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NONISOTHERMAL THERMOGRAVIMETRY OF POLYMERS

V. Bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide)

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Abstract

The model of weight loss taking place in each step of a scheme of consecutive reactions was applied to nonisothermal thermogravimetric records of bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide). The release of HBr was found to be faster in air than in nitrogen. A significant reduction in the apparent activation energy of dehydrobromination as compared with decomposition of the nonbrominated polymer was ascribed not only to a reduction in the activation energy of the initiation reaction, but also to an increase in the order of the termination reaction (from 1 for the nonbrominated polymer to 2 for the highly brominated polymer).

Keywords: bromination of methyl groups, effect of bromine atoms, model of consecutive reactions, nonisothermal thermogravimetry, poly(2,6-dimethyl-1,4-phenylene oxide), thermal and thermooxidation stability,

Introduction

Nonisothermal thermogravimetric (TG) records composed of reaction steps which are mutually superimposed require a modelling of the process with two or more temperature-dependent functions (rate constants). In recent papers [1–3], a model of two or three parallel reactions has been applied to the decomposition of blends of polyethylene, polypropylene and poly(methyl methacrylate) or polyethylene with inorganic additives such as aluminium and magnesium hydroxide. The kinetic independence of the respective reaction steps for this model must be assumed. It was found that such independence is an ideal case [2, 3]: even in mixtures of polymers with inorganic additives, the decomposition of each component is correlated with the decomposition of the rest of the system.

In the present paper, we submit an analysis of a nonisothermal model based on consecutive reaction steps in which volatile products are formed directly

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from the polymer itself and also from intermediates of polymer decomposition. As an experimental example of such behaviour, bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) (*PPO*) was chosen. This gives hydrogen bromide in the first step, while in a second step volatile products are formed from *PPO* residues. The thermal stability of bromomethylated *PPO* in a nitrogen atmosphere was investigated by Goh and Lee [4]. They indicated that the incorporation of bromine into the methyl groups leads to appreciable modifications in the decomposition [5, 6], but also to significant thermal destabilization of the polymer. The effects of an oxidation atmosphere, which have not been studied so far, also appear to be of interest.

Experimental

Materials

PPO was Nerafen (Spolana, Neratovice), $[\eta]=0.45$ dl/g (chloroform, 25°C), $M_n=21000$ (vapour phase osmometry). The polymer was purified by precipitation from chloroform solution into methanol, and dried in a vacuum oven.

Liquid bromine, dicumyl peroxide, chlorobenzene and methanol were all reagents of analytical grade purity (Lachema, Brno).

Methods

1 g ($8.33\cdot10^{-3}$ mol) of purified *PPO* was dissolved in 135 ml (1.33 mol) of chlorobenzene in a 250 ml four-necked flask equipped with a mechanical stirrer, a thermometer, a condenser and a nitrogen inlet, and heated to the reflux temperature (132°C) of chlorobenzene. A solution of 0.2 g ($7.4\cdot10^{-4}$ mol) of dicumyl peroxide in 8 ml (0.08 mol) of chlorobenzene was then added, followed by a solution of the required amount of molecular bromine in 0.36 mol of chlorobenzene, dropwise. The reaction mixture was kept at reflux temperature for 2 h. From the warm solution, the brominated polymer was precipitated and washed with methanol and dried under vacuum at 80°C for 12 h.

Analysis

All samples were subjected to elemental analysis (CHN/S/O, Carlo Erba 1106) and ^{1}H-NMR spectroscopy.

Bromine content was determined according to Schöniger [7].

^{1}H-NMR spectra were measured (Bruker AM-300 spectrometer) in $CDCl_3$ *vs.* TMS, at 300.13 MHz. The concentration of brominated methyl groups was calculated from the integral intensity of the proton signals of methylene (4.33 ppm) and methyl groups (2.09 ppm).

FTIR spectra (Fourier Transform Infrared Spectrometer Nicolet 20 DXB) were recorded with solvent (chloroform) cast films of bromomethylated *PPO* samples prepared on NaCl plates. FTIR was used as a qualitative tool to demonstrate bromomethylated groups, the presence of which was confirmed by the stretching frequencies at 590 and 1219 cm^{-1}.

Nonisothermal TG measurements were carried out on a derivatograph (Q 1500 D MOM, Hungary) either in nitrogen or in air (20 to 1000°C), at a heating rate of 10 $deg \cdot min^{-1}$. The sample mass was 50 mg.

