional data concerning the thermal decomposition of the acrylic anion-exchangers were also obtained by TG. Analysis was performed with the MOM derivatograph, Paulik-Paulik-Erdey type, on powdered polymer samples in mixtures with Al_2O_3 (20% sample) freshly calcined at 1100°, under the following conditions: sample weight 50 mg, heating rate 12 degree/min.

Results and discussion

The acrylic anion-exchangers undergo thermal decomposition by a complex degradation mechanism. On heating, the acrylic anion-exchangers first lose water and the decomposition proper starts at temperature above 100°. This fact is well illustrated by the experimental TG curves where the sample weight loss was recorded as a function of temperature (Fig. 1). For comparison, Fig. 1 also shows the TG curve for untransformed divinylbenzene-methyl acrylate-acrylonitrile (DVB-MA-AN) copolymer.

The experimental curves in Fig. 1 reveal that five chemical processes take place on the thermal decomposition of the acrylic anion-exchangers, in comparison with three processes in the case of the untransformed DVB-MA-AN copolymer. Moreover, the initial and final decomposition temperature of the aminated copolymers are lower than those of the untransformed copolymer. This indicates an apparent lower thermal stability of the aminated copolymers than that of the untransformed copolymer, and suggests that the thermal decomposition of the aminated copolymers starts by rupture of the functional group bonds attached on the backbone of the main copolymer.

Unfortunately, the gas chromatographic conditions used (FID detector) did not allow the detection of products which could possibly be evolved on heating of the acrylic anion-exchangers at temperatures below 200° (inorganic products).

The acrylic anion-exchangers yield a great number of products on thermal degradation at elevated temperatures. For instance, Fig. 2 shows the pyrograms of the gaseous and liquid products obtained on decomposition of sample A-44 at 490°.

The composition of the thermal degradation products of the acrylic anion-exchangers varies from one sample to another. This is clearly shown by the pyrograms in Figs 3 and 4, where there are important changes in the heights of given chromato-

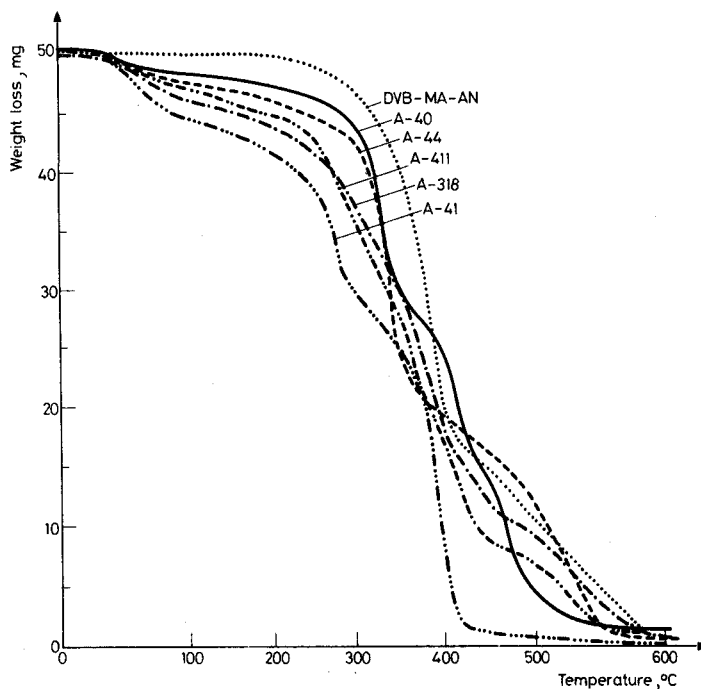


Fig. 1 TG curves for decomposition in air of both the acrylic anion-exchangers and of DVB-MA-AN copolymer

graphic peaks; in both cases the aminated copolymers had the same composition before aminolysis and the amines used for the chemical transformation (deethylenetriamine and triethylenetetramine) did not differ too much one from each other.

A more comprehensive view of the behaviour of the acrylic anion-exchangers on thermal degradation may be obtained from the data in Table 2, where a semiquantitative estimation of all the degradation products recorded in the pyrograms has been made.

The experimental data in Table 2 show that the products evolved on the thermal degradation of the acrylic anion-exchangers were formed in direct conjunction with the main structure of the aminated copolymer. Besides the saturated and unsaturated C_1 - C_4 hydrocarbons, the thermal decomposition of the acrylic anion-exchangers yields products characteristic of the starting comonomers. At the same time, it may be noted that the individual amine compounds produced on the thermal decomposition of the aminated copolymers are methylamine, dimethylamine and trimethylamine. However, while dimethylamine and trimethylamine are formed from all the analyzed copolymers, methylamine appears in small amounts on the thermal decomposition only of samples A-411, A-318 and A-40.

