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THERMOGRAVIMETRIC ANALYSIS OF POLY(DIALKYLPHENYL METHACRYLATES)

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ABSTRACT

The thermostability of poly(dialkylphenyl methacrylates) was studied by dynamic thermogravimetric (TG) analysis. The kinetic data obtained by TG show that the thermostability of these polymers decreases in the following order: PPh ≈ 2,6DPP ≈ 2,4DBP > 2,6DMP > 2,5DMP ≈ 2,4DMP ≈ 2,5DMP. The data suggest that the thermal stability of these polymers is not only influenced by the bulkiness and steric hindrance to rotation of the pendant group around the main chain, but also that other factors may influence the thermal decomposition at least in this family. The order of reaction for the thermal decomposition of this kind of polymer was found to be zero. The energy of activation of the decomposition for poly(dialkylphenyl methacrylates) was determined.

INTRODUCTION

The thermostability of polymers is a matter of current interest mainly due to the potential applications of polymers, particularly those of the organic types, as substitutes for metals and naturally occurring structural materials [1]. The trend towards the evaluation of the stability of polymeric substances over a wide range of conditions needs no detailed justification. By arbitrarily defining the thermal behaviour of polymers as a function of the amount of weight loss and the temperature specifying a particular environment, it is possible to establish a stability criterion of some value. The criterion for thermal stability is established as a weight loss criterion such as can be obtained from thermogravimetric (TG) analysis data. Because very significant changes in property occur without a noticeable weight change, this method is very limited and great caution must be exercised in drawing any conclusions concerning the apparent chemical ramifications from the data [1].

Three segments of the normal thermogram have often been used to contrast the degradation processes of various polymers. The first is the temperature at which degradation commences [1]. The second is the temperature region of maximum rate of volatilization of degradation fragments,

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which often roughly coincides with the third, namely the temperature at which 50% of the sample remains. There are at least two main modes of thermal decomposition [1–3]: depending on its structure, a polymer may either assume a random breakdown process or may decompose preferentially at reactive sites along the polymer chain. Steric repulsion effects between side groups are believed to be responsible for the low thermal stability of some polymers [3–5]. Therefore it would be interesting to study polymers which contain bulky side chains.

The aim of this work is to study the thermal degradation of several poly(alkylphenyl methacrylates), in order to determine the kinetic parameters of the decomposition and to correlate these parameters with the chemical structure of the polymers. For this reason we have analysed the following polymers: poly(phenyl methacrylate) (PPh), poly(2,4-dimethylphenyl methacrylate) (2,4DMP), poly(2,5-dimethylphenyl methacrylate) (2,5DMP), poly(2,6-dimethylphenyl methacrylate) (2,6DMP), poly(3,5-dimethylphenyl methacrylate) (3,5DMP), poly(2,6-diisopropylphenyl methacrylate) (2,6DPP) and poly(2,4-di-*tert*-butylphenyl methacrylate) (2,4DBP).

EXPERIMENTAL

Sample characterization

Polymer samples were characterized using methods reported previously [6,7]. All samples were characterized by IR and ^{1}H NMR spectroscopic techniques. Number average molecular weight ($\overline{M}_n$) was determined by membrane osmometry. Weight average molecular weight ($\overline{M}_w$) and the molecular weight distribution (MWD) were determined by size exclusion chromatography (SEC). Glass transition temperatures (T_g) were determined by differential scanning calorimetry (DSC) as has been previously reported [8].

Thermal decomposition

Dynamic thermogravimetric analyses were determined using a Perkin–Elmer TGS-1 thermobalance with a Perkin–Elmer UU-1 temperature program control. Samples (5–7 mg) were placed in the platinum sample holder and the thermal degradation measurements were carried out between 303 and 800 K at 20 °C min^{-1} under N_2.

