Thermochimica Acta, 211 (1992) 255–261
Elsevier Science Publishers B.V., Amsterdam

Thermal stability of poly(chloroalkyl methacrylate)s and poly(dichloroalkyl itaconate)s

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(Received 23 March 1992)

Abstract

Thermogravimetric analyses of fractions of poly(2-chloroethyl methacrylate) (P2CEM), poly(3-chloropropyl methacrylate) (P3CPM), poly(di-2-chloroethyl itaconate) (PD2CEI) and poly(di-3-chloropropyl itaconate) (PD3CPI) of similar molecular weight distribution were carried out. The effect of the nature and structure of the side chain on the thermogravimetric behaviour is investigated, together with the thermal behaviour of these two groups of polymers. The relative thermal stability of the polymers studied is PD3CPI > PD2CEI > P3CPM ≥ P2CEM, by comparison of the temperature of their initial thermal degradation. The results are discussed in terms of the nature and structure of the different side chains. The kinetic parameters for the thermal degradation process were established. All samples show a first-order kinetic model for the degradation process.

INTRODUCTION

The thermostability of polymers depends on several factors associated with the chemical structure of the macromolecule [1–3]. The effect of the side chain structure of polymers on the different types of properties has been studied extensively for a number of systems in solution [4–8] as well as in the solid state [9–11]. In particular, the flexibility of the macromolecule is reflected in its solution properties. The effect of the side chain structure and the glass transition temperature has been studied for different families of polymers [12–15]. The thermal stability of poly(methacrylates) containing different bulky side chains has recently been studied [1, 2]. Thermal stability studies on poly(itaconates), however, are scarce [16]. In poly(itaconates), there are two side groups per repeating unit. Depending on the structure, it is possible to distinguish at least three kind of poly(itaconates), i.e. poly(monoitaconates) in which only

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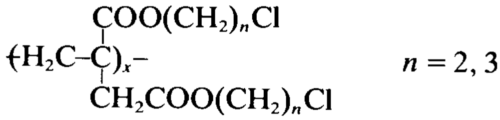

$$-\!\!\left(H_2C-\overset{\displaystyle COO(CH_2)_nCl}{\underset{\displaystyle CH_2COO(CH_2)_nCl}{C}}\right)_x\!\!- \qquad n = 2, 3$$

Scheme 1.

one of the carboxylic groups of the itaconic acid (2-methylenesuccinic acid) has been esterified, poly(diitaconates) with two similar ester groups and mixed poly(diesters) with two different esters groups per repeat unit [6].

Poly(monoitaconates) have been used in compatible polymer blends, but their stability in the blends is not known. Nevertheless, the annealing temperature for these blends is of fundamental importance in order to obtain miscible polymer blends. The miscibility of poly(2-choroethyl methacrylate) (poly[1-(2-chloroethyloxycarbonyl)-1-methyl ethylene]) (P2CEM), poly(3-chloropropyl methacrylate) (poly[1-(3-chloropropyloxy-carbonyl)-1-methyl ethylene]) (P3CPM), poly(di-2-chloropropyl itaconate) (poly[1-(2-chloroethyloxycarbonyl)-1-(2-chloroethyloxycarbonyl methyl) ethylene]) (PD2CEI) and poly(di-3-chloropropyl itaconate) (poly[1-(3-chloropropyloxycarbonyl)-1-(3-chloropropyloxycarbonyl methyl) ethylene]) (PD3CPI) (see Scheme 1), with poly(vinyl pyrrolidone) has recently been studied by our research group. For this reason we are interested in the thermal stability of these polymers.

The aim of this work is the thermogravimetric analysis of poly(chloralkyl methacrylates) and the corresponding poly(dichloralkyl itaconates) in order to obtain information about the thermal degradation of these chlorine-containing polymers and their compatibility with other acceptor polymers.