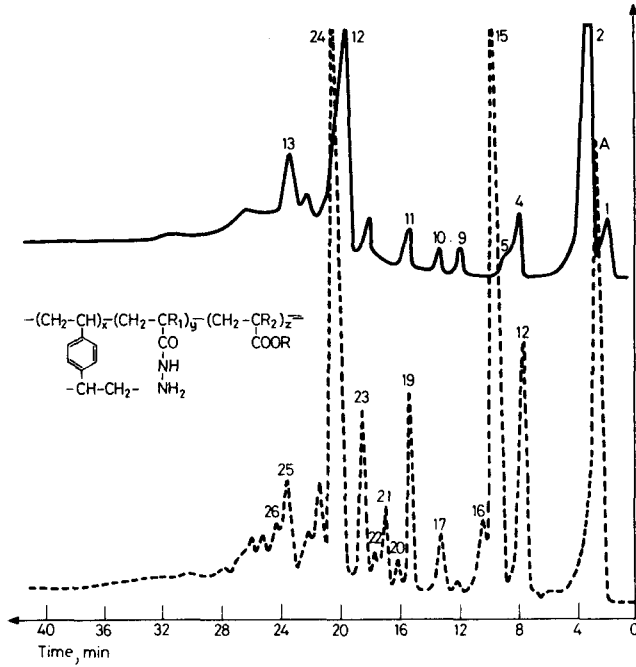


Fig. 2 Pyrograms of the sample A-44 at 490°C. - - - - FFAP; ——— Porapak Q. The peaks semnification is market in Table 2. Peak A correspond to C₁—C₄ hydrocarbons together with alkyl amines. Peaks not noted are unidentified

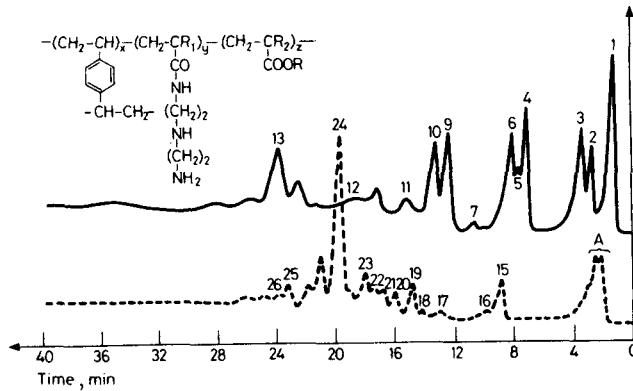


Fig. 3 Pyrograms of the sample A-318 at 490°C. - - - - FFAP; ——— Porapak Q. The peaks semnification is as in Fig. 1 and Table 2

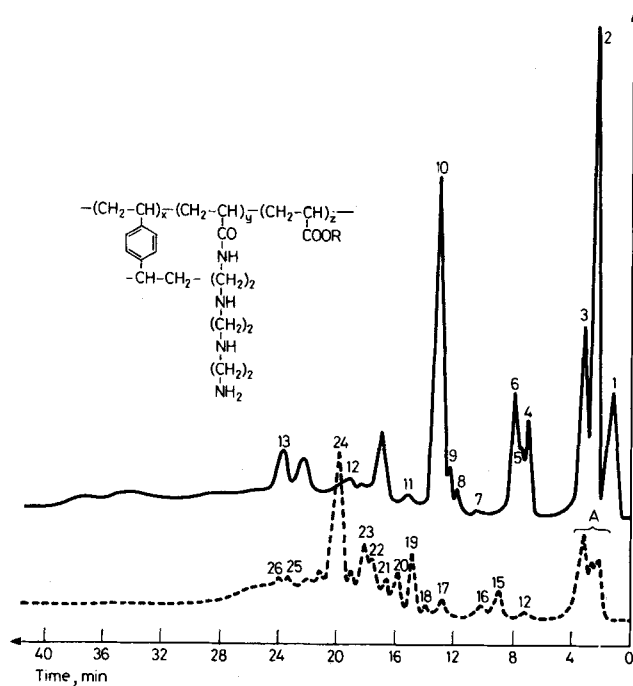


Fig. 4 Pyrograms of the sample A-411 at 490°C. - - - FFAP; — Porapak Q. The peaks semnification is as in Fig. 1 and Table 2

A high dimethylamine content appears on the thermal decomposition of sample A-411, due to the presence of the long functional group amine radicals attached to the backbone of the main copolymer. The same holds for sample A-318, though the percentage of dimethylamine is lower here.