RESULTS AND DISCUSSION

Figure 1 is a continuous tracing of the change in sample weight as a function of time and temperature when the seven poly(alkylphenyl

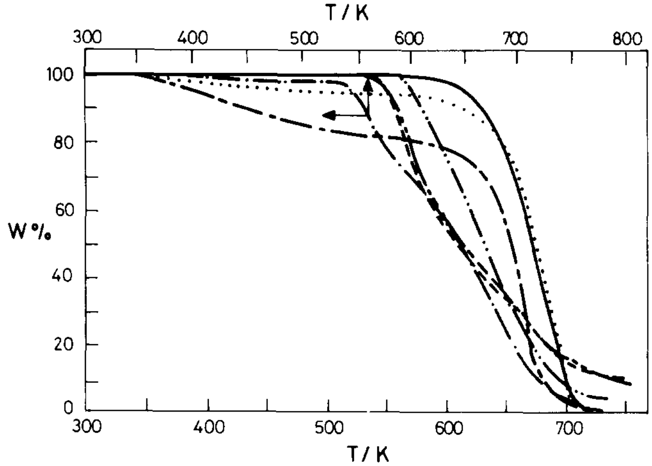

Fig. 1. Thermogravimetric curves of poly(alkylphenyl methacrylates): ———, PPh; — — —, 2,4DMP; –·–·, 2,5DMP; –··–··–, 2,6DMP; — — —, 3,5DMP; ······, 2,6DPP; — — — —, 2,4DBP.

methacrylates) are heated from 303 to 800 K. According to the results summarized in Fig. 1, all systems show similar profiles, but the decomposition of (2,4DBP), initiated at about 335 K, appears different from the other poly(alkylphenyl methacrylates) and suggests a two-stage weight loss on heating. In the first stage, losses are ~ 22% in the temperature range 390 $K < T < 515$ K. In the second stage, the decomposition of the residual weight (78%) takes place at $T = 603$ K. At $T = 686$ K, 50% of the residual weight has decomposed; therefore, this polymer can be considered stable [1].

If we take into account the structural unit of 2,4DBP, it is possible to consider that the 22% weight loss could be attributed to a migration or volatilization of one *t*-butyl group [$-C(CH_3)_3$] from the polymer repeating unit. This fact could be interpreted as a degradation or modification of 2,4DBP in the temperature range considered. It should be noted that more experimental evidence is needed in order to clarify this interesting problem especially because the TG data should be considered with caution; therefore, our interpretation may be highly speculative.

In the case of 2,6DPP, we found a slight change in its residual weight; the profile of the thermogram is very similar to that of the other poly(dialkylphenyl methacrylates). However, this polymer can be considered as stable by comparing its behaviour with, for instance, that of (PPh) [9] (see Table 1). Table 1 summarizes the initial decomposition temperature (T_D^i) observed by TG and the temperature at which 50% weight residual was observed ($T_D^{50\%}$). In this table we also list the pyrolysis kinetic parameters. According to the thermogravimetric results, it is not clear whether or not the nature, size and bulkiness of the side chain influence in the thermostabilities of these polymers. In fact, from the results of Fig. 1, the thermostability order for

TABLE 1

Initial decomposition temperature T_D^i, % of residual weight at T_D^i wt.%, temperature where 50% of residual weight is observed $T_D^{50\%}$, activation energy E_a, the reaction order n, and the frequency factor Z for the degradation of PPh; 2,4DMP; 2,5DMP, 2,6DMP; 3,5DMP; 2,6DPP and 2,4DBP

Polymer	Side chain	T_D^i (K)	Wt.%	E_a [a] (kcal mol^{-1})	n [a]	$T_D^{50\%}$ (K)	E_a [b] (kcal mol^{-1})	Z [b] (s^{-1})
PPh		603	97	4.79	0	672	4.85	97
2,4DMP		543	97	2.43	0	596	2.43	11068
2,5DMP		543	95	4.69	0	646	4.60	366
2,6DMP		563	96	0.31	0	627	2.62	2612
3,5DMP		543	96	7.61	0	605	7.48	6827
2,6DPP		603	93	4.65	0	671	4.34	72
2,4DBP		603	74	4.80	0	650	4.75	645

[a] Obtained from eqn. (5). [b] Obtained from eqn. (6).

this kind of polymers is: PPh ≈ 2,6DPP ≈ 2,4DBP > 2,6DMP > 2,5DMP ≈ 2,4DMP ≈ 3,5DMP. It is interesting to note that all poly(dimethylphenyl methacrylates) show a lower thermal stability than the other poly(phenyl methacrylates).

