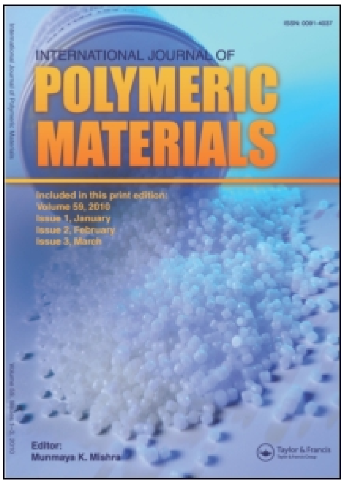

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Thermal Stability of Aromatic Poly(monoitaconates)

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Thermogravimetric analysis of poly(mono-benzyl itaconate), (PMBzI) poly(mono-ethylphenyl itaconate) (PMEPI) and poly(mono-*n*-propyl itaconate) (PMPPI), were performed by dynamic thermogravimetry. The thermal stability of these polymers depends on the side chain structure. The kinetic analysis of the degradation data shows that the thermal decomposition of these polymers follows a 0.5 kinetic order in all the cases.

KEY WORDS Poly(monoitaconates), aromatic, thermal analysis, stability, degradation, kinetics.

INTRODUCTION

Poly(monoitaconates) are a very interesting family of polymers whose behaviour in solution has been extensively studied[1-9] but less studied in the solid state.[10-12] The effect of the side chain structure on different properties of these polymers has been previously reported.[8-12] The nature, rigidity and bulkiness of the pendant groups, dramatically influence the physicochemical behaviour of poly(monoitaconates). In the case of aromatic side chains the photobehaviour of phenyl containing polymers and the influence of the length of the spacer group between the aromatic ring and the main chain, on the emission spectra is interesting.[13] The characteristics of the side chain in vinyl polymers are in general the main reason for their conformational behaviour.

We have recently reported[14] the effect of the side chain on the thermal degradation of aromatic poly(methacrylates) containing heteroatoms. In these systems, that show high rigidity factors, the degradation profiles are clearly affected by the rigidity of the side groups. Nevertheless, studies about the thermal degradation of aromatic poly(monoitaconates) are scarce.

In this work, we report the study of the thermal degradation of aromatic poly(monoitaconates) containing benzyl (PMBzI), 2-phenylethyl (PMEPI) and 3-phenylpropyl (PMPPI) groups as side chains (see Scheme I). These polymers present a

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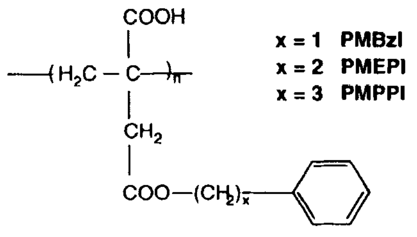

SCHEME I

flexible spacer group inserted between the main chain and the aromatic ring. Therefore, if the side groups are connected via a flexible spacer to the main chain the motions of the main chain and the side chains might be decoupled. On the other hand, if the side groups are directly fixed to the main chain, the ability to move and orient should be changed drastically.[14,15] This structural arrangement must be affect the thermal stability, influencing the relative stability of this family of polymers.

EXPERIMENTAL

Sample Characterization

Polymer samples were obtained by radical polymerization as was previously reported.[16,17] All samples were characterized by FTIR and ^{1}H NMR. Number average molecular weight (*Mn*) and weight average molecular weight (*Mw*) of the polymers were determined by osmometry and Light Scattering as previously reported.[16,17]

Thermal Decomposition

Dynamic thermogravimetric analysis was performed using a Mettler TA-3000 calorimetric system equipped with a TC-10A processor, and a TG-50 thermobalance with a Mettler MT5 microbalance. The samples were heated on Al_2O_3 pans. Measurements were carried out between 303 and 1000 K at a 20° min^{-1} under N_2.