Results and discussion

The losses in mass of bromomethylated samples of *PPO* in nitrogen (0, 6.5, 11, 21, 31 and 45 wt.% of bromine) at a heating rate of 10 $deg \cdot min^{-1}$ are shown in Fig. 1. As reported by Goh [4], two steps of mass loss can be distinguished in the nonisothermal TG record; the former obviously corresponds to the formation of HBr, while the latter is situated at a temperature where the pure polymer undergoes random chain splitting. The residual char, which is the final product of thermal degradation of both nonbrominated and brominated samples, changes in mass only slowly with increasing temperature, even at 900 K.

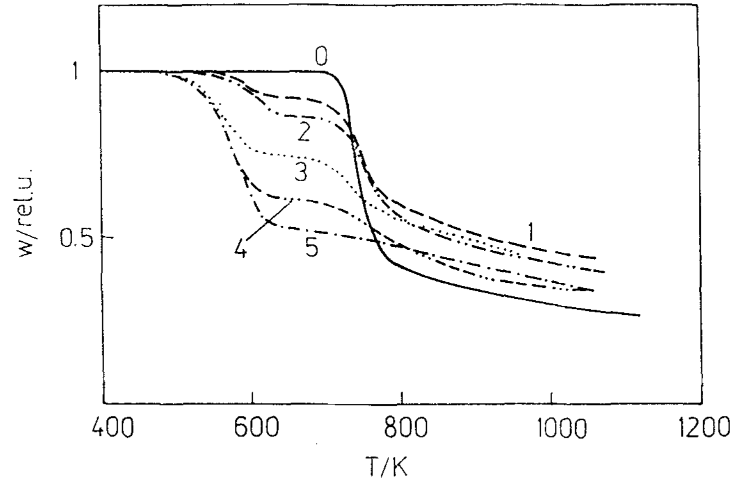


Fig. 1 Nonisothermal TG records of bromomethylated *PPO* in nitrogen. Content of bromine: 0 (0), 6.5 (1), 11 (2), 21 (3), 31 (4) and 40 (5) wt%

The initial temperature T_i of decomposition of bromomethylated *PPO* decreases with increasing content of bromine. The effect is similar to that for *PPO* brominated on the phenyl ring [8]. A relatively small content of aliphatically bound bromine (6.5 wt.%) leads to a reduction in T_i of 164 deg as compared with the pure polymer. On further increase of the concentration of bromomethylated groups (6.5–45 wt.%), an additional reduction in T_i of only 58 deg was found. Formally, the formation of volatile species from bromomethylated *PPO* can be represented by a model which involves both important reaction steps, dehydrobromination and degradation of the *PPO* residue:

$$PPO \xrightarrow{k_1} X + mV_1 \tag{1}$$

$$X \xrightarrow{k_2} CR + nV_2 \tag{2}$$

where X is the degradation intermediate, CR is the char residue, and V_1 (HBr) and V_2 are volatile species formed in the respective steps of the consecutive reaction scheme.

If the temperature dependence of the rate constants corresponding to steps 1 and 2 is expressed by the Arrhenius equation:

$$k_i = A_i \cdot \exp\left(-E_i / RT\right) \tag{3}$$

the formation of volatile products V_1 and V_2 can be described by the equation

$$\mathrm{d}V_1/\mathrm{d}t + \mathrm{d}V_2/\mathrm{d}t = mk_1\,PPO + nk_2\,X \tag{4}$$

or

$$\mathrm{d}V_1/\mathrm{d}T + \mathrm{d}V_2/\mathrm{d}T = m/\beta\;k_1\,PPO + n/\beta\;k_2\,X \tag{5}$$

where β is the rate of heating.

Table 1 The parameters determined by nonisothermal thermogravimetry of the bromomethylated *PPO* samples. The model of weight loss based on the scheme of subsequent reactions (in nitrogen)

Bromine / % wt	E_1/ kJ·mol^{-1}	E_2 /	A_1 / β	A_2 / β	m	n
0	338	3	$3.1 \cdot 10^{22}$	0.007	0.48	0.26
6.5	146	95	$5.8 \cdot 10^{11}$	$5.8 \cdot 10^{4}$	0.07	0.42
11	145	85	$2.6 \cdot 10^{11}$	$1.1 \cdot 10^{4}$	0.10	0.43
21	96	66	$2.9 \cdot 10^{7}$	508	0.23	0.27
31	91	39	$6.3 \cdot 10^{6}$	2	0.36	0.20
40	91	53	$3.9 \cdot 10$	20	0.47	0.16

Note: For bromomethylated *PPO* m is related to the relative weight of HBr released, n is the relative amount of *PPO* residuals which are decomposed into volatiles and 1-m-n is the relative weight of charred residue.