It can be concluded that the mechanism of decomposition of the acrylic anion-exchangers is very complicated, due to the great number of decomposition products, with important variations in the contents of evolved amine compounds.

Table 2 Yields of the pyrolysis products of the acrylic anion exchangers at 490°C

Peaks	Compounds	Sample content, %				
		A-411	A-318	A-41	A-44	A-40
1	Methane	6.49	13.40	2.54	2.40	2.99
2	Ethylene	18.54	9.89	7.37	19.20	2.70
3	Ethane	9.11	7.35	1.83	—	1.79
4	Propene	4.79	9.29	3.40	2.08	1.05
5	2-Methyl-propane	0.46	0.54	—	0.40	—
6	Propane	6.02	0.43	—	—	0.26
7	Methyl-amine	0.62	0.43	—	—	0.88
8	Butene	0.92	—	—	—	—
9	Butane	1.23	8.86	1.41	0.96	0.70
10	Dimethyl-amine	21.13	7.78	1.55	0.92	0.61
11	Trimethyl-amine	0.62	1.08	1.69	1.68	2.66
12	Ethyl acrylate	1.23	0.86	—	10.40	1.70
13	Methyl acrylate	3.71	7.78	3.98	1.44	2.88
14	Benzene	—	—	—	—	8.46
15	Methyl methacrylate Acrylonitrile	1.69	2.38	—	9.48	2.11
16	Toluene	0.62	0.65	0.84	0.50	1.70
17	<i>m, p</i> -Xylene	0.69	0.86	5.65	1.60	5.28
18	<i>o</i> -Xylene	0.23	0.65	—	—	—
19	Ethylbenzene	2.32	1.73	8.03	3.72	6.87
20	Isopropylbenzene	1.39	1.29	1.27	0.40	1.97
21	Ethyltoluene	0.92	0.86	5.65	2.40	3.25
22	α -Methylstyrene	0.77	0.43	—	0.24	—
23	Diethylbenzene	2.00	1.51	7.63	3.44	5.99
24	Ethylstyrene	9.27	14.05	31.90	26.08	24.66
25	<i>m</i> -Divinylbenzene	0.62	1.73	1.84	2.88	1.90
26	<i>p</i> -Divinylbenzene	0.46	1.08	1.27	0.80	1.20
	Unidentified	4.01	4.88	11.81	8.24	18.00

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Zusammenfassung — Pyrolyse-Gaschromatographie wurde bei der Untersuchung des thermischen Verhaltens einiger Anionenaustauscher auf Acrylbasis zur Identifizierung und zur Bestimmung des prozentualen Anteils der thermischen Zersetzungsprodukte verwendet. Die Anionenaustauscher wurden durch Aminolyse vernetzter Acrylester-Copolymeren mit bifunktionellen Aminen hergestellt. Pyrolyse-gaschromatographische Ergebnisse zeigen zusammen mit thermogravimetrischen Daten, dass Anionenaustauscher auf Acrylbasis zuerst das aus der Luft adsorbierte Wasser abgeben und die Zersetzung bei Temperaturen über 100° beginnt. Die grosse Anzahl der beim thermischen Abbau dieser Anionenaustauscher auftretenden, identifizierten Zersetzungsprodukte weist auf einen komplexen, beträchtliche Unterschiede in der Menge der in Freiheit gesetzten Aminoverbindungen bedingenden Zersetzungsmechanismus hin.

Резюме — Совмещенный пиролиз—газохроматографический метод был использован для идентификации продуктов термического разложения некоторых акриловых анионообменников и определения их процентного состава. Анионообменные смолы были получены аминолизом сополимера акрилового эфира с поперечными связями с различными аминами. Результаты совместного пиролиз—газохроматографического исследования и ТГ-данные показали, что акриловые анионообменники сначала теряют воду, легко адсорбированную из воздуха, а затем начинают разлагаться при температуре выше 100°. На пирограммах термического распада акриловых анионообменников идентифицировано большое число продуктов разложения со значительным изменением содержания выделяющихся аминоксоединений. Все это указывает на сложный характер процесса разложения.