Journal of Thermal Analysis, Vol. 6 (1974) 53–58

THERMAL DECOMPOSITION OF POLYMETHYLMETHACRYLATE SYNTHESIZED WITH ANIONIC CATALYSTS

YU. N. SAZANOV, E. P. SKVORTSEWICH and E. B. MILOVSKAYA

Institute of High Molecular Weight Compounds,
Academy of Sciences of the USSR, Leningrad, USSR

(Received July 3, 1972; in revised form October 8, 1972)

TG and DTA data are used to show that the thermal decomposition of polymethylmethacrylate (PMMA) synthesized with anionic catalysts depends on the nature of the catalyst. It is found that the thermal stability of PMMA obtained by using anionic amide catalysts is higher than that of radical PMMA and of PMMA obtained with other anionic catalysts, and depends on the temperature of polymerization and on the molecular weight of the polymer.

Present methods of thermal analysis afford ample possibility for the investigation of polymer behaviour at elevated temperatures. The results of thermal analysis permit not only the determination of the limits of thermal stability, but also the establishment of a correlation between the method used for the synthesis of the polymer and the character of its thermal decomposition. The polymethylmethacrylate (PMMA) chosen for our investigations differs from the samples previously investigated in the nature of the catalyst, which is known to determine the polymer structure. A combined TG – DTA method of observing the thermal decomposition process makes it possible to choose optimum methods for synthesizing PMMA with favourable properties.

Although many papers deal with PMMA, only a few of these are concerned with the problems of its thermal decomposition [1 – 5], the decomposition being studied under isothermal conditions. Thermogravimetry was carried out only by McNeill [6], who discussed the results for several PMMA samples synthesized under different conditions. It should also be noted that, with the exception of McNeill's work, thermal analysis was carried out on PMMA samples synthesized in the presence of radical catalysts.

We chose PMMA obtained by using Et_2AlNPh_2 (aluminium-amide) as the main object of this investigation. In contrast to alkyls of alkali and alkaline earth metals, alkyl aluminium cannot initiate anionic polymerization of vinylic monomers. This is due mainly to the low polarity of the Al – C bond. Compounds with a more polar bond, such as aluminium mono-, di- and triamides, may be used as initiators of ionic polymerization [7, 8]. It is noteworthy that data on the mechanism of chain initiation and propagation in polymerization with aluminium amides as catalysts are scarce, and the characterization of the thermal decomposition of polymers obtained by this method is completely lacking.

Simultaneously with a study of the details of polymerization with aluminium amide (this work is in progress), we have made an attempt to determine the effect of changes in the nature of the anionic initiator used on the character of the decomposition of the polymer obtained with this initiator. Many circumstances indicate the possibility of this effect. First, the polymer synthesized in the presence of aluminium amide is more stereospecific (syndiotactic) than the polymer obtained by using BuLi in a polar medium. Secondly, the process taking place under the effect of aluminium amide is very peculiar. Thus, the influence of electron donors on the polymerization differs profoundly from their effect on the usual anionic polymerization. The introduction of catalytic amounts of strong electron donors (THF, HMPA, DMF) both in the initiation and in the propagation step completely inhibits polymerization, and the introduction of the weak electron donor Bu_2O suppresses it to a considerable extent [9]. These facts suggest that the monomer takes part in the chain initiation and propagation as an electron donor. Probably as a result of complex formation, both the monomer double bond and the organoaluminium compound are activated and this ensures effective development of the polymerization. This mechanism of polymer chain formation presumably leads to a more regular structure. This, in turn, should affect the characteristics of the thermal composition. Finally, the introduction of specific end-groups should also affect the thermal decomposition.

To elucidate the specificity of PMMA synthesized by using aluminium amide catalyst we have studied the thermal decomposition of PMMA samples obtained with common anionic (BuLi and $LiNPh_2$) and free radical (benzoyl peroxide and the system benzoyl peroxide – $AlEt_3$) catalysts [10].