EXPERIMENTAL

Sample characterization

Polymer samples were characterized according to methods previously reported [17] by FTIR and ^{1}H-NMR spectroscopic techniques. Number-average molecular weight (Mn) values were determined by membrane osmometry using a Hewlett-Packard high-speed osmometer, model 502. The weight-average molecular weight (M_w) and the molecular weight distribution (MWD) were determined by size exclusion chromatography (SEC). Glass transition temperatures and the annealing temperatures for the samples studied were determined by differential scanning calorimetry (DSC) in a Mettler TA 3000 system equipped with a TC-A10 processor, as previously reported [17].

Thermal decomposition

Dynamic thermogravimetric analyses were determined using a Perkin-Elmer TGS-1 thermobalance with a Perkin-Elmer UU-1 temperature program control. Samples (8–10 mg) were placed in a platinum sample holder. Measurements were carried out between 303 and 1000 K at a heating rate of 20° min^{-1} under N_2.

RESULTS AND DISCUSSION

Figure 1 shows the thermogravimetric curve for fractions of P2CEM, P3CPM, PD2CEI and PD3CPI of narrow molecular weight distribution (MWD) and similar molecular weights ($M_W \approx 1.5 \times 10^5$), in which the change in sample weight as a function of time and temperature is measured in the temperature range between 293 and 933 K. All the samples show similar profiles, with a single weight loss on heating, but there is a quantitative difference between the decomposition curves for the poly(chloroalkyl methacrylate) and the poly(dichloroalkyl itaconate) analogues. If we consider the $T_D^{50\%}$ values, i.e. the temperature at which 50% weight residual is observed by thermogravimetry, for the different polymers, it is possible to observe that the poly(dichloroalkyl itaconates) show higher decomposition temperatures than those of the corresponding poly(chloroalkyl methacrylates). Similar results can be observed throughout for the initial decomposition temperature (T_D^i). Table 1 summarizes the T_D^i and $T_D^{50\%}$ values obtained from Fig. 1 and also the characteristic ratio C_∞, determined from solution measurements [17]. The relative thermal stability of these polymers can be obtained by comparing their decomposition behaviour, which according to the results shown in Table

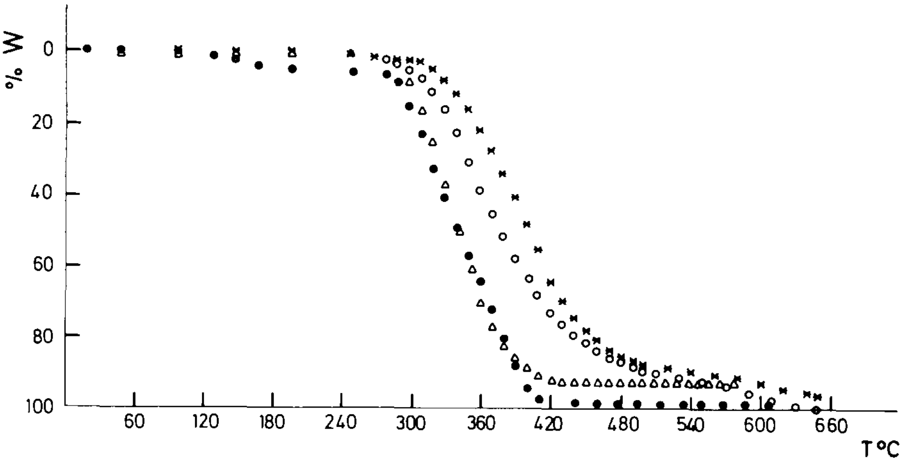

Fig. 1. Thermogravimetric curves for P2CEM (●), P3CPM (△), PD2CEI (○) and PD3CPI (*).

TABLE 1

Initial decomposition temperature T_D^i, temperature at which 50% of residual weight is observed $T_D^{50\%}$ and the steric hindrance to rotation expressed by the characteristic ratio C_∞ determined in solution [17] for P2CEM, P3CPM, PD2CEI and PD3CPI

Polymer	T_D^i (K)	$T_D^{50\%}$ (K)	C_∞
P2CEM	555	610	17.80[a]
P3CPM	563	614	20.02[a]
PD2CEI	583	646	31.20[a]
PD3CPI	603	673	33.13[a]

[a] In THF and chloroform, from ref. 17.