The steric repulsion effects between side groups believed to be responsible for low thermal stability [4], are apparently not observed here. It has been observed in other systems, for instance in the case of linear poly(ethylene), that this polymer is more resistant to thermal degradation than polypropylene. Polypropylene, in turn, is more resistant to thermal degradation, than the polymer of 5-phenyl-1-pentene (poly[(3-phenyl-propyl)-ethylene]) which has larger side chains [4]. If we extrapolate these results to our observation in the poly(alkylphenyl methacrylates), 2,6DPP would be the most thermally unstable, due to the high steric hindrance imposed by the two isopropyl groups in the *ortho* position. However, the thermal stability of 2,6DPP is surprisingly high relative to the rest of the polymers of this family.

In the case of dimethylphenyl derivatives, the relative thermal stability of the polymers can be obtained by comparing their decomposition behaviour, which according to the results shown in Fig. 1, follows the order: 2,6DMP > 2,5DMP ≈ 2,4DMP ≈ 3,5DMP. Therefore, in this particular set of isomeric polymers we can assume that the higher the steric hindrance to rotation, (due to the size of the side chain), the higher the stability of the polymer.

The data suggest that the thermal stability of these polymers is not only influenced by the bulkiness and steric hindrance to rotation of the pendant group around the main chain, but also that other factors may influence the thermal decomposition, at least in this family (see Table 1).

The decomposition reaction is irreversible so that the rate dependent parameters such as energy of activation and order of reaction may be calculated from a single experimental curve [1,10]. The specific rate constant (k) can be expressed in the Arrhenius form

$$k = Z\,\mathrm{e}^{-E/RT} \tag{1}$$

where Z is the frequency factor, E is the energy of activation, R is the gas constant [10] and T is the absolute temperature.

According to Freeman and Carroll [10], if we consider a reaction in the liquid or solid state, where one of the products B is volatile and all other substances are in the condensed state

$$a\mathrm{A} \rightarrow b\mathrm{B(g)} + c\mathrm{C} \tag{2}$$

the rate expression for the disappearance of reactant A from the mixture is

$$-\mathrm{d}X/\mathrm{d}t = kX^n \tag{3}$$

where X is the amount of reactant A, k is the specific rate constant and n the order of the reaction with respect to A. It is assumed that the specific rate may be expressed as eqn. (1). Solving for k in eqn. (3), and substituting eqn. (1) for k gives

$$Z\,\mathrm{e}^{-E/RT} = [-(\mathrm{d}X/\mathrm{d}t)]/X^n \tag{4}$$

Following Freeman and Carroll's method [10], it is possible to determine the order of the reaction n and the energy of activation E. This can be done by taking the logarithm of eqn. (4), differentiating with respect to $\mathrm{d}X/\mathrm{d}t$, X and T, and then integrating the resulting equation to obtain

$$\frac{\Delta \ln(-\mathrm{d}X/\mathrm{d}t)}{\Delta \ln X} = \frac{-(E/R)\,\Delta(1/T)}{\Delta \ln X} + n \tag{5}$$

From eqn. (5), we can see that plots $[\Delta(1/T)/\Delta \ln X] = A$ against $[\Delta \ln(-\mathrm{d}X/\mathrm{d}t)/\Delta \ln X] = B$ should result in a straight line where the slope is $-E/R$ and the intercept is n, the kinetic order of the thermal degradation. These equations are very useful for the determination of the kinetic parameters for thermal degradation. Equation (5) has the advantage that it can be used to calculate the order of the thermal degradation directly, without any previous assumption about the value of n, as is the case in eqn. (4).

