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THERMODEGRADATION OF ISOMERIC POLYBUTYLMETHACRYLATES

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The thermodegradation of polybutylmethacrylates synthesized from all four isomers of butyl methacrylate has been investigated by TG and DTA methods in oxidative, inert and self-generating atmospheres. It was established that the influence of the atmosphere surrounding the polymer on the temperature characteristics of the samples depends on the degree of branching of the substituents in the polybutylmethacrylate (PBMA). It is assumed that the difference in thermodegradation of isomeric polybutylmethacrylates is related to the difference in the degree of substitution of the α-carbon in the ester substituent.

The thermodegradation of polyalkylmethacrylates has been described in many papers, but these deal mainly with the processes occurring in the thermodegradation of polymethylmethacrylate [1–6]. Information concerning the thermodegradation of other derivatives of the methacrylic series is far more scarce [7], and no comparison at all has been made of the thermal characteristics of polyalkylacrylates in isomeric series. This comparison would provide information on the changes in the character of the thermodegradation of acrylic polymers as a function of the qualitative structure of the elementary polymer unit with a constant quantitative ratio of the molecules in this unit.

The present paper deals with the thermodegradation of all the isomeric polybutylmethacrylates (normal, iso, secondary and tertiary-PBMA) synthesized under identical conditions.

Experimental

Polymerization

The polymerization of the isomeric butyl methacrylates was carried out by the same method, irrespective of the monomer structure [8]. The monomer, distilled under vacuum, was placed in an ampoule and 0.2% by weight of cyclohexyl peroxydicarbonate was introduced. After the ampoule had been flushed three times with dry argon, it was sealed and placed in a thermostat at 20–22°. It was maintained at this temperature for 72 hr, and the reaction mixture was then heated according to the following schedule: at 65° for 10 hr, at 100° for 10 hr, at 130°

for 3 hr and at 160° for 3 hr. After polymerization had been completed, the ampoules were opened and the polymer was dissolved in an appropriate solvent and precipitated into methanol. The polymers were washed and dried under vacuum at 50° to constant weight.

Thermogravimetric analysis

Thermodegradation of the polymers was carried out with a Derivatograph. The sample size was 50 mg, and the heating rate 6°/min. For the determination of the effect of the atmosphere, the experiments were carried out under different conditions as follows:

1. Oxidative atmosphere: the polymer was heated in a standard crucible in air both under static conditions and in an air flow of 170–200 ml/hr.
2. Inert atmosphere: a helium flow of 300–400 ml/hr.
3. Self-generating atmosphere: a closed volume was achieved by using a large crucible with a lid or with a layer of an inert substance (alumina) above the sample.

The T_0 value [9], the starting temperature of polymer thermodegradation at which the TG curve begins to deviate, was used as a criterion of the thermostability of the polymers.

Apart from the thermoanalysis schedules reported above, the effect of the annealing of the polymers on the change in the value of T_0 was also investigated. The polymers were annealed for 400 min. under static air conditions at temperatures 40° below the value of T_0 for the corresponding polymer which did not undergo annealing.

Results and discussion

Fig. 1 shows the thermal analysis results. The abscissa gives the experimental conditions. The order of the conditions along the axis was established on the assumption that the thermostability of samples of isomeric polybutylmethacrylates increases in the following order: oxidative atmosphere → inert atmosphere → self-generating atmosphere → after annealing. The indices on the abscissa indicate that the analysis was carried out:

1 – in an air flow in a small open crucible
2 – without an air flow in a small crucible
3 – in a helium flow in a small crucible
4 – without an air flow in a closed small crucible
5 – with a helium flow in a closed small crucible
6 – without an air flow in a closed large crucible
7 – under an alumina layer in a large open crucible
8 – after annealing, in a large closed crucible
9 – after annealing, in a small closed crucible.

Poly-n-butylmethacrylate

Curve 1 in Fig. 1 shows that when an oxidative atmosphere is replaced by a self-generating atmosphere, a certain increase is observed in the thermostability of poly-n-butylmethacrylate.