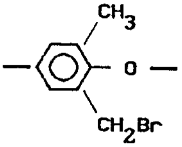
The nonisothermal kinetics of transformation of *PPO* and *X* can be expressed as

$$\mathrm{d}\,PPO/\mathrm{d}T = -k_1/\beta\ PPO \tag{6}$$

$$\mathrm{d}\,X/\mathrm{d}T = k_1/\beta\ PPO - k_2/\beta\ X \tag{7}$$

Numerical integration of Eq. (4) together with Eqs (6) and (7), the model being fitted to experimental mass *vs.* temperature runs by a nonlinear regression method, permits the determination of parameters such as E_1, E_2, A_1, A_2, m and n. The results are given in Table 1.

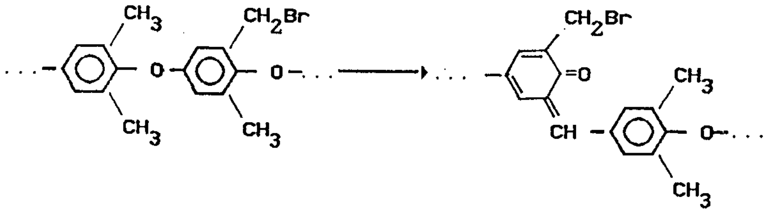
The activation energy of the dehydrobromination (step 1) is higher (ca 140 kJ/mol) for a lower content of bromine. For a higher content of bromine in *PPO*, it is about 90 kJ/mol. This may demonstrate the fact that different CH_2Br groups can take part in the dehydrobromination process, *e.g.* those with a regular character:



I)

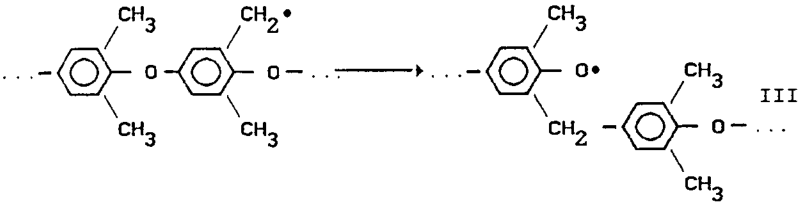
but also CH_2Br groups formed after the structural rearrangement of *PPO*, *e.g.*

II)



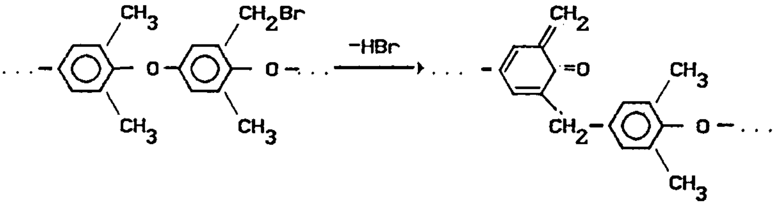
Rearrangement of Fries type prior to random splitting has been reported for *PPO*; for the pure polymer [9], the process occurs at higher temperature. This does not appear to be the case during the halogenation or dehydrohalogenation of *PPO*. In fact, structure II should release bromine more easily than structure I, and the activation energy of its dehydrobromination should be lower. Many other anomalous *PPO* units [10] can be proposed, but the ^{1}H-NMR spectra show that their concentration is negligible.

The process of dehydrobromination represents an interesting alternative from the viewpoint of the mechanism. Following the primary homolysis of the C–Br bond, methylene radicals and bromine atoms are apparently formed. The problem is whether the bromine atoms abstract hydrogen from other methyl group on the polymer chain, or whether this is a process involving only the same phenyl ring. It may be supposed that the methylene radical has a strong tendency to the following rearrangement:



III)

It homolysis of the C–Br bond and rearrangement take place within one meric form, the conjugated structure IV is likely to be formed during dehydrobromination:



IV)

Similarly as in paper [1], with testing of the losses in mass of parallel processes, we attempted here to test the unambiguity of the model of consecutive steps where volatile compounds are formed. The procedures were performed so that the theoretical lines of residual mass *vs.* temperature were constructed for a set of chosen parameters (Fig. 2). The procedure of nonlinear regression was then applied to a given curve, assuming considerably different values of the initial parameters. It was found that the convergency of the method to the minimum sum of the least squares was rather fast. The iterations usually ended in a set of parameters corresponding to the correct values (Table 2). In this way, acceptable values of E_1, E_2, A_1 and A_2 can be found for a given experimental curve.