In order to determine the thermal decomposition kinetic order we have used eqn. (4), assuming a first-order reaction model ($n = 1$), and a polynomial regression program. Kinetic parameters were determined from a linear least-squares fit of the data in a semilogarithmic plot of k against $1/T$ with $k = [(-\mathrm{d}X/\mathrm{d}t)/X]$. Figure 2 shows these plots. As can be seen, straight lines are not obtained, indicating that n differs from unity. For this reason, we have used Freeman and Carroll's method [10] in order to determine the real kinetic parameters for the thermal decomposition.

Figure 3 shows the plots of $\Delta \ln(-\mathrm{d}X/\mathrm{d}t)/\Delta \ln X$ against $\Delta(1/T)/\Delta \ln X$, according to eqn. (5), using the same program mentioned above. As

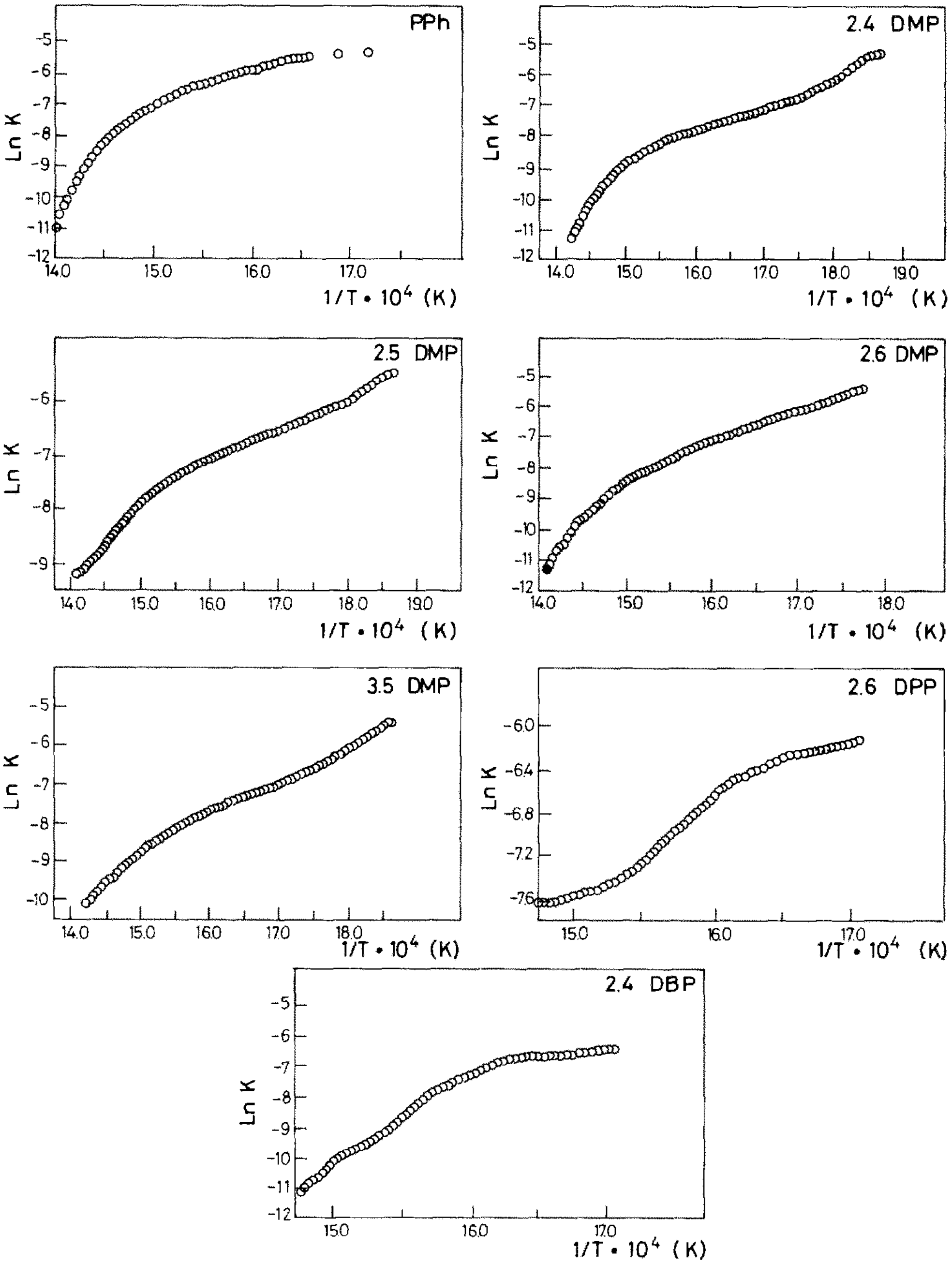

Fig. 2. Plots of the degradation of poly(alkylphenyl methacrylates) according to eqn. (4) and assuming $n = 1$.

can be seen, good straight lines ($R^2 = 0.9999$) are obtained for all the systems studied. In the case of 2,6DMP, there is scattering of the points but the intercept i.e. the order of the reaction, is zero. These results suggest that

