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THERMAL STABILITY OF POLY(MONO-*n*-ALKYL-ITACONATES) AND MONO-*n*-ALKYLITACONATE-co-VINYLPYRROLIDONE COPOLYMERS I.

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Abstract

Poly(monoitaconates) containing octyl, decyl and dodecyl groups and random monoalkylitaconate-co-vinylpyrrolidone copolymers were studied by thermogravimetric analysis. Copolymers of mono-*n*-octylitaconate (MOI), mono-*n*-decylitaconate (MDI), and mono-*n*-dodecylitaconate (MDoI), respectively, with N-vinyl-2-pyrrolidone (VP) of different compositions were studied by dynamic thermogravimetric analysis. The thermal stability of the copolymers depends on the structure of the monoitaconate comonomer and on the composition of the copolymer. The kinetic analysis of the degradation data shows that the thermal decomposition of these copolymers can be described by several kinetic orders depending on the copolymer and on the composition. The relative thermal stability of the copolymers increases as the VP content increases and as the length of the side chain of the itaconate increases, following the same trend as the flexibility of the copolymers in solution.

Keywords: copolymers, kinetic order, poly(monoalkylitaconates), side chain, specific degradation temperature, thermal stability

Introduction

The thermogravimetric behaviour of polymers depends, as it is well known, on the polymer structure and the type of substituents in the main chain [1–3]. The influence of the nature and structure of the substituents on different types of properties has been extensively studied for a number of systems in solid state [4–6] as well as in solution [7–11], particularly on the flexibility of the macromolecule which is reflected by its solution properties. In fact, the effect of the

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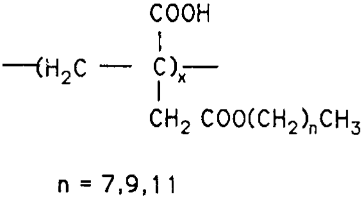
side chain structure on the glass transition temperature (T_g) has been studied for different families of polymers [12–15].

The thermal decomposition of poly(methacrylates) containing different bulky side chains and some poly(itaconic acid derivatives) has been recently studied [1, 2, 16]. In the case of poly(itaconates) the studies about the thermal stability are scarce [17].

The aim of this work is the thermogravimetric analysis of a series of poly(mono-*n*-alkylitaconates) i.e. poly(1-carboxy-1-octyloxycarbonylmethyl-ethylene) (PMOI), poly(1-carboxy-1-decyloxycarbonylmethylethylene) (PMDI) and poly(1-carboxy-1-dodecyloxycarbonylmethyl ethylene) (PMDoI) (see scheme I) and of the corresponding random copolymers with vinylpyrrolidone, in order to correlate the thermal degradation behaviour of these copolymers with their solution properties. The correlation with the chain rigidity was reported previously [18]. The insertion of a flexible comonomer such as vinylpyrrolidone in the poly(monoitaconate) chain has demonstrated an important flexibilization of the main chain [18], but maintaining the high rigidity of the parent homopolymers [9, 19, 20]. It should be interesting to analyze how the insertion of a flexible comonomer in a polymer structure influences the degradation process of these kinds of material.



$$-\!\left(H_2C - \overset{COOH}{\underset{CH_2\,COO(CH_2)_nCH_3}{C}}\right)_x\!-$$

$n = 7,9,11$

Scheme 1

Experimental

Sample characterization

Monomer reactivity ratios of the copolymers were previously reported and all the samples can be considered as random copolymers with small tendency to alternance [18].

Polymer samples were characterized according to methods previously reported [18]. Number average molecular weights (M_n) were determined by membrane osmometry, weight average molecular weights (M_w) and the molecular weight distribution (*MWD*) by size exclusion chromatography (SEC) [18].

Thermal decomposition

Dynamic thermogravimetric analyses were carried out using a Perkin-Elmer TGS-1 thermobalance with a Perkin-Elmer UU-1 temperature program control unit. Samples (8–10 mg) were placed in the platinum sample holder. Thermogravimetry was also performed using a Mettler TA-3000 calorimetric system equipped with a TC-10A processor, a TG-50 thermobalance with a Mettler MT5 microbalance and samples were heated on Al_2O_3 pans. the results obtained from both instruments are in good agreement. Measurements were carried out between 303 and 1000 K at a heating rate of 20 $deg \cdot min^{-1}$ under N_2.