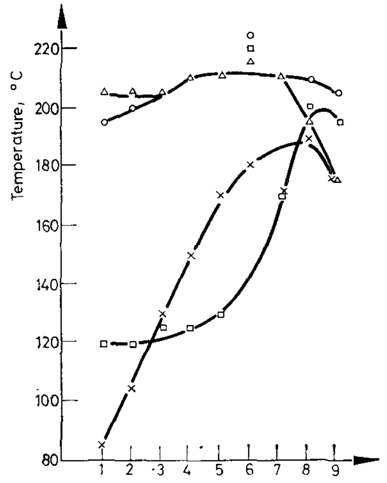
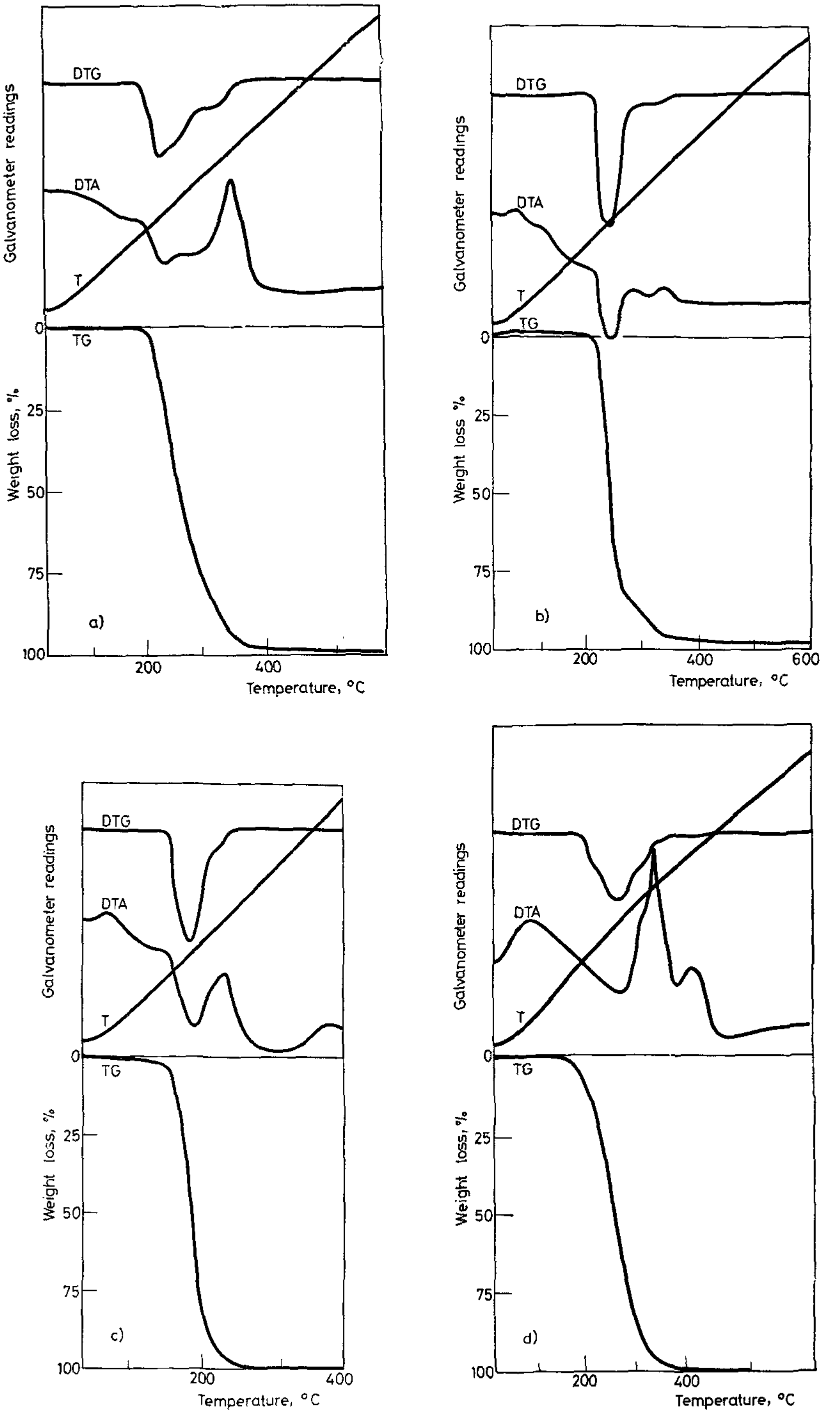