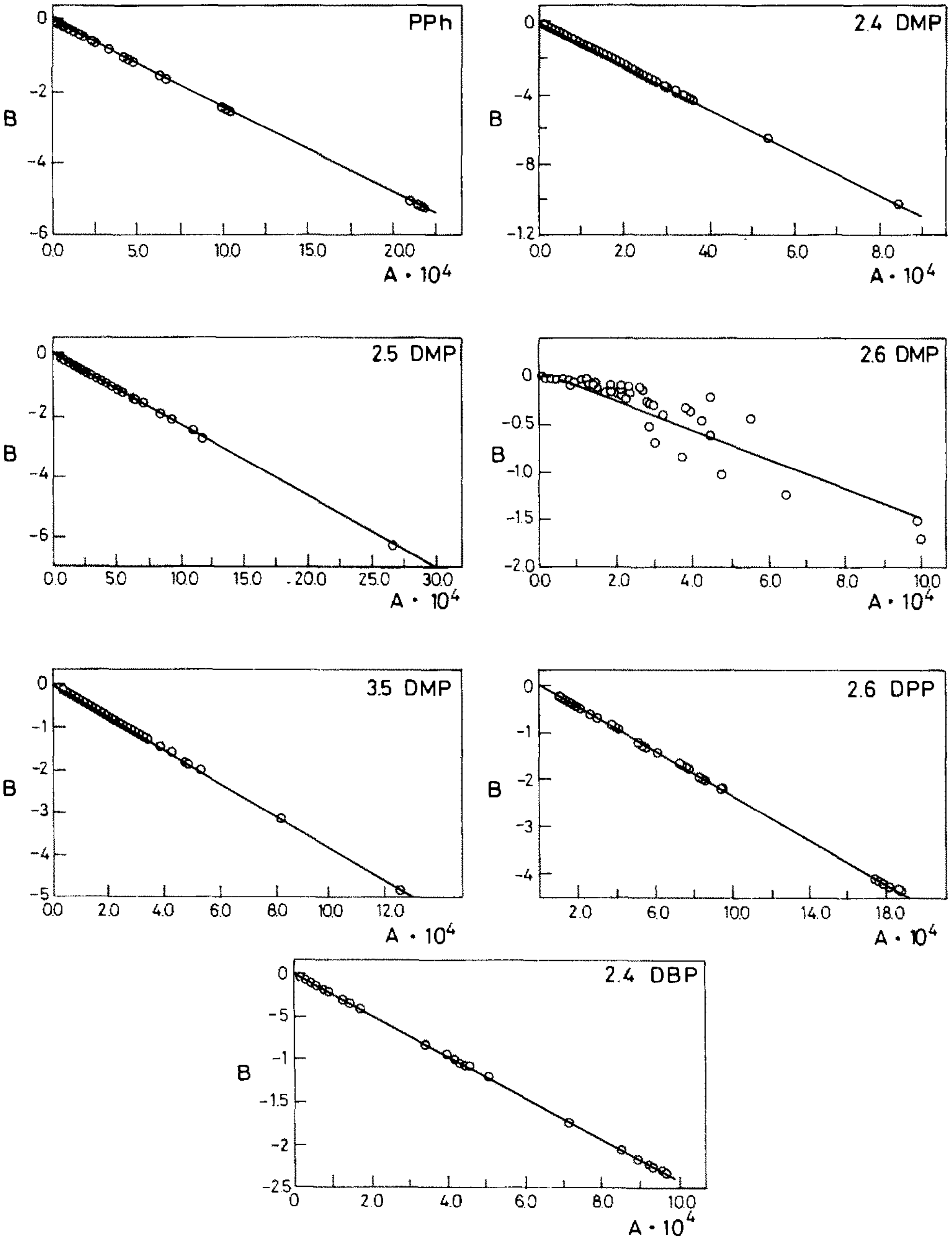

Fig. 3. Plots of the degradation of poly(dialkylphenyl methacrylates) according to eqn. (5).

the thermal decomposition kinetic order is zero for all the poly(dialkylphenyl methacrylates) studied. However, the slope of these plots i.e. the energy of activation for the process *E*, is different for each system. In order to confirm the zero-order model, if we solve eqn. (4) for $n = 0$, the logarithmic form gives