Results and discussion

Figure 1a shows the thermogravimetric curves corresponding to PMOI, PMDI, PMDoI and PVP of similar weight average molecular weights (M_w) in order to compare the degradation behaviour of the polymers. The relative thermal stability of these polymers can be appreciated by comparing their decomposition temperatures, TD^i and $TD^{50\%}$, i.e. the initial decomposition temperature and the temperatures of 50% weight loss. According to the results shown in Fig. 1a and also summarized in Table 1, $TD^{50\%}$ follows the order:

$$PVP > PMDoI > PMDI > PMOI.$$

This is a very interesting result because it was expected that poly(monoitaconates) being semirigid or rigid polymers [7, 17–22], show higher thermal stability than PVP, which is considered to be a flexible polymer. Flexibility of the polymer chain is a very important factor influencing the thermal stability but its real effect is not well known, at least in this family of polymers. Later we will discuss this aspect taking into account the results involving copolymers [18]. Figs 1b, 1c and 1d show the thermogravimetric curves for random copolymers containing MOI/VP, MDI/VP and MDoI/VP of three different compositions. All the copolymers used in this study were selected in such a way that they present the most similar weight average molecular weight (M_w) in order to avoid the influence of this factor in the thermogravimetric analysis. All samples show similar curves with one or two stage weight loss on heating. Table 1 also summarizes the main characteristics of the polymer samples analyzed in this work. Figure 1 represents the change in sample weight as function of temperature, using a given heating rate in the temperature range between 323 and 903 K. If we analyze these figures we can observe that in general all of the curves show a similar behaviour with small differences which will be discussed later. But, all the copolymers degrade apparently in the usual way. Let us discuss the thermogravimetric curves of the different copolymers.

Figure 1b represents a common degradation curve for copolymers containing MOI of three different compositions i.e. copolymers having 90, 52 and 13 mol% of MOI. Qualitative differences between the copolymers of different compositions can be observed. The copolymer with high VP content (13 mol% of MOI) shows a TG curve which seems to reflect at least two or three steps in the degradation process. The degradation temperatures for these copolymers show that $TD^{50\%}$ increases as the mole fraction of VP increases (Table 1). Similar behaviour is observed in Figs 1c and 1d for the degradation of copolymers containing 82, 46 and 17 mol% of MDI and 82, 48 and 20 mol% of MDoI. As in Fig. 1b, copolymers showing higher VP content present a different behaviour with a shape of the curves similar to those with more than one degradation step [1, 2] and also similar to that of PVP. In Fig. 1d, this trend is more pronounced, nevertheless it can be considered as a normal degradation curve compared with the classical ones.

Table 1 Copolymer composition, weight average molecular weight, as well as initial decomposition temperature TD^{i}, and temperature of 50% weight loss $TD^{50\%}$ for PMOI, PMDI, PMDoI, PVP and MI/VP copolymers of different compositions

Copolymer	Composition / mol% MI	$Mw \cdot 10^{-5}$	TD^{i} / °C	$TD^{50\%}$ / °C
MOI	100	1.00	150	225
	90	0.99	160	270
MOI/VP	52	0.85	170	288
	13	1.10	190	320
MDI	100	0.90	175	270
	82	0.70	165	275
MDI/VP	46	0.60	190	320
	17	0.40	210	430
MDoI	100	0.75	225	365
	82	0.70	180	285
MDoI/VP	48	0.80	175	285
	20	–	190	370
PVP	0.0	0.40	165	460

If we consider the values of the temperatures involved in the degradation processes we can observe an increase of these temperatures as the VP content of the copolymer increases. Among the copolymers the temperature of thermal degradation increases as the length of the side chain of the monoitaconate in-