Fig. 1. Temperature of start of thermodegradation vs. experimental conditions. ○ normal-PBMA, △ iso-PBMA, □ secondary-PBMA, X tertiary-PBMA. Symbols of the abscissa are explained in the text

However, a change in the atmosphere surrounding the polymer causes only a slight change in the rate of the depolymerization processes characteristic of the thermodegradation of lower polyalkylacrylates. The predominance of depolymerization is confirmed by endothermal effects accompanying the loss in weight in the first stage of degradation, which was found to be about 85% in all the experiments. An example of the thermodegradation of poly-n-butylmethacrylate is shown in Fig. 2a.

Iso-polybutylmethacrylate

The thermodegradation of this polymer is very similar to that of the normal isomer, both in the T_0 values under different experimental conditions (Fig. 1, curve 2) and in the TG and DTA curves (Fig. 2b). Similarly to the degradation of poly-n-butylmethacrylate, the degradation of its isomer occurs as a result of rapid depolymerization of the macromolecule up to high conversion (85–90%). Only in the later stages of the thermodegradation or after a prolonged period at high temperature is it possible to discern some differences in the degradations of these polymers.


Galvanometer readings
DTG
DTA
T
TG
0
25
50
75
100
Weight loss, %
a)
200
400
Temperature, °C
b)
200
400
600
Temperature, °C
c)
200
400
Temperature, °C
d)
200
400
Temperature, °C

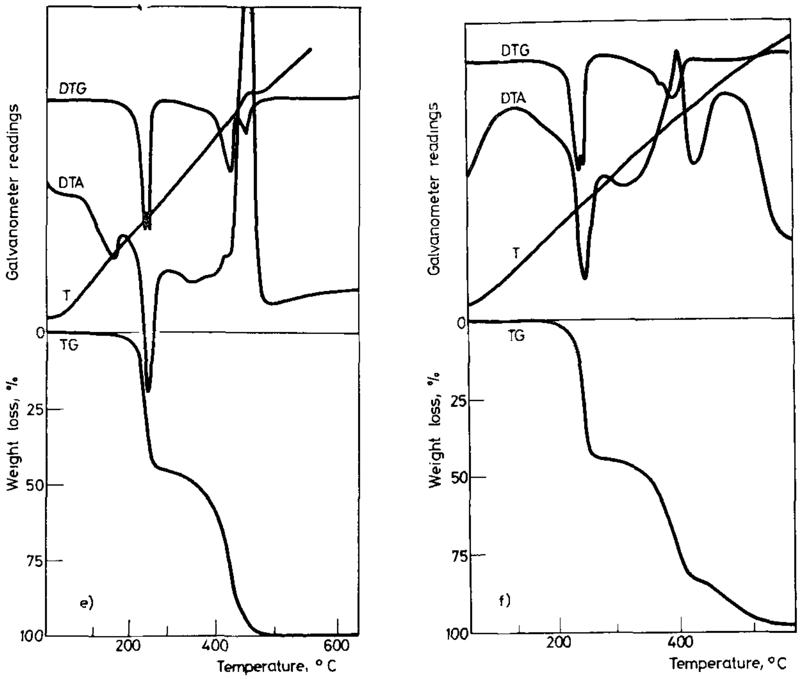


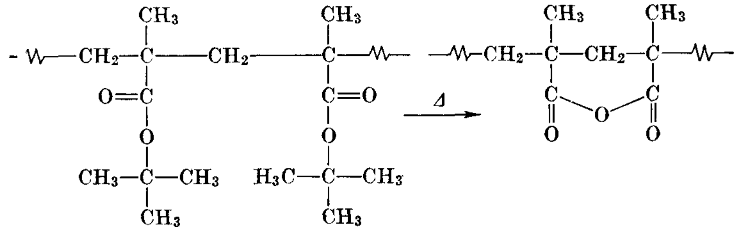
Fig. 2. Thermal analysis curves obtained by Derivatograph on samples of isomeric polybutylmethacrylates in a small open crucible in an air flow (Figs a, b, c, e) and in a large closed crucible after annealing (Figs d, f). The sample size was 50 mg, and the heating rate 6°/min. a) normal-PBMA, b) iso-PBMA, c) and d) secondary-PBMA, e) and f) tertiary-PBMA