RESULTS AND DISCUSSION

Figure 1 shows the thermogravimetric curves for fractions of narrow molecular weight distribution and similar molecular weights (*Mw* ~ 200.000) of PMBzI, PMEPI and PMPPI. According to these profiles all the polymers show a qualitative similar behaviour in the sense that the loss weight apparently follows a single one-stage decomposition process. In order to compare in a relative way the degradation behaviour of these polymers we determined the initial decomposition temperatures TD^i and the temperatures of 50% weight loss $TD^{50\%}$. Table I summarizes the TD^i and $TD^{50\%}$ values together with the molar volume of the side groups of the polymers. According to the results shown in Figure 1 and also summarized in Table I, TD^i and $TD^{50\%}$ follow the order:

$$\text{PMPPI} \approx \text{PMEPI} > \text{PMBzI}.$$

and the polymers can be considered as thermally stable. The thermal stability of the polymers decreases as the molar volume of the side chain decreases. This result is contrary to that reported for a family of related chalcogenides containing poly(methacrylates),[18] poly(alkyl methacrylates),[19] poly(alkyl acrylates)[20] and poly(N(*n*-alkyl) maleimides).[21] In these polymers there is a correlation between the temperatures of the decomposition and the polymer structure in the sense that TD decreases as the molar volume of the side chain increases.

Poly(monoitaconates) are rigid or semirigid polymers[7,22-25] therefore, the polymer structure plays an important role in the thermal stability but its real effect is not well known. If we pay attention to the structures of the polymers studied, some influence should be expected of the nature, bulkiness and structure of the side groups on the thermogravimetric profiles and on the degradation temperatures. No important differences in TD^i or $TD^{50\%}$ are observed at least between the first two polymers but in

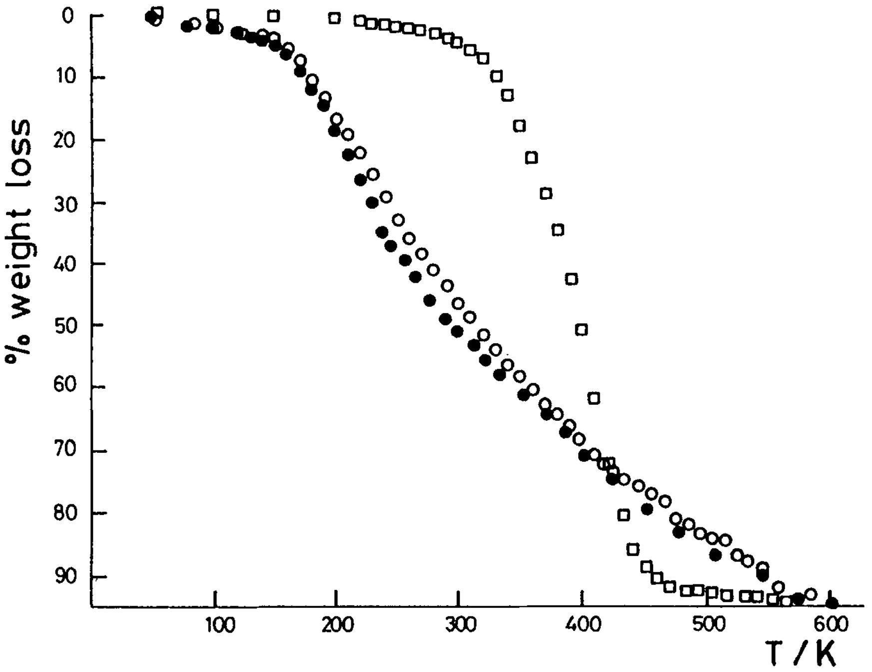

FIGURE 1 Thermogravimetric curves for: (○) PMBzI, (●) PMEPI and (□) PMPPI.

TABLE I

Initial decomposition temperature TD^i and temperature of 50% weight loss $TD^{50\%}$ for PMBzI, PMEPI and PMPPI

Polymer	V	TD^i	$TD^{50\%}$
	cm^3	°C	°C
PMBzI	103.8	175	324
PMEPI	119.8	178	320
PMPPI	135.1	336	400