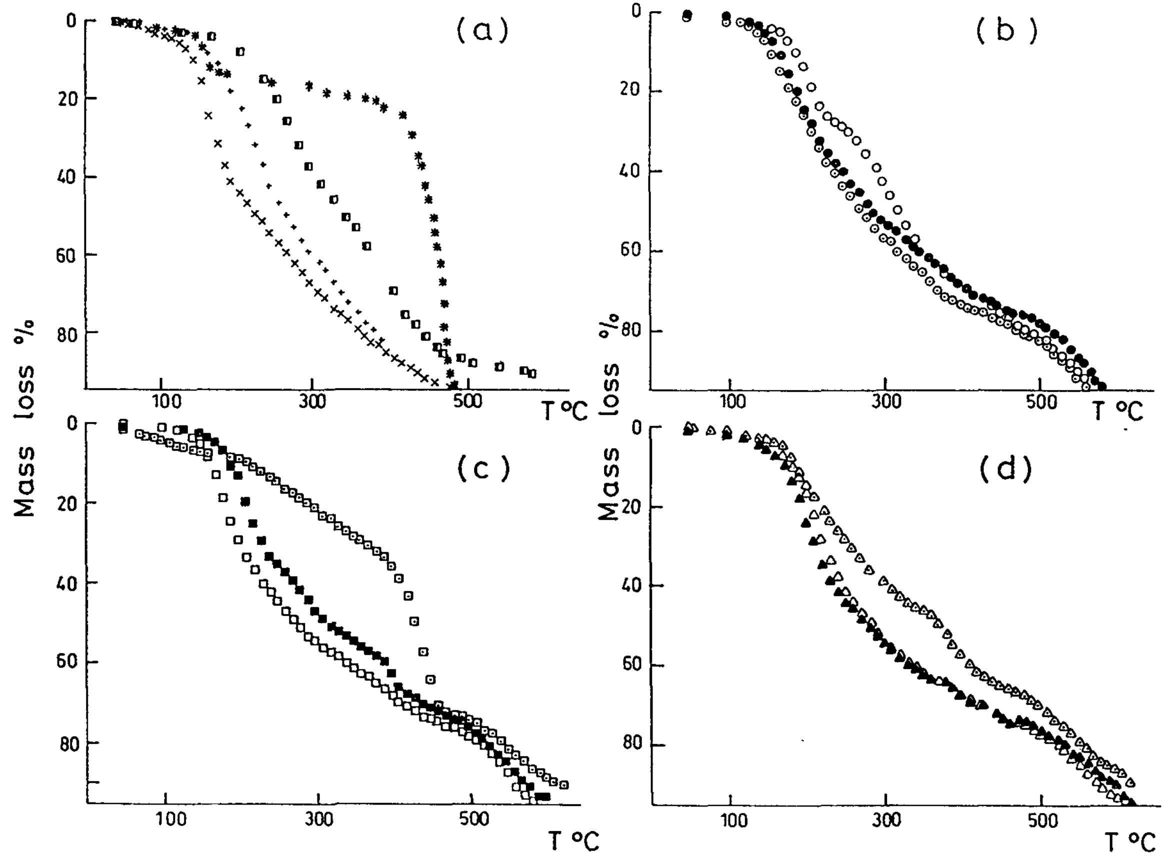


Fig. 1 Thermogravimetric curves for: a) PMOI (x); PMDI (+); PMDoI (◧) and PVP (∗). b) MOI/VP Copolymers 90% MOI (⊙); 52% MOI (•); 13% MOI (o). c) MDI/VP copolymers 82% MDI (□); 46% MDI (■); 17% MDI (⊡). d) MDoI/VP Copolymers 82% MDoI (Δ); 48% MDoI (▲); 20% MDoI (Δ)