Secondary-polybutylmethacrylate

In contrast to the polymers synthesized from the first two isomeric butyl methacrylates, the polymer of secondary-butyl methacrylate is more sensitive to changes in the surrounding atmosphere at high temperature (Fig. 1, curve 3). The increase in thermostability of the polymer is particularly marked when the analysis is carried out in a self-generating atmosphere, and also after annealing under isothermal conditions. When high temperature is maintained for a prolonged period, the polymer evidently undergoes cross-linking, and its rate in a self-generating atmosphere is comparable with the rate of depolymerization from the chain-ends. A comparison of the TG and DTA curves for annealed and untreated samples of secondary-polybutylmethacrylate (Fig. 2c and d) shows differences in the characters of their thermodegradations. In an untreated sample rapid loss in weight up to 80% conversion is observed in the first stage, with heat absorption similar to the processes of thermodegradation of normal and isopoly-butylmethacrylate. In an annealed sample a loss in weight of about 60% occurs in the first stage and the degradation of the remainder is highly exothermal.

Tertiary-polybutylmethacrylate

The last representative of the polybutylmethacrylate isomeric series illustrates clearly the influence of the qualitative change in the polymer structure upon its thermodegradation, and the corresponding effect of the experimental conditions upon the thermal characteristics of the product. Curve 4 in Fig. 1 shows a marked and steadily-growing increase in the value of T_0 on passing from an oxidative to an inert atmosphere and further to a self-generating atmosphere. Examples of TG and DTA curves in Fig. 2e and f, obtained in an oxidative and in a self-generating atmosphere, show that a pronounced three-stage character of the process is a general feature of the thermodegradation of tertiary-polybutylmethacrylate, in marked contrast to the thermodegradation of the three other polymers. Curve 4 in Fig. 1 shows that the value of T_0 (which in this case characterizes the beginning of the first process) increases with the resistance to removal of volatile products from the polymer in the first stage of thermodegradation. It is characteristic that, irrespective of the experimental conditions, the loss in weight in the first stage is always 46% and is accompanied by a constant endothermal effect. As to the following stages of thermodegradation, their rates and the accompanying thermal effects vary with the experimental conditions (Fig. 2e and f). The occurrence of a pronounced plateau region in the temperature range between 240 and 290°, in which the polymer loses hardly any weight, suggested that in the course of thermodegradation a new and more thermostable structure is formed. Annealing of tertiary-polybutylmethacrylate at 240° for 400 min. gave a product with a yield of about 52–53% and with T_0 = 330°. The infrared spectrum of this compound exhibited the presence of anhydride units (strong absorption bands in the region of 1760 and 1805 cm^{-1}), while theoretical calculations and calculations from the data of the TG curves showed that the volatile product of the thermodegradation of tertiary-polybutylmethacrylate in the first stage is di-butyl ether. The initial stage of thermodegradation of this polymer may thus be represented as follows: When tertiary-polybutylmethacrylate was subjected to thermal treatment at lower temperatures (130, 180, 230°), this did not change the character of the process:



+ $(CH_3)_3C-O-C(CH_3)_3$

in all cases the thermostability of the polymer did not increase above 190–200° until all dibutyl ether was removed.

Thus, if we compare the results of TG and DTA for the isomeric polybutylmethacrylates, it may be inferred that the thermodegradation of this group of polymers depends on the structure of the butyl radical. The isomerism of the monomer not only affects the thermal characteristics of the polymers, but also leads to great changes in their behaviour in different gaseous media at high temperature.