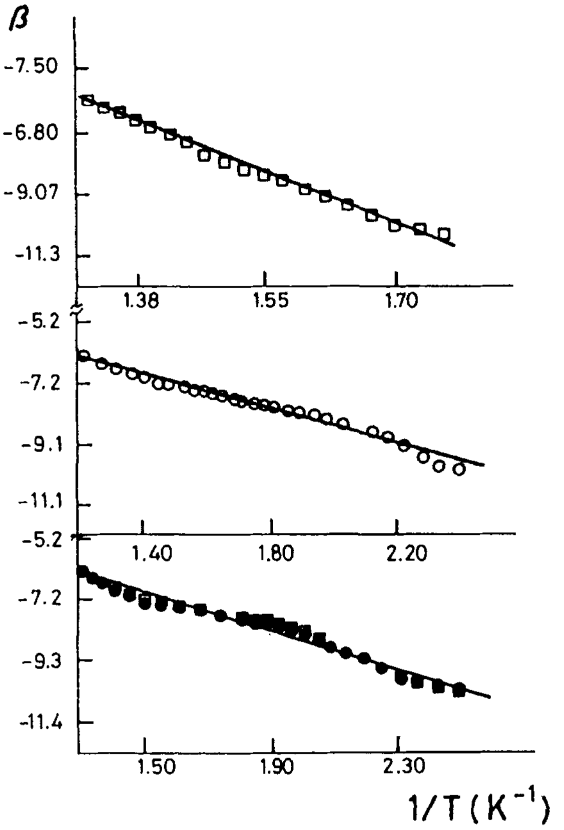

FIGURE 2 Plots of β vs 1/T for: (○) PMBzI, (●) PMEPI, (□) PMPPI.

the case of PMPPI the decomposition temperature is notably higher. Therefore, this behaviour could be due to the differences in the side chain structure. The presence of the free carboxylic group in poly(monoitaconates) could also play some role in the degradation behaviour.

In order to determine the kinetic parameters of the decomposition of the polymers studied we have considered that this reaction is irreversible, therefore the reaction rate $d\alpha/dt$ can be expressed as function of the degree of conversion α, according to the classical equations for this purpose. By this way it is possible to know the kinetic parameters expressed by:

$$\beta = \text{Ln}\left[\left(\frac{-\frac{d\alpha}{dt}}{(1-\alpha)^n}\right)\right] = \text{Ln}\, Z - \frac{E_a}{RT} \tag{1}$$

where n is the kinetic order, Z is the frequency factor, E_a the activation energy, T is the absolute temperature and R the gas constant. Using these equations and a linear

TABLE II

Activation energy, E_a, frequency factor, Z, and degradation order, n, for PMBzI, PMEPI and PMPPI

Polymer	Ea Kcal/mol	Z s^{-1}	n
PMBzI	6.76	0.029	0.5
PMEPI	6.31	0.0062	0.5
PMPPI	2.44	0.004	0.5

multiple regression program it is possible to obtain E_a and Z from a linear least-square fit of the data in a semilogarithmic plot of β against $1/T$.

Figure 2 show the plots of β vs $1/T$ for PMBzI, PMEPI and PMPPI respectively. Straight lines are obtained for a 0.5 order kinetic model. Table II summarizes the order of the degradation process, (n) the activation energy (E_a) and the frequency factor (Z) for all the polymers studied.

The activation energies are rather similar for PMBzI and PMEPI but quite different for PMPPI. Nevertheless, E_a decreases as the molar volume of the polymer increases following the same behaviour as that observed for the degradation temperatures. The values of the frequency factor Z, are low but in good agreement with those frequently found for polymers of similar structure. What is noteworthy is the 0.5 order found for the degradation process. It is not common to find these values. It is important to remark that from data in solution the chain rigidity in this family of polymers decreases as the molar volume increases which is attributed to the flexibilization effect of the spacer groups.[17] In fact, in this series of polymers there are at least two different factors which would exert opposite effects. On one hand, the increases of the volume of the lateral group (V) which would enlarge the value of the activation energy for decomposition and on the other hand, the rigidity of the chain (σ), which would contribute to diminish the activation energy for the thermal degradation of the polymer. The effect of the free carboxyl group on the thermal degradation is unknown but it is possible to think that this group could play some role in the thermal stabilization of poly(monoitaconates). In order to investigate the thermal stability of this kind of polymers, thermal degradation of copolymers containing itaconate moiety are in progress.

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