$$\ln(-\mathrm{d}X/\mathrm{d}t) = \ln Z - E/RT \tag{6}$$

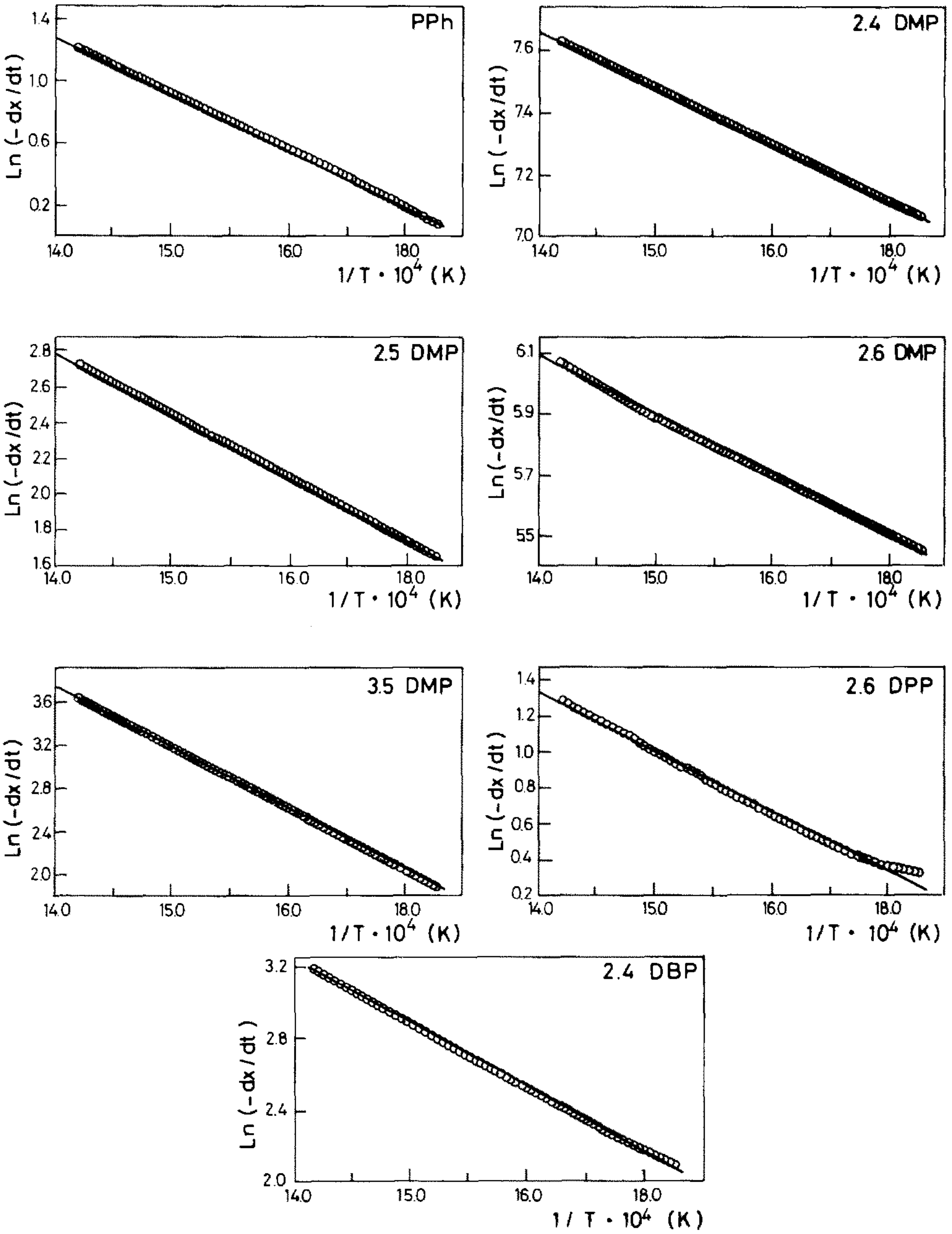

Fig. 4. Plots of the degradation of poly(dialkylphenyl methacrylates) according to eqn. (6) for $n = 0$.

Therefore plots of $\ln(-\mathrm{d}X/\mathrm{d}t)$ against $1/T$ should give a straight line with slope $-E/R$ and intercept $\ln Z$.

Figure 4 shows these plots, where we can see that all the values obtained for each polymer from Fig. 1 fit well onto a straight line with a good correlation ($R^2 = 0.999$). Also it is interesting to note that there is no scatter of the values over the length of the curve (except for 2,6DPP). Therefore, the zero-order model is the best fit for the kinetic data of each poly(dialkylphenyl methacrylate). The kinetic parameters derived from the plots of fig. 4 are summarized in Table 1.

From eqns. (5) and (6), we can obtain the values of $-E/R$ from the slopes of the corresponding plots. These values are also summarized in Table 1. The values of $-E/R$ obtained from both equations are in good agreement, as can be seen in Table 1, except for 2,6DMP, which can be explained by noting that the plots of Fig. 3 show significant scattering and therefore the determination of E using eqn. (5) is very uncertain.

The kinetic parameters obtained for the thermal decomposition of these polymers do not show any relationship between the polymer side chain structure and the energy of activation. Nor is there any correlation between the frequency factor Z and the energy of activation E. The values of the frequency factor are low, corresponding to zero-order kinetics.

According to our results, it is interesting to note that the (T_D^i) for the different polymers cannot be clearly correlated with the structure of the polymers because, apparently, there is no relation between the bulkiness and steric hindrance of the side chain and the thermal decomposition of these polymers. However, in the case of 2,4DBP there is a thermal decomposition at very low temperatures that can be attributed to the *tert*-butyl group; however, no further analysis of the degradation products has been performed. Finally, we can conclude that the order of reaction for the decomposition of poly(dialkylphenyl methacrylates) is zero. Although no previous literature references have been found concerning the kinetics of the decomposition of this family of polymers, it is interesting to remark that generally the order of the reaction of the decomposition of polymers is unity [11–13]. But, in this case, it is zero with no scatter of the values either at the head or the tail of the plots which comprise 90 points taken from the original thermogravimetric curves. Further investigations on the mechanism of the degradation of these poly(dialkylphenyl methacrylates) are proceeding.

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