These differences in the thermodegradation of the isomeric polymers investigated may probably be ascribed to the different bonding energies of the primary, secondary and tertiary carbon atoms in the butyl radical attached to the ether oxygen. It is known from the literature [10, 11] that the energy of abstraction of isomeric radicals from a polymer molecule or from another organic molecule decreases in the following order: normal-PBMA > iso-PBMA > tertiary-PBMA, and for the C–H bond it is equal to 94, 92 and 89 kcal/mole, respectively.

If we consider the structure of the elementary unit of each isomeric polybutylmethacrylate, we can see that for normal and iso-butyl-methacrylate the α-carbon of the butyl radical bonded to the ether oxygen is a secondary carbon, i.e. it is attached to two hydrogen atoms, whereas in secondary-butyl methacrylate only C–H bond remains for the α-carbon, and in tertiary-butyl methacrylate it is attached merely to carbon atoms. Hence the behaviour of the α-carbon in the process of thermodegradation is similar for normal and iso-polybutylmethacrylates and differs from the behaviour of the other isomers, as was found by thermal analysis.

In normal and iso-polybutylmethacrylates the energy of abstraction of the monomer molecule from the chain-end is evidently lower than the energy of breaking of the C–O bond, i.e. the depolymerization process predominates. The decrease in the energy of the C–O bond for the tertiary isomer leads to the predominance of C–O bond-breaking at high temperature and to a qualitative change in the whole thermodegradation process. The values of the activation energies in the initial process of thermodegradation of all the polymers under investigation, determined from the TG curves by a well-known method [19], confirm this suggestion quantitatively. Calculation of E_a yields the following values: normal-PBMA 46 ± 4, iso-PBMA 42 ± 2, secondary-PBMA 40 ± 5, tertiary-PBMA 33 ± 5 kcal/mole. These figures show that the thermodegradation of tertiary-PBMA differs greatly from that of its isomeric analogs because depolymerization is absent.

Conclusions

1. TG and DTA methods were used to investigate the process of thermodegradation of polybutylmethacrylates synthesized from all the isomers of butyl methacrylate under conditions of oxidative, inert and self-generating atmospheres.

2. The isomerization of the initial monomers was shown to affect the thermal characteristics of the polybutylmethacrylates, in particular for the polymers with branched substituents.

3. It was shown that it is possible to increase the thermal stability of tertiary-polybutylmethacrylate by thermal treatment.

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Résumé — On a étudié, par TG et ATD, dans des atmosphères oxydantes, inertes et autogénérées, la dégradation thermique des polybuthylmétacrylates synthétisés à partir des quatre isomères du butylmétacrylate. On a établi que l'influence de l'atmosphère autour du polymère sur les caractéristiques thermiques des échantillons dépend du degré de réticulation des substituants dans le polybutylmétacrylate (PBMA). On suppose que les différences de dégradations thermiques respectives des PBMA isomères sont à relier aux différences de degré de réticulation du carbone-α dans l'ester substituant.

Zussammenfassung — Die thermische Zersetzung der aus sämtlichen vier Butylmethacrylat-Isomeren synthetisierten Polybutylmethacrylate wurde unter Anwendung der TG und DTA Methoden unter den Bedingungen oxidativer, inerter und selbst entwickelter Atmosphären studiert. Es wurde festgestellt, daß die Wirkung der das Polymer umgebenden Atmosphäre auf die Temperaturcharakteristika der Proben vom Verzweigungsgrad der Substituenten im Polybutylmethacrylat (PBMA) abhängt. Es wird angenommen, daß die Unterschiede in der thermischen Zersetzung isomerer Polybutylmethacrylate mit jenen des α-Kohlenstoffsubstituierungsgrades im Estersubstituenten verbunden sind.

Резюме — На основании данных ТГ и ДТА показана зависимость термостабильности изомерных полибутилметакрилатов от строения эфирного заместителя в макромолекуле, а так же установлено влияние окужающей полимер газовой среды на количественные и качественные характеристики процессов термодеструкции исследованных полимеров.