

# Thermal Behavior of Aliphatic–Aromatic Poly(ether-amide)s

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**ABSTRACT:** The thermal properties of a set of experimental aliphatic–aromatic polyamides containing ether linkages were examined as a function of their chemical structure. Variations of the glass transition temperature ( $T_g$ ) and melting temperature ( $T_m$ ) could be correlated with the length of the aliphatic spacers and with the orientation of the phenylene rings. Polymers with a high concentration of *p*-oriented phenylene units showed a higher  $T_g$  than those containing mainly *m*-oriented ones;  $T_g$  values ranged from 110 to 155°C. Surprisingly, a negligible dependence of  $T_g$ s on the nature of flexible spacers was observed. For all of the polymers, the thermal stability was virtually the same, about 440°C, when tested by dynamic thermogravimetric analysis (TGA). However, quite different levels of thermal stability were found by isothermal TGA analysis for polyamides with different flexible spacers. Moreover, the poly(ether-amide)s described here compare fairly well with wholly aromatic polyamides when measured by dynamic TGA; but isothermal TGA measurements clearly demonstrated that they decompose faster than aromatic polyamides. Treatment of the TGA curves by the method of McCallum provided kinetic data that confirmed a better long-term stability for poly(ether-amide)s with a higher proportion of *para*-oriented phenylene rings.  
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**Key words:** poly(ether-amide)s; melting temperature; glass transition temperature; differential scanning calorimetry; thermogravimetric analysis; thermal decomposition kinetics; mesophase

## INTRODUCTION

Wholly aromatic polyamides, e.g., poly(*m*-phenyleneisophthalamide) and poly(*p*-phenyleneterephthalamide), are well known for their superior resistance to heat, outstanding mechanical resistance, and poor solubility in common solvents.<sup>1–3</sup> This extreme behavior is a severe limiting factor for the processing of these materials, which do not melt and are virtually insoluble. Thus, due to the technical relevance of these materials, the im-

provement of their solubility, and their melting behavior has attracted considerable attention.

Approaches traditionally applied to enhance the processibility of intractable polymers include copolymerization and chemical modification of the original polymers. Segmented block copolymers, containing rigid and flexible sequences, offer an average of the properties of the corresponding homopolymers; thus, it is possible that the processing problems described above could be overcome by properly designed block copolymers. Segmented block polyamides are considered as a family of new thermoplastic elastomers with unique physical and processing properties<sup>4,5</sup> that can show good thermal properties and, occasionally, thermotropic behavior.<sup>6</sup> In this article, a

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study is presented of the influence of the chemical structure on the thermal properties of poly(ether-amide)s containing short sequences of aromatic polyamides alternating with short sequences of poly(ethyleneglycol) (PEG) or alkylene glycol. The aim of this study was directed towards the search for aliphatic–aromatic polyamides that could offer a balance of properties between those of tractable aliphatic nylons and the virtually insoluble and nonmelting wholly aromatic polyamides.

In order to obtain some insight into the structure–properties relationships that govern the behavior of these polymers, a set of homologous polyamides has been studied, in which the various polymers differ from each other in the orientation of the rigid moieties (*m*- or *p*-phenylene rings) and in the nature and length of the flexible (aliphatic) spacer. We have extended the study to 16 poly(ether-amide)s synthesized by low temperature methods, reported in our previous articles.<sup>7,8</sup> The evaluation of the thermal behavior of these polymers as a function of their chemical structure has been carried out using the data obtained from measurements of glass transition temperature, ( $T_g$ ), melting temperatures ( $T_m$ ), decomposition temperatures ( $T_d$ ), and thermal degradation kinetics.

## EXPERIMENTAL

The poly(ether-amide)s were synthesized by low temperature polycondensation methods from diamines and diacid chlorides. Isophthaloyl and terephthaloyl chlorides were combined with eight original aromatic diamines containing aliphatic sequences, as was previously reported.<sup>7,8</sup> Repeating units and inherent viscosities are listed in Table I.