1, follows the order PD3CPI > PD2CEI > P3CPM ≥ P2CEM. This result seems to indicate that there is a detectable effect of the side chain structure on the relative thermal stability of these polymers, in good agreement with the results obtained in solution for the same family of polymers [17]. In fact, for these polymers the rigidity factor (σ), the characteristic ratio (C_∞) and the molar volume (V_m) of the side chain increase in the same way as the characteristic degradation temperatures, $T_D^{50\%}$ and T_D^i, i.e. they increase as the molar volume of the side chain increases. Similar results have been reported for other sets of polymeric systems [2]. These results are important in that the volume and the bulkiness of the side chain play an important role in the degradation of these polymers, if we consider that substitution in the lateral chain by a chlorine atom appreciably increases the volume and rigidity of the polymer sample.

It is also very interesting that the thermal behaviour of these polymers is qualitatively similar; this is not surprising because of the similarities in structure, but the monotonic variations in the thermogravimetric analysis can clearly be attributed to the differences in the size and volume of the lateral group. Therefore, the two families of polymers, being different yet similar in structure, represent a good example of the relationship between structure and physical behaviour. Nevertheless, it is necessary to analyse this behaviour to determine if it follows a similar trend from a kinetic point of view.

In order to obtain the kinetics parameters for the decomposition processes for these polymers, we have followed a classical approach, assuming that the degradation process is irreversible. Therefore, the rate-dependent parameters such as the energy of activation (E_a) and order of reaction (n), may be calculated from a single experimental curve [18, 19]. Thus it is possible to express the specific rate constant (k) in terms of an Arrhenius-type equation

$$k = A\mathrm{e}^{-(E_a/RT)} \quad (1)$$

where A is the pre-exponential factor (frequency factor), E_a is the activation energy, R is the gas constant and T the absolute temperature. According to the previous treatment of data for similar systems in which the reaction rate in the solid or liquid state follows a reaction model similar to those described in the literature [1, 2, 18, 19], we can express the reaction rate $d\alpha/dt$ as function of the degree of conversion α by

$$-\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{2}$$

where k is the specific rate constant, α is the fraction of the sample weight-loss at time t, which can be obtained directly from the thermograms, and n is the order of the reaction. The reaction rates can be calculated using a differential technique, directly incorporating the heating rate (20°C min^{-1}) into the data of temperature against sample weight fraction [20]. By combining eqns. (1) and (2) and using the logarithmic form, one obtains

$$\beta = \ln\left[\frac{d\alpha/dt}{(1-\alpha)^n}\right] = \ln A - \frac{E_a}{RT} \tag{3}$$

According to this equation the kinetics parameters can be determined by using a linear multiple-regression program, which allows the calculation of the activation energy E_a and the frequency factor A from a linear least-squares fit of the data in a semi-logarithmic plot of β against T^{-1}. In this way, we obtain a first-order kinetic model for the four polymers under study. The results are listed in Table 2.

Figures 2 and 3 show the plots of β against T^{-1} for poly(chloroalkyl methacrylates) and poly(dichloroalkyl itaconates) respectively. Good straight lines are obtained with a good correlation ($R^2 = 0.999$) in all cases for a first-order kinetic model. The active energies for the system studied are very similar, but are lower for poly(dichloroalkyl itaconates) than for the corresponding poly(methacrylates). Although these differences are not significant, they can be interpreted in terms of the differences in the

TABLE 2

Activation energy values E_a, frequency factor A and order of reaction n for P2CEM, P3CPM, PD2CEI and PD3CPI

Polymer	E_a (kcal mol^{-1})	A (s^{-1})	n	Temperature range (°C)
P2CEM	29	1.42×10^7	1	290–400
P3CPM	39	4.7×10^{10}	1	300–360
PD2CEI	23	2.5×10^4	1	340–420
PD3CPI	27	2.65×10^6	1	340–450