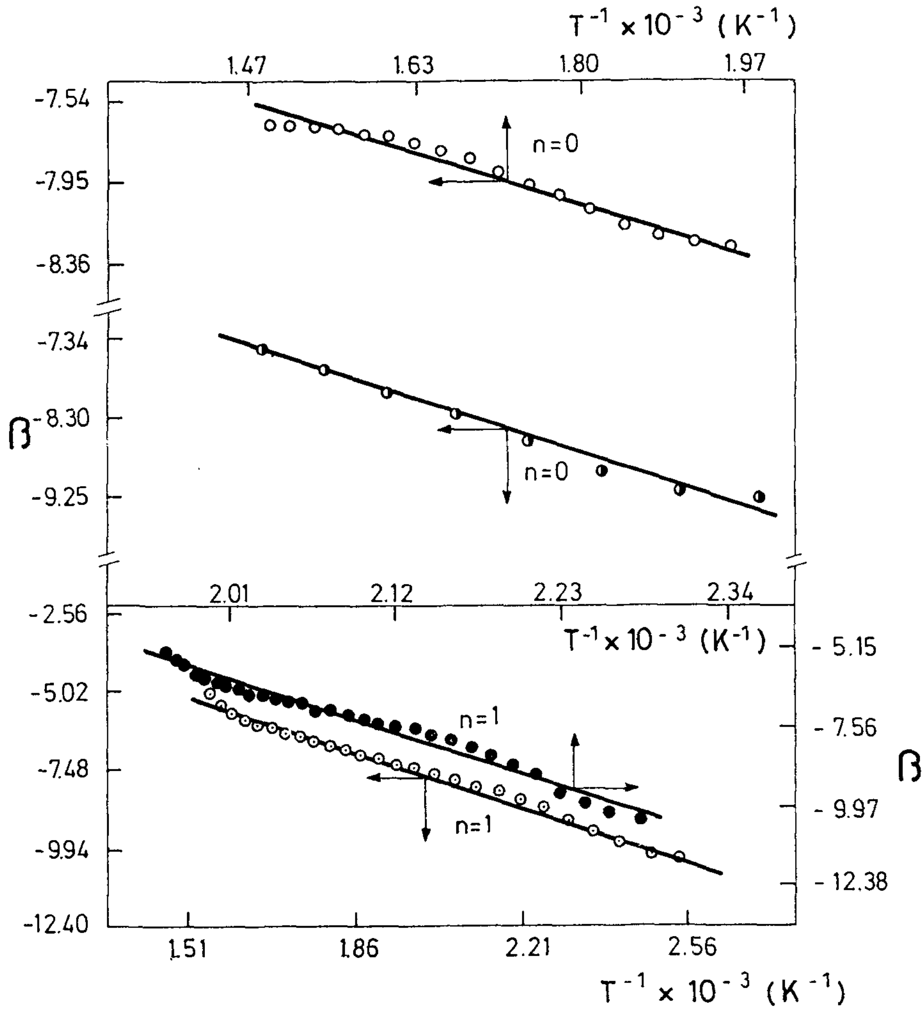


Fig. 2 Plots of β *vs.* $1/T$ for MOI/VP copolymers. (⊙) 90% MOI; (●) 52% MOI; (o) 13% MOI (n = 0, 513–673 K; (◐) 13% MOI (n = 0, 423–493 K)

creases. These results are in good agreement with those corresponding to the thermogravimetric behaviour of the respective homopolymers. Degradation temperatures increase from PMOI to PMDoI and it is the highest for PVP. In all cases the introduction of VP units in itaconate chains leads to macromolecules with higher thermal stability.

An effect of the side chain structure of the itaconate on the relative thermal stability of the copolymers is observed. There is a good agreement with the flexibility results obtained in solution for the same family of copolymers [18].