Experimental

Commercial methyl methacrylate and commercial solvents were purified in the usual manner [11] with subsequent degassing and drying over butyl lithium. The catalysts Et_2AlNPh_2 and Ph_2NLi were synthesized according to Murahashi et al. [8]. The second catalyst was used in toluene suspension, butyl lithium was synthesized by the method described in reference [12], commercial benzoyl peroxide was purified in the usual manner, and $AlEt_3$ was used without additional purification. Polymerization was carried out in single-chamber ampoules, monomer, solvent and catalyst solution being introduced consecutively. After the completion of the process the polymer was precipitated into petroleum ether, washed, and dried to constant weight. For subsequent investigations the polymer was reprecipitated from chloroform solution into petroleum ether. The viscosity was determined in chloroform at 25°. The molecular weight was calculated from the equation $[\eta] = 3.4 \cdot 10^{-5} M^{0.83}$ [13].

Thermogravimetry was carried out with a Paulik – Paulik – Erdey derivatograph in air at a heating rate of 6°/min and with a sample weight of 50 mg. The NMR spectra were recorded with a Varian – 60 spectrometer in orthodichlorobenzene solution at 182°.

Results and discussion

The PMMA samples which had not been previously investigated were synthesized with anionic catalytic systems. PMMA samples obtained with common radical catalysts and under low-temperature conditions [10] were used for simultaneous comparative investigations. The results of thermogravimetric analysis shown in Table 1 indicate that the initial temperature of the thermal decomposition of anionic PMMA samples is in many cases much higher than for samples synthesized by radical mechanism. In extreme cases this difference attains 90°.

The thermal curves of samples 3 and 11 show considerable differences in character (Fig. 1). The two-stage process of the thermal decomposition of "radical" PMMA (Fig. 1a) agrees with the mechanism suggested previously [4], according to which in the thermal decomposition of PMMA two reactions compete: random degradation of polymer chains and depolymerization of both the initial chains and the fragments.

In contrast to this, the thermal decomposition of sample 3 (Fig. 1b) is monomodal and presumably* consists only in depolymerization accompanied by a pronounced endothermic effect.

The conditions of methacrylate polymerization in the presence of an ionic catalyst prevent the formation of unsaturated double bonds at the chain-ends of the PMMA macromolecules. As a rule, the initiation of the thermal decomposition of PMMA obtained with radical catalysts occurs on these bonds. It may be assumed that in the case of the catalysts investigated the terminal $N(Ph)_2$ groups in the polymer play the part of traps for free radicals, or that the amide group reacts with the peroxide formed, destroying it without the generation of free radicals [14]. This favours the increase of the initial temperature of thermal decomposition.

When radical catalysts are replaced by anionic ones, a change occurs in the whole process of the thermal decomposition of PMMA, with a considerable increase in the initial temperature of the decomposition (point of weight loss deflection).

In contrast to this, a change in the polymerization conditions in the presence of anionic catalysts does not alter the general picture of the process, but causes a proportional increase in the initial temperature of decomposition both when the polymerization temperature is lowered (samples 1–3) and when the molecular weight is increased to a certain limit (samples 3–5). For PMMA synthesized on BuLi (in THF or in toluene) (samples 9–10) the picture of the thermal decomposition differs both from that for the "radical" PMMA (Fig. 1a) and from that for the PMMA obtained in the presence of Et_2AlNPh_2 and $LiNPh_2$ (Fig. 1b and d). It is of interest to note the character of degradation of PMMA synthesized on butyl lithium: the consecutive decompositions of chain fragments with different thermal stabilities (DTG curve, Fig. 1c).

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* The products of the thermal decomposition were not investigated.