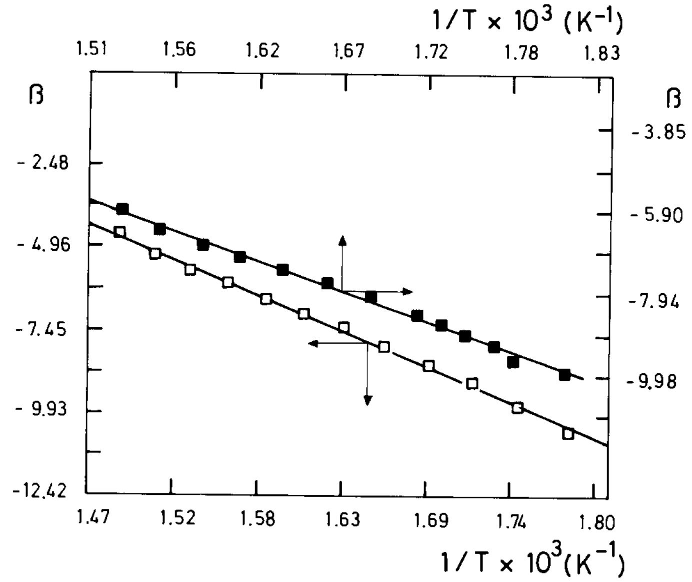

Fig. 2. Plots of β against $1/T$ for P2CEM (■) and P3CPM (□).

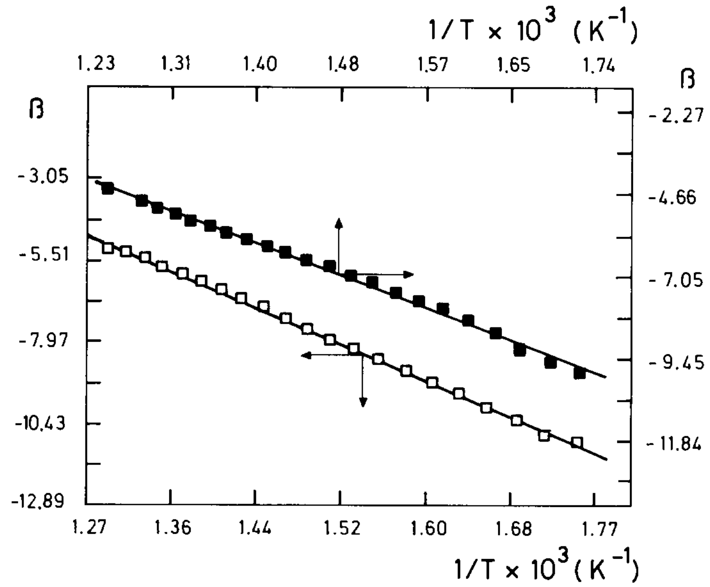

Fig. 3. Plots of β atainst $1/T$ for PD2CEI (■) and PD3CPI (□).

structure between poly(methacrylates) and poly(diitaconates). In the case of poly(diitaconates) where the repeat unit has two ester groups and, therefore, the monomer unit is more bulky and sterically hindered than that of the corresponding poly(methacrylates), this could be one of the factors leading to the differences in activation energy. As in other poly(methacrylates) in the same family of polymers [1, 2], the frequency factor decreases as the side chain structure of the polymer increases.

Finally, it is possible to conclude that the thermal degradation of these polymers depends on the bulkiness of the side chain and on the rigidity factor, and follows a first-order kinetic model.

ACKNOWLEDGEMENTS

We express our thanks to Mrs. Claudia Dañin V. for her help in the synthesis and characterization of the polymers, to Dirección de Investigación, Pontificia Universidad Católica de Chile (DIUC) and Fondo Nacional de Desarrollo Científico y Tecnológico (Fondecyt) for partial financial support.

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