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THE THERMAL DEGRADATION OF POLYMETHACRYLONITRILE WITH DIFFERENT END GROUPS

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Abstract

Polymethacrylonitrile (PMAN) was prepared by bulk, solution and precipitation polymerization. The thermal stability of the polymer, which is affected by the structure of the chain end groups, was studied by non-isothermal thermogravimetry (TG). On the basis of the differential TG curves of samples prepared by polymerization in the presence of chlorinated solvents, it may be concluded that, in addition to end-chain and random main chain scission initiated depolymerization, hydrogen chloride evolution also occurs during the thermal degradation of PMAN.

Keywords: end groups, polymethacrylonitrile, thermogravimetry

Introduction

Polymethacrylonitrile (PMAN) thermally degrades predominantly by the depolymerization mechanism. The thermal degradation of PMAN has been studied by several authors [1–7]. It was established that depolymerization is initiated by end chain and random main chain scission. The terminal double bonds, responsible for end chain initiated depolymerization, originated from termination by disproportionation and chain transfer to monomer ($C_{\mathrm{MAN}}^{60^\circ\mathrm{C}}=5.81\times10^{-4}$) [8] during radical polymerization. Conjugated structures can be formed to a lesser extent by internal cyclization [9].

The thermal stability of polymers degrading predominantly by depolymerization can be changed by varying the nature and amount of end groups in the polymer, such as chain-end double bonds and/or initiator or transfer agent residues, or the presence of weak links, such as head-to-head bonds.

As has been demonstrated in the case of poly(methyl methacrylate) (PMMA) [10] and poly(di-*n*-alkyl itaconates) [11], the depolymerization initiation modes can be identified and followed by analysis of the shapes of the differential thermogravimetric (DTG) curves. Depending on the ease of chain transfer reactions during degradation, which can be evaluated by means of the apparent kinetic length of de-

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propagation Z (zip length) [12], the shapes of the DTG curves can vary or remain unchanged depending on the initial molar mass of the polymer. Thus, the shapes of the DTG curves of PMMA are dependent on the initial molar mass, while the DTG curves of poly(di-*n*-alkyl itaconates) remain unchanged. McNeill and Mahmood [13] have established that the shapes of the DTG curves of PMAN also change with initial sample molar mass.

The goal of this investigation was to study changes in the thermal stability of PMAN with modified end groups by means of non-isothermal differential thermogravimetry.

Experimental

PMAN samples were prepared by radical polymerization in bulk in the absence and presence of *n*-dodecyl mercaptan (DDM) and in solutions of dichloromethane, chloroform, carbon tetrachloride or benzene. The only true solution polymerizations were the ones in dichloromethane. The bulk polymerizations and polymerizations in chloroform were precipitation polymerizations in which swollen insoluble polymer formed in the reaction system, whereas the polymerizations in carbon tetrachloride and in benzene were classic precipitation polymerizations during which the formed polymers precipitated as white powders in the monomer/solvent mixture.

Methacrylonitrile (MAN) (Merck, p.a.) was distilled prior to use, as were the commercial solvents of various origin. DDM (Aldrich, p.a.) was used as received. α,α'-Azobisizobutyronitrile (Merck), recrystallized in methanol, was used to initiate the polymerizations. The solutions were prepared in volumetric flasks by first adding the required amount of MAN and then filling the remaining volume with the chosen solvent. DDM was added by means of a Hamilton microlitre syringe. The reaction mixtures were transferred to glass ampoules, bubbled for 20 min with nitrogen and then sealed under vacuum. The polymerizations, performed at 40 or 60°C, were taken to low yields. The obtained polymers were purified by multiple dissolution/precipitation in acetone/methanol and dried to constant mass under vacuum at room temperature.

The PMAN samples were characterized by determining the limiting viscosity number (LVN) in N,N-dimethyl formamide at 29.2°C. The viscosity average molar masses, $\overline{M}_v$, of the samples were calculated by means of the Kuhn-Mark-Houwink-Sakurada equation taking literature values for the constants K and a [14].

The polymerization conditions and $\overline{M}_v$ of the prepared PMAN samples are given in Tables 1 and 2.

Table 1 Polymerization conditions and viscosity average molar masses, $\overline{M}_v$, of PMAN synthesized by bulk polymerization in the presence of DDM at 40°C, [AIBN] = 0.01 mol dm^{-3}

Sample No.	[DDM]/[MAN]$\times10^3$	$\overline{M}_v$/g mol^{-1}
D0	0	89100
D1	0.9	34500
D2	2.6	19500

Table 2 Polymerization conditions and molar masses, $\overline{M}_v$, of PMAN synthesised in the presence of various solvents

Sample No.	Solvent	[S]/[MAN]	[AIBN] mol dm^{-3}	T_{Pol}/ °C	t_{Pol}/ min	$\overline{M}_v$ g mol^{-1}
S0	none	0	0.005	60	1080	49000
S1	CH_2Cl_2	1.92	0.005	40	5830	31000
S2	$CHCl_3$	1.50	0.005	60	1200	15000
S3	CCl_4	1.28	0.002	60	80	175000
S4	C_6H_6	0.91	0.005	60	1080	1765000

A Perkin Elmer TGS-2 instrument was used for non-isothermal experiments in a dynamic nitrogen atmosphere (30 cm^3 min^{-1}) in the temperature interval 30–600°C applying heating rates of 2.5, 10, 20 and 40°C min^{-1}.