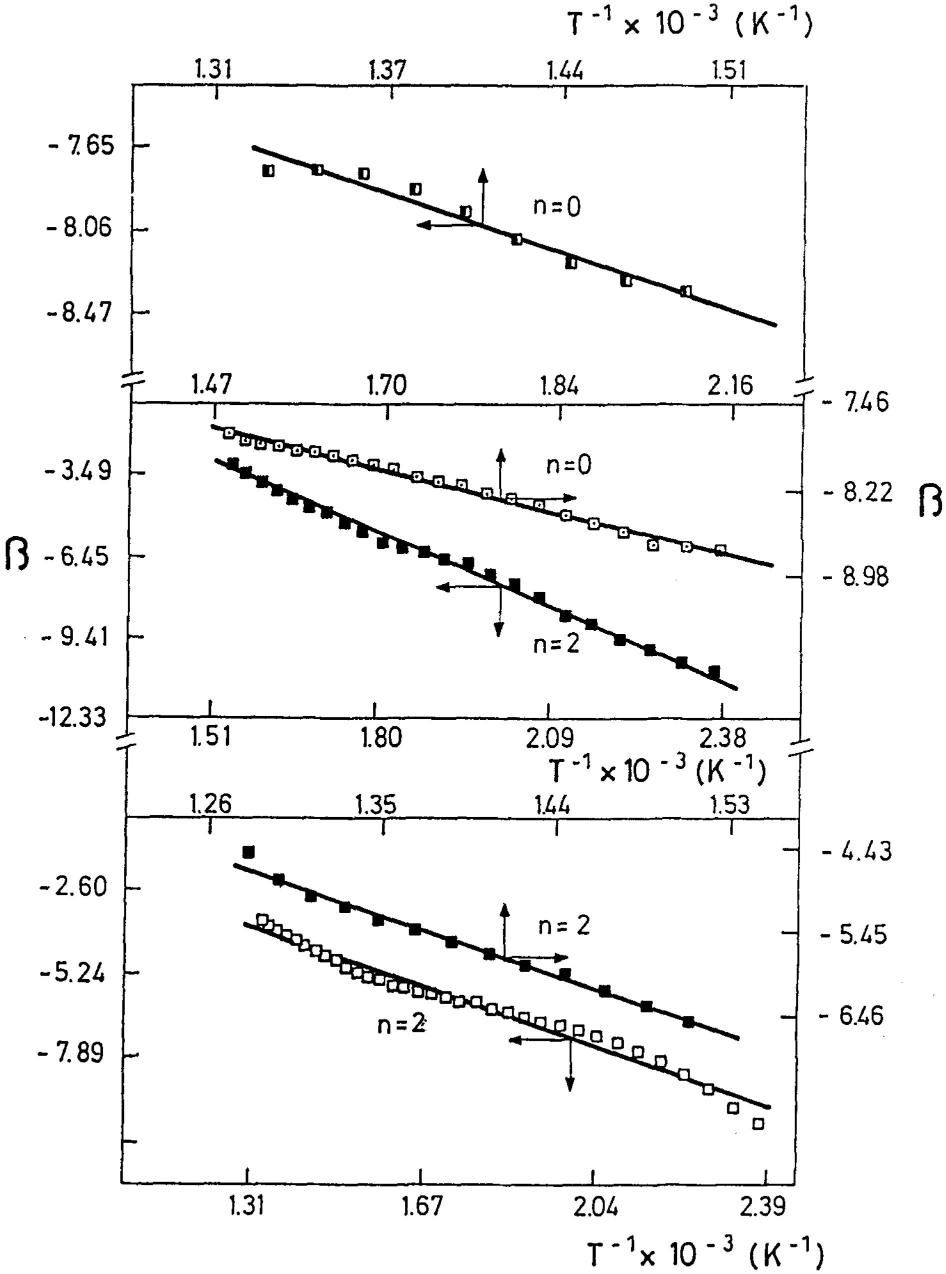


Fig. 3 Plots of β *vs.* 1/T for MDI/VP copolymers. (□) 82% MDI; (■) 46% MDI; (◧) 17% MDI (n =0, 673–753 K); (⊡) 17% MDI (n =0, 463–763 K)

In fact, the flexibility of these copolymers estimated through the rigidity factor (σ), and the characteristic ratio (C_∞) diminishes in the same way as the characteristic degradation temperatures, $TD^{50\%}$ and TD^{i}. On the other hand, the flexibility among the copolymers increases as the molar volume of the side chain increases [18], following a similar trend as $TD^{50\%}$ and TD^{i}. However, in the corresponding homopolymers the rigidity increases as the molar volume of bulkiness of the side chain increases, PVP being the most flexible one [18]. The differences in rigidity of the homopolymers and the corresponding copolymers has been explained in terms of the separation of the itaconate units by VP units, leading to a less compact structure unfavourable for hydrophobic interactions which seems to be responsible for their conformation behaviour [18].

Similar results have been reported for other sets of polymeric systems [2]. Hence the volume and the bulkiness of the side chain seems to play an important role in the degradation of these polymers, if we consider that the bulkiness of the lateral chain increases appreciably as the length of the substituents increases.

It is very interesting to remark in the thermal behaviour of these systems that they behave qualitatively in a similar way, which is not surprising because of the similarities in structure, but clearly the monotonous variations in the thermogravimetric analysis can be attributed to the differences in the size and volume of the lateral group. Nevertheless, it is necessary to analyze if this behaviour follows a similar trend from a kinetic point of view.