It is of interest that the values of apparent activation energy of *PPO* dehydrobromination reported by Goh [4] vary within the interval 185–110 kJ/mol, depending on the amount of bromine bound, while we found it to be 140–90 kJ/mol for approximately the same interval of bromine concentrations. We take this as a demonstration that the one-step approach used in the former case suffers from errors due to the superposition of the consecutive reaction steps.

As we have indicated, in a kinetically controlled region of the reaction [2], the apparent activation energy E of decomposition of the polymer into volatile products may be expressed as

$$E = E_f + 1/n(E_i - E_t)$$

where E_f is the activation energy of fragmentation of polymer macroradicals into lighter fragments, E_i is the activation energy of initiation of polymer cleavage, and E_t is the activation energy of free radical termination with order n.

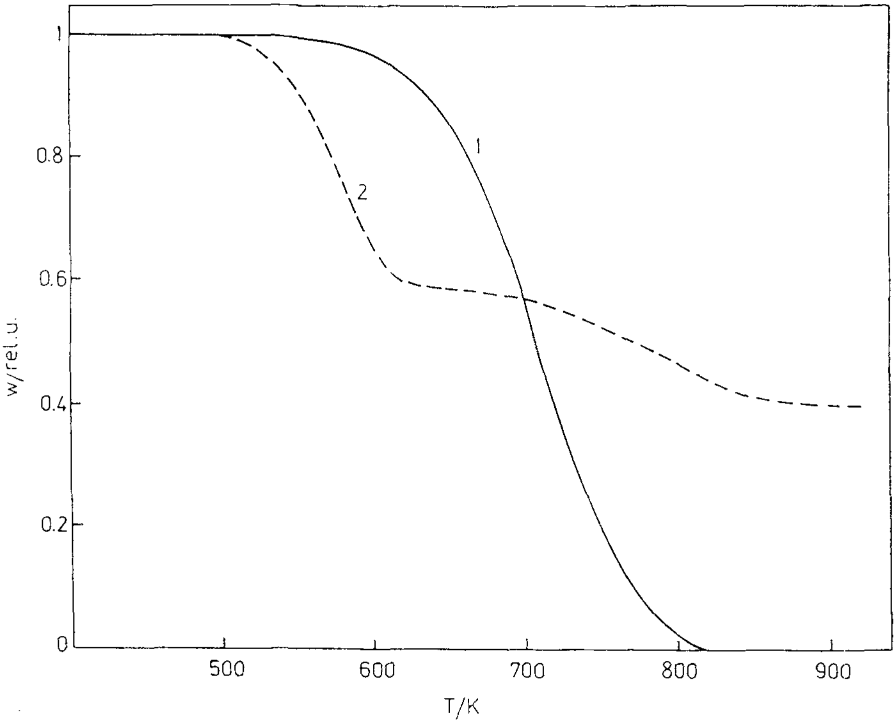


Fig. 2 Theoretical residual mass *vs.* temperature lines calculated for the model based on the scheme of consecutive reactions. The parameters used for calculation are as in Table 2

	Line 1	Line 2
E_1, J/mol	100 000	110 000
E_2, J/mol	80 000	80 000
A_1 / β	$1 \cdot 10^6$	$3 \cdot 10^8$
A_2 / β	$1 \cdot 10^4$	3 000
m	0.5	0.4
n	0.5	0.2

β is the rate of heating

The reduction in apparent activation energy of *PPO* decomposition (from a value well above 300 kJ/mol for the pure polymer to 90 kJ/mol for bromomethylated *PPO*) for a large degree of reaction indicates that, in parallel with the reduction in activation energy of polymer decomposition into radicals (E_i), an increase in the order of termination n occurs. Obviously, the pure polymer has a value of n close to 1, while with an increasing degree of bromination n approaches 2.