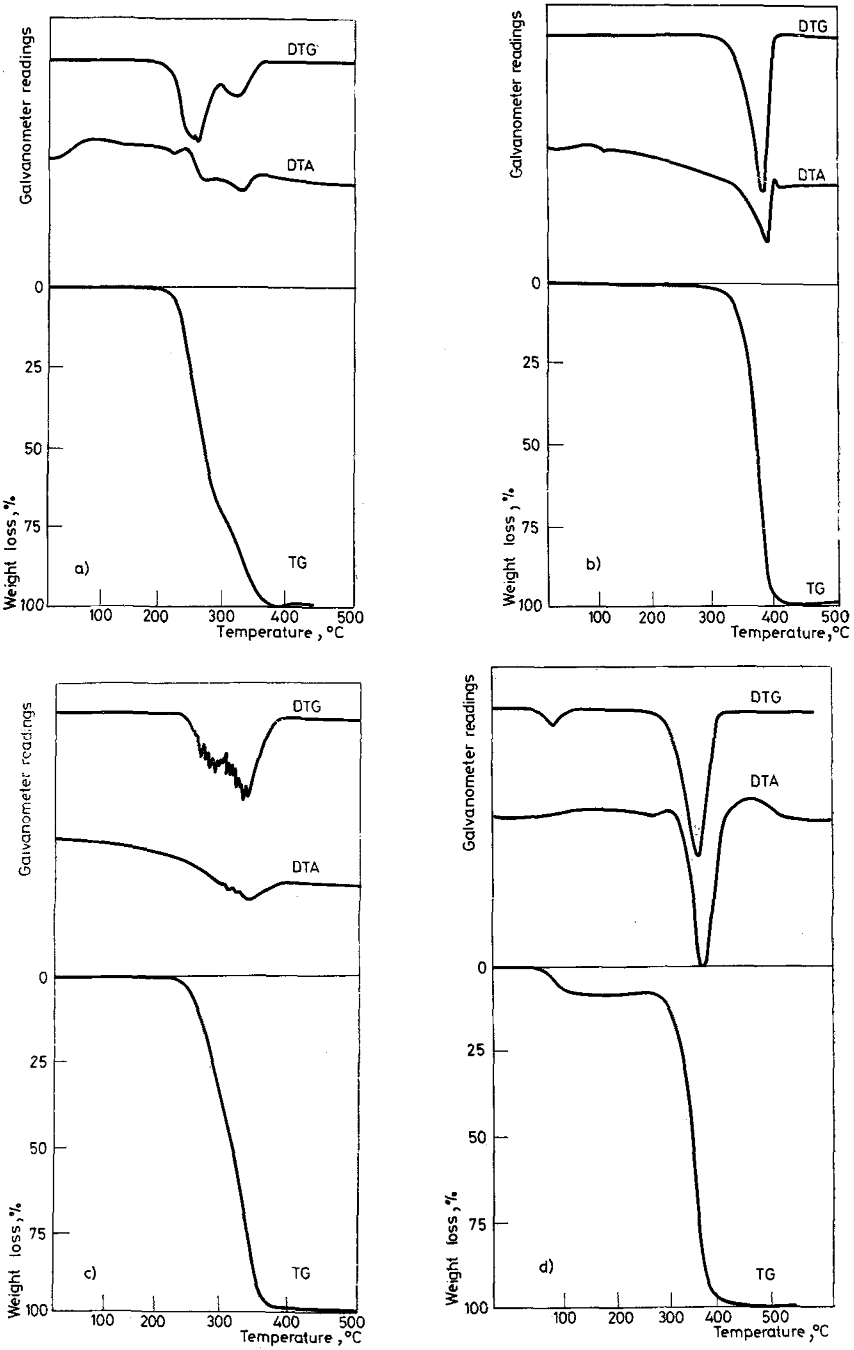

Fig. 1. Thermal curves of a) sample 11; b) sample 3; c) sample 9; d) sample 8

Thus, the considerable differences in the characters of the thermal decomposition of the PMMA samples synthesized with radical, anionic (BuLi) and anionic amide catalysts illustrate the effect of the nature of the initiator on the structure of the PMMA macromolecule. A marked increase in thermal stability, and the high stereoregularity of the PMMA obtained in the presence of Et_2AlNPh_2 are the advantages of this catalyst as compared to radical and common anionic catalysts. It may be added that this catalyst is more convenient to work with than are the catalysts insoluble in hydrocarbon solvents, in particular $LiNPh_2$.