In fact, the rate dependent parameters such as activation energy (E_a), and order of the reaction (n) may be calculated from a single experimental curve [1, 2, 19]. It is possible to express the specific rate constant (k) in terms of an Arrhenius type equation:

$$k = Ae^{-\frac{E_a}{RT}} \tag{1}$$

where A is the frequency factor, E_a is the activation energy, R is the gas constant and T the absolute temperature. Following a reaction model like the one described in references [1, 2, 16, 23, 24] we can express the degradation rate $d\alpha/dt$ as function of the degree of weight loss 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, which can be obtained directly from the curves and n is the order of the degradation process. By introducing directly the heating rate (20 deg·min^{-1}) into the data of temperature against sample weight fraction [25], the reaction rates can be calculated. From Eqs (1) and (2) it is possible to obtain:

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

By this way the kinetics parameters are determined using a linear multiple regression program, which allows to calculate the activation energy E_a, and the frequency factor A, from a linear least-square fit of the data in a semilogarithmic plot of β *vs.* T^{-1}. They are, however, valid for the used conditions only, because of the complexity of the reaction.

Figures 2, 3 and 4 show plots of β *vs.* T^{-1} for copolymers containing MOI, MDI and MDoI of three different compositions. Straight lines are obtained in all cases by using different order kinetic models. In fact, for some samples, good correlations are obtained considering at least two different reaction orders. Table 2 summarizes the kinetic parameters obtained from the plots of Figs 2, 3 and 4 and those for the corresponding homopolymers. As can be seen for PMOI and the copolymers containing 90 and 52% of MOI, the best fit is obtained for $n=1$, but for the copolymers rich in vinylpyrrolidone, the best fit is for $n=0$. For copolymers derived from MDI there are several n values resulting good fits, depending on the composition of the copolymer and on the temperature range. For PMDI and the copolymer containing 46% of MDI in the high temperature range, the fits are good for $n=1$ whereas for copolymers with 82 and 46% of MDI in the whole temperature range. For copolymers with 46% of MDI in the high temperature range, good fits are obtained for $n=2$. For MDoI derivatives, we find similar results as it can be seen in Table 2, where we obtain fits wit $n=2$ for the copolymers richer and poorer in MDoI and $n=1$ for copolymers with 50% of MDoI and also for the copolymer with 20% of MDoI. The corresponding homopolymer fits well with $n=1/2$, and PVP with $n=1$ or $n=0$ depending on the temperature range. These are very surprising results because for some samples we obtain good fits with two n values in the same temperature range and for other samples with different n values for different temperature ranges.

The activation energies for the systems studied are very similar, but some differences are observed for systems with more than one degradation step. Although these differences could not be significant they can be interpreted in terms of the differences in the structure between the copolymers where the repeating unit could play an important role in the degradation process.