Results and discussion

The obtained non-isothermal thermogravimetric (TG) curves of all the PMAN samples show similar trends. The amount of carbonaceous residue at 500°C increases at lower heating rates and the DTG peaks are better resolved at higher heating rates. Such behavior is in accordance with the results of Hill *et al.* [15], implying that PMAN is more susceptible to the side reaction of internal cyclization at lower heating rates and that the two depolymerization initiation modes are only discernible at higher heating rates.

The effect of DDM end groups on the thermal stability of PMAN

The TG curves of PMAN synthesized in the absence and presence of DDM are very similar. The characteristic mass loss temperature, $T_{5\%}$, $T_{50\%}$ and $T_{90\%}$, are shifted toward slightly lower temperatures in the presence of DDM (Table 3). With increasing amount of DDM added during the polymerizations, there is a small increase in the amount of carbonaceous residue. The differences in the samples are better seen in the DTG curves (Fig. 1a). The PMAN sample prepared without DDM has a clearly visible shoulder originating from chain end initiated depolymerization, while the main peak corresponds to main chain scission initiated depo-

Table 3 Characteristic TG data for PMAN synthesized in the presence of DDM, heating rate 10°C min^{-1}, N_2 flow rate 30 cm^3 min^{-1}

Sample	$T_{5\%}$/°C	$T_{50\%}$/°C	$T_{90\%}$/°C	% Residue at 500°C
D0	305	365	392	3.0
D1	300	355	390	4.3
D2	295	353	390	5.8

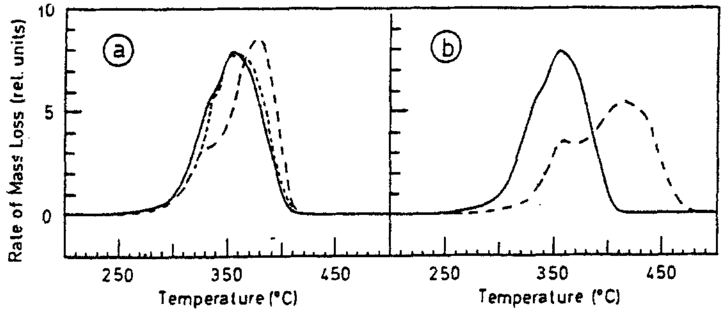


Fig. 1 The DTG curves of PMAN samples synthesized in the presence of DDM: a) D0 (– – –), D1 (- - -), D2 (—), heating rate 10°C min^{-1}, b) D2, heating rates 10°C min^{-1} (—) and 40°C min^{-1} (– – –), N_2 flow rate 30 $\text{cm}^3\ \text{min}^{-1}$

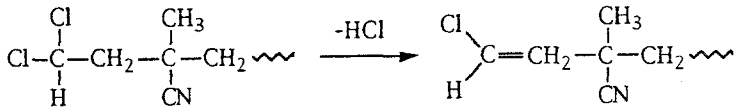
lymerization. The DTG curves of samples prepared in the presence of DDM consist of a broad peak consisting of two unresolved peaks originating from the two depolymerization initiation modes. When a higher heating rate is applied, the two peaks separate, as seen in Fig. 1b.

There are two factors affecting the shapes of the DTG curve due to the effect of the chain transfer agent. The size of the first should decrease because of the reduced number of chain end double bonds formed in the polymer because of the predominance of chain transfer to DDM as opposed to chain transfer to monomer and termination by disproportionation during the polymerization. On the other hand, because of the resulting lower polymer molar mass, the size of the second peak should decrease. Thus, the overall effect on the overall thermal stability of the polymer is negligible.

The effect of chlorinated solvent end groups on the thermal stability of PMAN

Due to the relevant differences in polymerization conditions, it is difficult to obtain PMAN samples that are readily comparable. However, the trends in polymer stability are similar in the same monomer/solvent systems, so characteristic TG curves of PMAN samples synthesized in the presence of chlorinated solvents are presented in Fig. 2.

