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THERMAL DEGRADATION OF SOME POLYMERS BASED ON ETHYLENE GLYCOL DIMETHACRYLATE

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Thermogravimetric analysis and pyrolysis in combination with gas chromatography were used to study the thermal behaviour of some cross-linked polymers of ethylene glycol dimethacrylate. The investigated polymers show a complex thermal degradation mechanism. The complexity of the reaction increases together with increase of the ethylene glycol chain in the macromolecule and with increase of the pyrolysis temperature. At low temperature, the thermal decomposition products of the analyzed polymers are mainly the constituent monomers. At high temperatures, besides the monomer, other decomposition products are formed as a result of thermal cracking reactions, i.e. secondary reactions of decomposition and recombination.

Polymers based on ethylene glycol dimethacrylate find important use as chromatographic packings in both gas and liquid chromatography. The cross-linked macroporous packings based on methacrylic ersters (mono- and divinylics) have a special advantage, as they can directed to products for precise purposes [1–3].

The characterization of reactive macroporous packings, with special reference to the morphological aspects and the macroporous structure, has formed the subject of many publications [4–9].

Pyrolysis has recently been widely used to evaluate the structure, composition and thermal stability of many cross-linked macromolecular compounds [10–15].

The present paper deals with the thermal behaviour of some cross-linked macroporous adsorbents based on ethylene glycol dimethacrylate: polyethylenedimethacrylate (PEDM), polydiethylenedimethacrylate (PDEDM) and polytriethylenedimethacrylate (PTEDM).

The polymers were studied via thermogravimetry (TG), derivative thermogravimetry (DTG), differential thermal analysis (DTA) and pyrolysis in combination with gas chromatography (P–GC).

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Experimental

The monomers, mono-, di- and triethylene glycol dimethacrylate (technical purity), were freshly distilled before use and then polymerized in suspension.

The polymerization was carried out in a cylindrical vessel provided with a stirrer and a refrigerating system. 400 ml water, a suspension stabilizer (6 g ammonium salt of styrene-maleic anhydride and 0.4 g gelatine) and 1.2 g sodium chloride were added to the vessel.

A solution containing 50 g monomer, 50 g toluene and 1.0 g initiator (benzoyl peroxide) was prepared separately. This solution was added to the dispersion medium, the latter being heated to 70°. The suspension was stirred for 16 h at 74°. At the end of the process the polymer spheres, with sizes between 0.2 and 1.0 mm, were washed with water and extracted with methyl alcohol in a Soxhlet apparatus for 24 h. The next operation was drying under vacuum at 50° for 50 h.

The polymer spheres were characterized physically, the measured data being listed in Table 1.

Table 1 Some physical characteristics of polyethylenedimethacrylates studied

Polymer	Apparent density, g/ml	Porosity, %	Pores volume, md/g	Pores diameter, Å	Specific area, m^2/g
PEDM	0.4218	66.30	1.57	227.4	276.20
PDEDM	0.8050	35.60	0.44	395.5	44.50
PTEDM	0.7492	30.04	0.40	924.8	17.30

The thermal behaviour of the synthesized polymers was studied by means of a derivatograph and P–GC. The TG, DTG and DTA curves were recorded simultaneously together with the temperature variation curve. In all cases, the experimental conditions were as follows: sample weight 20 mg; heating rate 12 deg/min; atmosphere air; reference material α-Al_2O_3.

The separation and the analysis of the thermal decomposition products were carried out with a Siemens–L–400 gas chromatograph provided with a flame ionization detector, under the following operating parameters: the stainless steel chromatographic column (2 × 3 mm i.d.) was packed with Chromosorb W (60–80 mesh) coated with 10% w/w Apiezon L; the column temperature was programmed from 50 to 180° at a rate of 7 deg/min; the weight of sample pyrolyzed was below 0.5 mg; argon was used as carrier at a flow rate of 26 ml/min.

Results and discussion

The thermal behaviour of polyethylenedimethacrylates shows the involvement of a complex degradation mechanism, as evidenced by both thermogravimetric and P–GC studies.

As an illustration of this, Fig. 1 presents TG curves recorded for the three polymer samples, while Fig. 2 gives DTG curves.

The shapes of both the TG and the DTG curves suggest that the complexity of the thermal degradation mechanism increases in the following sequence: PEDM, PDEDM and PTEDM (the number of thermal degradation stages increases).

Some thermogravimetric characteristics evaluated from the curves for the samples are listed in Table 2.

It can be seen from Table 2 that there is a common stage for the three polymer samples, between 40 and 110°. This first decomposition stage could be assigned to the volatilization of undesirable components, present in the starting samples.