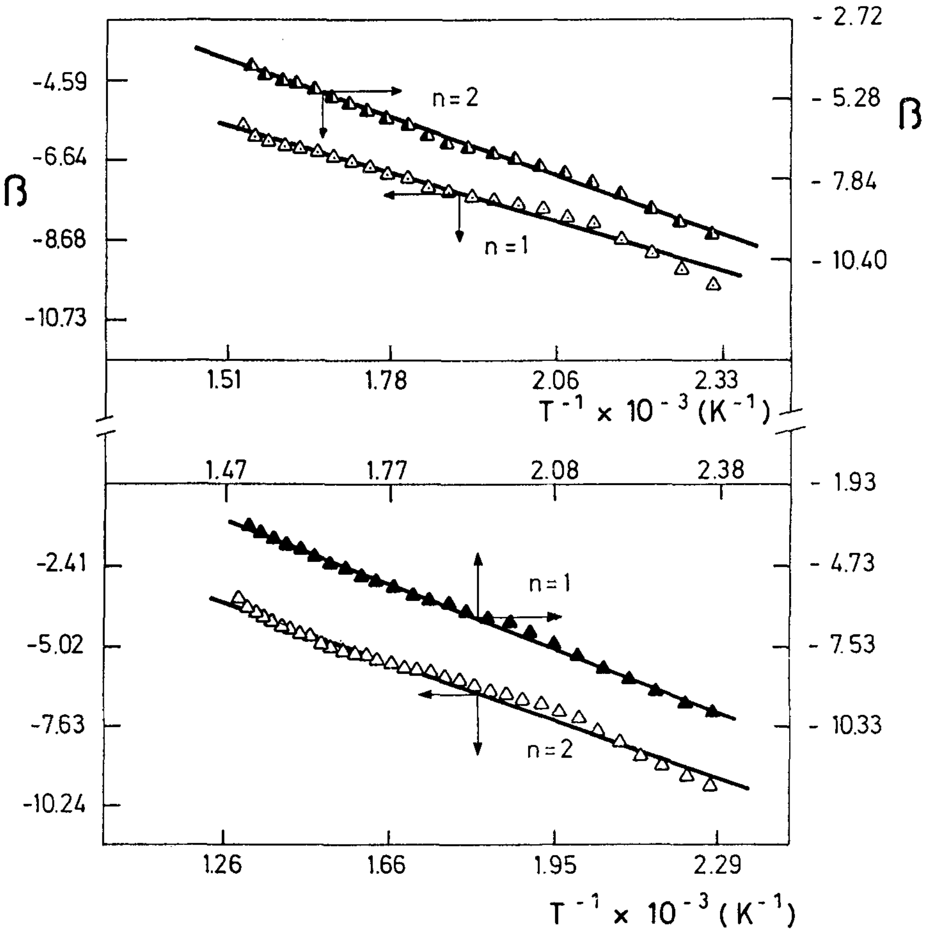


Fig. 4 Plots of β *vs.* $1/T$ for MDoI/VP copolymers. (Δ) 82% MDoI; (▲) 48% MOI; (Δ) 20% MDoI (n = 2, 443–773 K); (▲) 20% MDoI (n =1, 443–653 K)

Finally it is possible to conclude that the thermal degradation of these copolymers depends on the monomer composition and on the nature of the comonomers. The degradation temperatures increase as both the length of the side chain of the itaconate and the vinylpyrrolidone content increases. The thermal behaviour of these random copolymers shows the same trend as the corresponding poly(monitaconates) and the specific degradation temperatures can be correlated with the flexibility of the copolymers in solution.

Table 2 Thermogravimetric kinetic parameters of the decomposition process and the temperature range analysed, for copolymers of MOI/VP, MDI/VP, MDoI/VP and the corresponding homopolymers PMOI, PMDI, PMDoI and PVP respectively

Polymer	Composition / % MI	E_a / kcal·mol^{-1}	A / s^{-1}	n	Teperatures / K
PMOI	100	8.20	1.71	1	130–470
	90	10.18	16.11	1	393–653
MOI/VP	52	9.18	4.11	1	403–703
	13	11.54	77.9	0	423–493
		3.19	$5.77{\cdot}10^{-3}$	0	513–673
MDI	100	8.65	1.77	1	143–453
	82	10.74	37.11	2	423–753
	46	18.15	$6.42{\cdot}10^{4}$	2	423–653
MDI/VP		16.09	310.7	1	663–783
		31.67	$1.66{\cdot}10^{8}$	2	663–783
	17	3.22	$5.1{\cdot}10^{-3}$	0	463–763
		8.95	0.192	0	673–753
MDoI	100	10.0	5.78	0.5	150–380
	82	11.78	68.7	2	443–773
MDoI/VP	48	15.11	4225	1	423–673
	20	9.42	4.98	1	433–653
		14.38	1337	2	433–653
PVP	100	28.94	$3.03{\cdot}10^{11}$	1	413–463
		10.21	0.2178	0	673–823

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Zusammenfassung — Poly(monoitaconate), die Octyl-, Decyl-und Dodecylgruppen enthalten, sowie statistische Monoalkyl-itaconate-co-vinylpyrrolidon Copolymere und Copolymere des N-vinyl-2-pyrrolidons mit Mono-*n*-octylitaconaten (MOI), Mono-*n*-decylitaconaten (MDI) und Mono-*n*-dodecylitaconaten (MDoI) verschiedener Zusammensetzungen wurden durch dynamische TG Analyse untersucht.

Die thermische Beständigkeit der Copolymere hängt von der Struktur der Monoitaconatecomonomere und von der Zusammensetzung der Copolymere ab. Die kinetische Auswertung der TG-Kurven ermöglicht eine Beschreibung der thermischen Zersetzung der Copolymere nach verschiedenen kinetischen Ordnungen, je nach Copolymerart und Zusammensetzung. Die Copolymere sind thermisch stabiler, wenn die VP-Gehalt bzw. die Seitenkettenlänge zunimmt. Dieses Verhalten zeigt im Grunde genommen die gleiche Tendenz, wie die Beweglichkeit dieser Copolymere in Lösung.