The common feature of all the TG curves is a small mass loss starting at about 220°C, non-existent in the bulk polymer TG curve. Thus, all of these PMAN samples have lower thermal stability than bulk polymerized PMAN. These differences are even better evidenced in the corresponding DTG curves (Fig. 2). In all three cases a small new peak is visible with a maximum at about 230–250°C. It may be assumed that this peak originates from a chain end dehydrochlorination reaction. The availability of chlorine atoms at the chain ends due to transfer reactions during sample preparation allow the occurrence of an elimination reaction, similar to the thermal dehydrochlorination of PVC. For example:



Zutty and Welch [16] have observed an intramolecular reaction in copolymers of methyl methacrylate and vinyl chloride at around 150°C in which γ-lactone rings are formed with the elimination of HCl. A corresponding reaction in PMAN with end groups from the applied chlorinated solvents does not seem likely.

It is also not probable that this peak can be ascribed to depolymerization initiated by the scission of head-to-head bonds, as such behavior has not been found in the thermal degradation of bulk PMAN. In order to confirm that the low temperature DTG peak originates from chlorine containing structures, a PMAN sample obtained by the precipitation polymerization of MAN in benzene was analysed by DTG. The obtained DTG curve is presented in Fig. 3. The absence of the low temperature peak is evident.

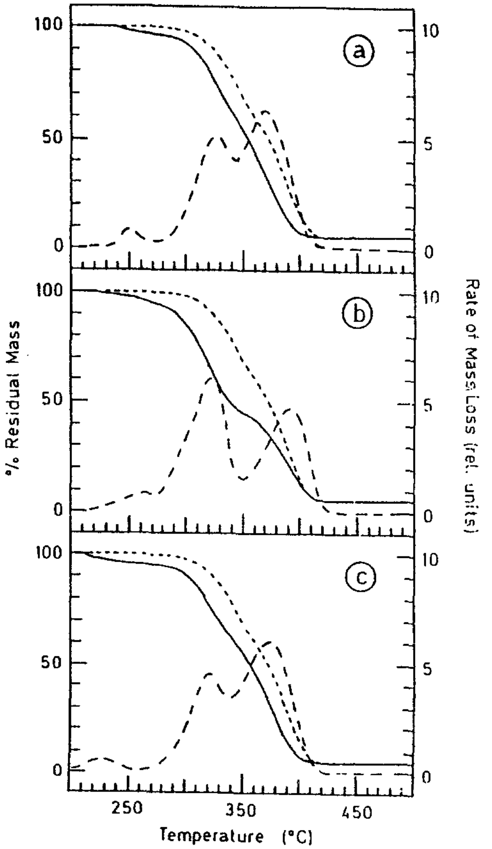


Fig. 2 The TG (—) and DTG (– – –) curves of PMAN samples synthesized in the presence of chlorinated solvents: a) CH_2Cl_2, S1, b) $CHCl_3$, S2 and c) CCl_4, S4; TG curves S0 (- - - -) sample S0, heating rate 10°C min^{-1}, N_2 flow rate 30 cm^3 min^{-1}

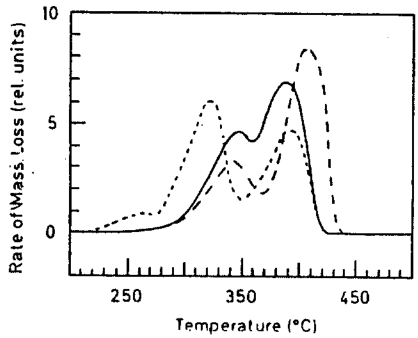


Fig. 3 The DTG curves of PMAN samples synthesized in the presence of benzene, S4 (– – –), $CHCl_3$, S2 (- - - -) and in bulk, S0 (—), heating rate 10°C min^{-1}, N_2 flow rate 30 cm^3 min^{-1}

Preliminary non-oxidative isothermal degradation experiments of PMAN samples with chlorinated solvent end groups were performed at 250°C and the volatile degradation products were passed through aqueous NaOH solutions and changes in the solution *pH* were measured. According to these experiments, the amounts of emitted acidic volatiles were equivalent to the expected calculated amounts of evolved HCl.

The second and third DTG peaks in PMAN samples with chlorinated solvent end groups correspond to chain end and main chain scission initiated depolymerization. However, the ratios of the heights of these peaks are different to that of bulk PMAN, with a noticeable increase of the second peak. This increase can be explained by the generation of new chain end double bonds by the dehydrochlorination reaction.

It could be expected that the size of both the first and second DTG peaks could increase with increasing number of chlorine atoms in the end group available for HCl elimination. This trend holds for PMAN samples synthesized in CH_2Cl_2 and $CHCl_3$. In the case of PMAN samples prepared in CCl_4, the additional effect of the very high initial molar mass of the sample (Table 2), due to the nature of precipitation polymerizations, does not allow discussion of this trend.

Further, more detailed investigations of the thermal degradation of PMAN with chlorinated solvent end groups are currently under way.

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