Significant percentage mass losses are recorded during the second thermal

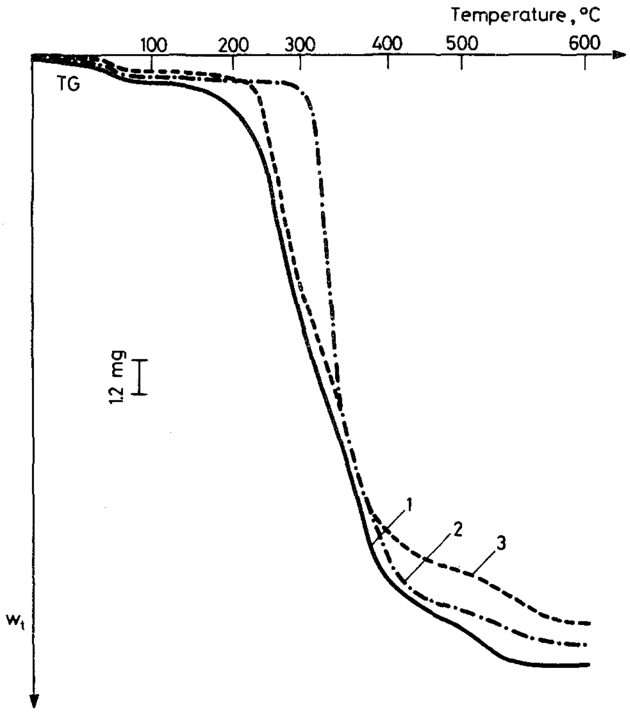

Fig. 1 TG curves for decomposition in air of polyethylenedimethacrylates: 1 – PEDM; 2 – PDEDM and 3 – PTEDM

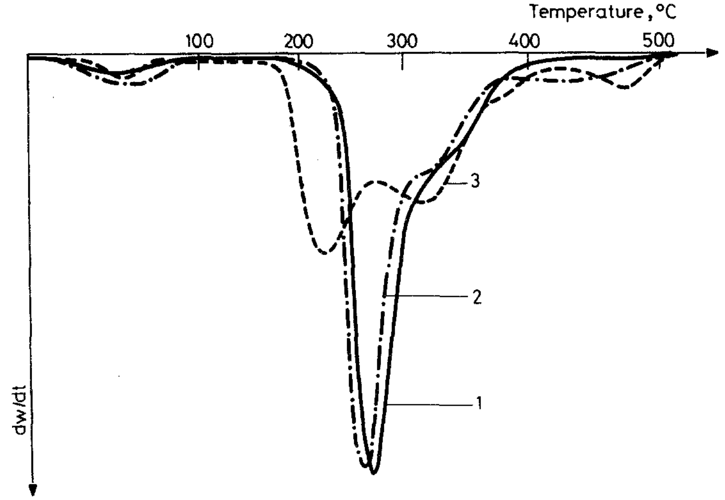

Fig. 2 DTG curves for decomposition in air of polyethylenedimethacrylates: 1 – PEDM; 2 – PDEDM and 3 – PTEDM

Table 2 Thermogravimetric characteristics of polyethylenedimethacrylates studied

Polymer	First stage		Second stage		Third stage		Fourth stage	
	T, °C	W, %*	*T*, °C	W, %	*T*, °C	W, %	*T*, °C	W, %
PEDM	40– 60	2	220–450	98	—	—	—	—
PDEDM	40–110	3	220–400	87	400–525	10	—	—
PTEDM	40–110	3	210–310	46	310–455	47	455–550	4

* W – weight loss given in percentages

degradation stage, especially for the PEDM and PDEDM samples. Table 2 reveals that there is a third thermal degradation stage only for PDEDM and PTEDM, and a fourth thermal degradation stage only for PTEDM.

With the object of estimating the thermal stabilities of the samples, the activation energy (E_a) was evaluated by means of the differential method of Freeman and Carroll [16].

The kinetic data obtained for the three polymers, E_a, reaction order (n) and the temperature corresponding to the medium decomposition rate (T_m), are listed in Table 3.

It can be seen from Table 3 that PEDM and PDEM have somewhat similar stabilities. From the experimental data in Table 3, the following sequence can be established for the thermal stabilities of the polymers: PEDM > PDEM > PTEDM.