So far the NMR data on the stereoregularity of the polymers under investigation given in Table 1 do not permit any suggestion as to the effect of tacticity on the parameters and the character of the thermal decomposition of PMMA. Further investigations and interpretation of the structural effects on the thermal stability are required. Nevertheless, even at this stage far greater possibilities of regulating the structure of PMMA in the course of synthesis are provided by the method of anionic polymerization, which permits an increase of the thermal stability of the polymers considered.

Table 1

Conditions of synthesis and PMMA properties

Sample No.	Catalyst	Polymerization temperature, °C	Mol. weight 10^{-3}	Stereoregularity			Initial temperature of thermal decomposition, °C
				syndio	iso	hetero	
1	Et_2AlNPh_2	−30	60	77	0	23	240
2	Et_2AlNPh_2	−50	64	79	—	21	250
3	Et_2AlNPh_2	−78	57	77	0	23	280
4	Et_2AlNPh_2	−78	10	73	9	18	245
5	Et_2AlNPh_2	−78	32	77	0	23	270
6	Et_2AlNPh_2	−78	100	—	—	—	265
7	Et_2AlNPh_2	−78	175	82	2	15	255
8	$LiNPh_2$	−78	207	8	63	29	260
9	LiBu (in toluene)	−78	140	13	70	17	230
10	LiBu (in THF)	−78	66	64	4	32	210
11	Benzoyl peroxide	+20	2000	—	—	—	190
12	Benzoyl peroxide + $AlEt_3$	−20	35	74	2	24	200

Conclusions

1. TG and DTA results have been used to illustrate the effect of the nature of the catalyst in PMMA synthesis on the character of the thermal decomposition of the PMMA.
2. It has been found that the thermal stability of most PMMA samples synthesized with anionic catalysts is higher than that of "radical" PMMA.

3. A decrease in the polymerization temperature of methyl methacrylate with anionic catalysts and an increase in the molecular weight of the PMMA (up to a certain limit) contribute to the increase of the thermal stability of the PMMA.

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The authors are indebted to A. I. Koltsov and V. M. Denisov for recording the NMR spectra of the polymers.

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Résumé — On montre, à partir des données TG et ATD, que la dégradation thermique du polyméthylmétacrylate (PMMA) synthétisé avec des catalyseurs anioniques dépend de la nature de ceux-ci. La stabilité thermique du PMMA obtenu avec des catalyseurs anioniques de type amide est plus élevée que celle du PMMA obtenu avec d'autres catalyseurs anioniques et elle dépend de la température de la polymérisation ainsi que de la masse moléculaire du polymère.

Zusammenfassung — An Hand von TGA und DTA-Angaben wurde gezeigt, daß die thermische Zersetzung des durch anionische Katalysatoren synthetisierten Polymethylmethacrylats (PMMA) von der Beschaffenheit des Katalysators abhängt. Es wurde gefunden, daß die Thermostabilität des unter Anwendung von anionischen Amid-Katalysatoren erhaltenen PMMA höher ist als die des radikalen PMMA oder des mit anderen anionischen Katalysatoren erhaltenen PMMA und daß sie darüberhinaus von der Polymerisationstemperatur und dem Molekulargewicht des Polymers abhängt.

Резюме — На основании данных TGA и DTA показано, что процесс термической деструкции полиметилметакрилата, синтезированного на анионных катализаторах, зависит от природы использованного в полимеризации катализатора. Установлено, что термостабильность PMMA, полученного на амидных анионных катализаторах выше термостабильности радикального PMMA и PMMA, полученного на других анионных катализаторах и зависит от температуры полимеризации и молекулярного веса полимера