Table 2 The starting and end values of parameters for the iteration process (theoretical lines 1 and 2 on Fig. 2)

Parameters Starting	Line calculated for	Final	Units
Line 1			
E_1 = 150 000	100 000	99 963	J/mol
E_2 = 150 000	80 000	79 995	J/mol
$A_1 / \beta = 1{\cdot}10^{11}$	$1{\cdot}10^{6}$	$9.95{\cdot}10^{5}$	
$A_2 / \beta = 1{\cdot}10^{11}$	$1{\cdot}10^{4}$	$1{\cdot}10^{4}$	
m = 0.2	0.5	0.5	
n = 0.8	0.5	0.5	
Line 2			
E_1 = 150 000	110 000	109 957	J/mol
E_2 = 150 000	80 000	79 978	J/mol
$A_1 / \beta = 1{\cdot}10^{10}$	$3{\cdot}10^{8}$	$3{\cdot}10^{8}$	
$A_2 / \beta = 1{\cdot}10^{10}$	3000	2994	
m = 0.7	0.6	0.6	
n = 0.2	0.2	0.2	

From this viewpoint, the dependence of the apparent activation energy of formation of the volatile products on the bromine content [4] is not justified. It should be recalled that in paper [4] the thermogravimetry records indicated that the order of decomposition of the polymer was equal to 1 for all samples, regardless of the fact that the mechanism of the reaction was changing.

Thermogravimetry of bromomethylated PPO in air

The effect of atmospheric oxygen on bromomethylated *PPO* samples containing the same amount of bromine as in the previous case is clear (Fig. 3). Except for the sample containing 6.5 wt.% of bromine, the process of dehydrobromination (the first process in the TG records) is shifted to lower temperatures. This is particularly clear for samples with the maximal amount of bromine present. The second loss in mass is a superposition of the oxidation of charred and probably crosslinked residues and the random chain splitting of the original *PPO*.

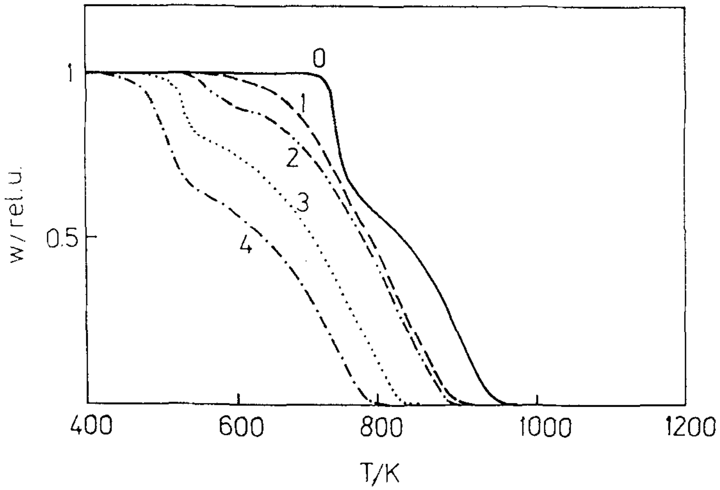


Fig. 3 Nonisothermal TG records of bromomethylated *PPO* in air. Content of bromine: 0 (0), 6.5 (1), 11 (2), 21 (3), 40 (4) wt%

Table 3 The parameters determined by nonisothermal thermogravimetry for bromomethylated *PPO* samples in air. The model of weight loss based on the scheme of subsequent reactions

Bromine /	E_1 /	E_2 /	A_1 / β	A_2 / β	*m*	*n*
% wt	kJ·mol^{-1}					
0	335	118	$3.6\cdot10^{22}$	$1.8\cdot10^{5}$	0.36	0.64
6.5	95	66	$2.1\cdot10^{6}$	260	0.06	0.94
11	104	65	$9.1\cdot10^{7}$	261	0.10	0.90
21	134	57	$7.3\cdot10^{11}$	135	0.20	0.80
31	79	58	$4.9\cdot10^{6}$	328	0.35	0.65
40	104	64	$2.0\cdot10^{8}$	381	0.41	0.59

Note: *m* is the same as in Table 1

The kinetic parameters obtained according to the model of consecutive reactions are given in Table 3. To allow a comparison of the stabilities of pure and brominated *PPO*, the rate constant of decomposition of a given sample corresponding to 500 K, i.e. to the region of occurrence of the first loss in mass, was calculated (Table 4). As expected, the process of formation of HBr is appreciable faster in air than in nitrogen. It can be seen that in both cases the rate constant of HBr release from bromomethylated *PPO* attained its maximum for samples with a bromine content somewhere between 20 and 30 wt%.