Table 3 Kinetical and thermogravimetric characteristics of the polyethylenedimethacrylates studied

Polymer	Kinetical characteristics		T_m, °C
	n	E_a, kJ/mol	
PEDM	4	212	310
PDEDM	4	206	280
PTEDM	4	164	270

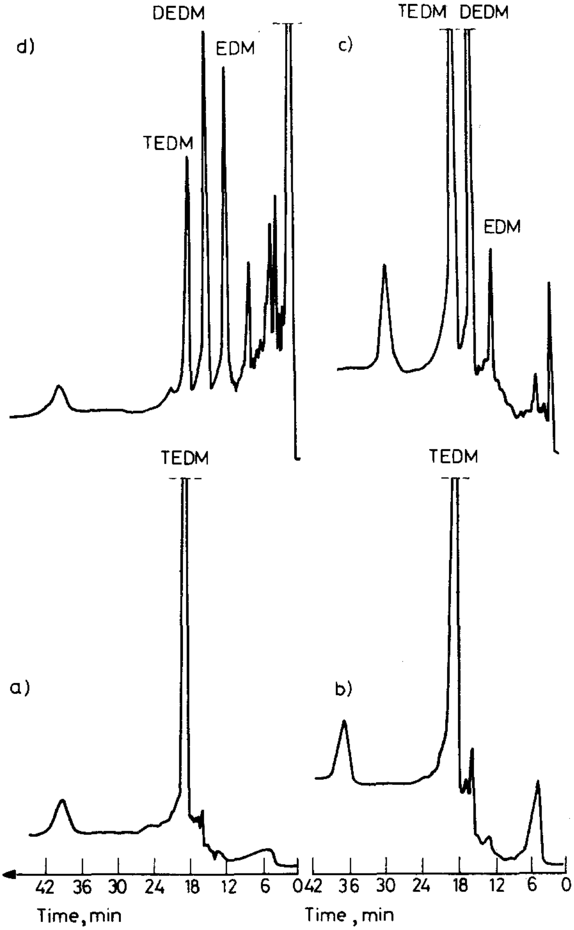

Fig. 3 Typical pyrograms for PTEDM, recorded at various temperatures: (a) 220°; (b) 310°; (c) 480° and (d) 660°. Peaks: EDM (ethylenedimethacrylate); DEDM (diethylenedimethacrylate) and TEDM (triethylenedimethacrylate)

The thermal stability of the coross-linked dimethacrylate with ethyleneglycol polymers decreases with increase of the length of the glycol chain in the macromolecule. This observation is in good agreement with the data previously reported by Asejeva et al. [17] for the thermal behaviour of some cross-linked polymers based on unsaturated esters with ethylene glycol.

The high value of n found for the present polymers suggests a complex degradation mechanism, involving chain reactions.

Below 400°, the data obtained by P–GC show depolymerization processes of the polymers studied, with monomers evolved in a proportion of 96–98%.

At temperatures higher than 400°, besides monomers, the other products appear due to cracking reactions. As an example, Fig. 3 a–d show some typical pyrograms for PTEDM, obtained at increasing decomposition temperatures.

Conclusions

The thermal decompositions of the polymers based on ethylene glycol dimethacrylate take place via a complex degradation mechanism. The complexity increases in the sequence PEDM, PDEDM and PTEDM. The same sequence is also observed for the decrease in thermal stability.

At low temperature, the thermal decompositions of polyethylenedimethacrylates take place by a depolymerization process, which yields the monomers in high proportion. On increase of the temperature, the depolymerization is accompanied by secondary processes of decomposition and recombination, and by advanced cracking. This results in various chemical products, those with low molecular weights prevailing among them.

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Zusammenfassung — Zur Untersuchung des thermischen Verhaltens einiger quervernetzter Polymere auf Äthylenglykoldimetacrylatbasis wurden thermogravimetrische Analyse und Pyrolyse in Zusammenhang mit der Gaschromatographie angewendet. Die untersuchten Polymere zeigten einen komplexen thermischen Zersetzungsmechanismus. Die Komplexizität der Reaktion nimmt mit Zunahme der Anzahl der Äthylenglykolketten im Makromolekül und mit Zunahme der Pyrolysentemperatur gleichermaßen zu. Bei niedrigeren Temperaturen stellen die Hauptzerfallsprodukte der analysierten Polymere hauptsächlich deren Monomere dar. Bei höheren Temperaturen werden als Ergebnis thermischer Krackreaktionen, z. B. sekundäre Zersetzungs- und Rekombinationsreaktionen, neben den Monomeren auch andere Zersetzungsprodukte gebildet.

Резюме — Термогравиметрический анализ и пиролиз в комбинации с газовой хроматографией были использованы для изучения термического поведения некоторых сшитых полимеров этиленгликоля с диметилакрилатом. Полимеры показали сложный механизм термического разложения. Сложность реакций увеличивается с увеличением в макромолекуле этиленгликольной цепи и увеличением температуры. При низкой температуре глаавными продуктами разложения полимеров были мономерные компоненты. При высоких температурах, наряду с мономерами, образуются и другие продукты разложения, как результат протекания вторичных реакций разложения и рекомбинации.