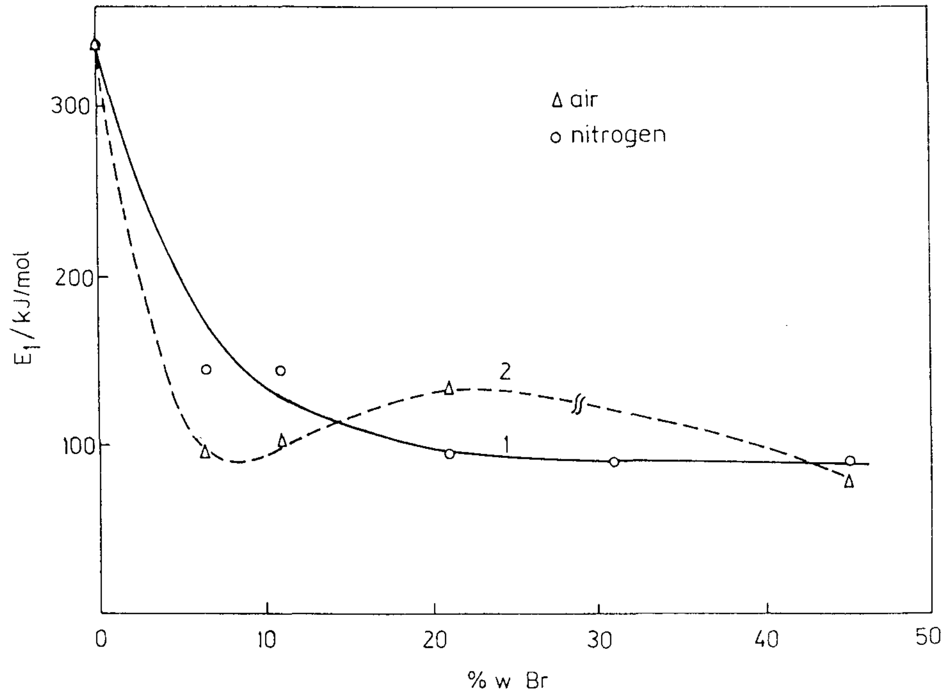


Fig. 4 Plot of activation energy E_1 for release of volatiles from bromomethylated *PPO* *vs.* initial content of bromine in sample. Line 1 – nitrogen, line 2 – air

The higher rate constants for the dehydrobromination of samples decomposed in air supports the idea that bromine atoms formed by homolysis of CH_2–Br bonds do not abstract hydrogen only within one mer. Benzyl radicals $P^{\bullet}$ reaction with oxygen to form peroxy radicals, which enter into a fast reaction with HBr, and the stage of propagation of the dehydrobromination is accelerated due to the increased length of the chain reaction caused by a partial regeneration of bromine atoms:

$$P^{\bullet}+O_2 \rightarrow PO_2^{\bullet}$$

$$PO_2^{\bullet}+HBr \rightarrow POOH+Br^{\bullet}$$

$$Br^{\bullet}+PH \rightarrow HBr+P^{\bullet}$$

An apparently higher stability, which does not correspond to the activation energy values of the samples (Fig. 4), for the highest content of bromine may be caused by the back-hydrobromination of the phenyl rings, which occurs in competition with the loss of HBr. The subsequent decomposition of brominated phenyl rings, which occurs in one step, will thus be slower. Moreover, the char residue formed from the *PPO* is converted into volatile products much more easily in air than in nitrogen (Fig. 3). In air, the overall mass of the sample is totally 'evaporated' and $m+n=1$.

Conclusions

It has been demonstrated that bromination of the methyl groups of poly(2,6-dimethyl-1,4-phenylene oxide) (*PPO*) leads to a considerable destabilization of the polymer in both nitrogen and air atmospheres. Analysis of the nonisothermal TG mass loss curves for modified *PPO* samples on the basis of a model of consecutive reactions, in which volatile products are formed in each step of polymer tansformation into the charred residue, yields reasonable values of the apparent activation energies.

* * *

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Zusammenfassung — An nichtisothermen TG-Aufnahmen von brommethyliertem Poly(2,6-dimethyl-1,4-phenylenoxid) wurde ein Modell mit Massenverlust in jedem der Schritte eines Systemes von konsekutiven Reaktionen angewendet. Die Freisetzung von HBr erfolgte in Luft schneller als in Stickstoff. Die beträchtliche Verminderung der scheinbaren Aktivierungsenergie der Dehydrobromierung im Vergleich zum nichtbromierten Polymer wurde nicht nur der Verringerung der Aktivierungsenergie der Anfangsreaktion zugeschrieben, sondern auch der Zunahme der Ordnung der Abschlußreaktion (von 1 für nichtbromiertes Polymer auf 2 für hochbromiertes Polymer).