For comparison purposes, poly(*m*-phenylene isophthalamide) (MPD-I) was prepared from isophthaloyl chloride and *m*-phenylenediamine by the classical low temperature polycondensation method in a solution of *N,N*-dimethylacetamide. MPD-I was attained in quantitative yield, with an inherent viscosity of 1.85 dL/g, measured in *N*-methylpyrrolidinone at  $25.0 \pm 0.1^\circ\text{C}$ .

Differential Scanning Calorimetry (DSC) analyses were performed on a Perkin–Elmer DSC7 calorimeter at a heating rate of  $20^\circ\text{C}/\text{min}$  under nitrogen. Two runs were needed, in general, be-

cause water absorbed and/or solvent traces greatly disturbed the first run.

Thermogravimetric analyses (TGA) were performed on a Perkin–Elmer TGA7 thermobalance. The dynamic measurements were performed with  $3 \pm 1$  mg samples heated in flowing nitrogen at  $10^\circ\text{C}/\text{min}$ . The samples were dried under vacuum at room temperature for 24 h over  $\text{P}_2\text{O}_5$ . Isothermal measurements were recorded with  $3 \pm 1$  mg samples at 400, 425, and  $450^\circ\text{C}$  in nitrogen.

X-Ray diffraction (XRD) patterns were obtained using a Geigerflex D/max device, with nickel-filtered  $\text{CuK}_\alpha$  ( $\lambda = 0.1542$  nm) radiation. The  $2\theta$  scan range was  $2\text{--}35^\circ$  using a scan rate of  $1^\circ/\text{min}$ .

Microscope observations were made with an Olympus BH-2 optical microscope fitted with crossed polarizers. The temperature was controlled in  $1^\circ\text{C}$  range by means of a computerized Linkam THM 600 heat controller.

## RESULTS AND DISCUSSION

The repeating unit of the polymers studied is depicted in Table I. They constitute a set of 16 different poly(ether-amide)s where the orientation of the phenylene rings and the nature and length of the flexible spacers were systematically changed. Samples having inherent viscosity values as near the same as possible were chosen for this study in order to avoid the influence of molecular weight.

DSC results obtained in the determination of  $T_g$ s indicate that the transitions fall in a temperature range that is intermediate between those of the conventional aliphatic polyamides and those of aromatic polyamides, as was expected from the nature of the chain backbone. As an example, the DSC curves of polymer PM8 are shown in Figure 1.

The data summarized in Table II actually confirm that the separation of the amide groups by lengthening the flexible sequences brings about an effective decrease of the hydrogen bond density and a lowering of the  $T_g$ s. Thus, polymers with pentamethylene and bis-oxyethylene units show higher  $T_g$ s than polymers with octamethylene or trioxyethylene units. In addition, it was expected that the higher conformational mobility of the oxyethylene moieties relative to that of the alkyl moieties should make for a lower  $T_g$  in the former polymers. However, polymers containing pentamethylene units show  $T_g$ s very close to those of

**Table I** Repeating Units and Inherent Viscosities of Poly(ether-amide)s

Polymer	Ar <sub>1</sub>	<i>n</i>	Ar <sub>2</sub>	$\eta_{inh}^a$ (dL/g)
$\left[ \text{HN}-\text{Ar}_2-\text{O}(\text{CH}_2\text{CH}_2\text{O})_n-\text{Ar}_2-\text{NHOC}-\text{Ar}_1-\text{CO} \right]_x$				
MM2O2	<i>m</i> -Ph	2	<i>m</i> -Ph	1.29
PM2O2	<i>p</i> -Ph	2	<i>m</i> -Ph	1.33
MP2O2	<i>m</i> -Ph	2	<i>p</i> -Ph	0.66
PP2O2	<i>p</i> -Ph	2	<i>p</i> -Ph	0.50
MM2O2O2	<i>m</i> -Ph	3	<i>m</i> -Ph	1.01
PM2O2O2	<i>p</i> -Ph	3	<i>m</i> -Ph	0.89
MP2O2O2	<i>m</i> -Ph	3	<i>p</i> -Ph	2.37
PP2O2O2	<i>p</i> -Ph	3	<i>p</i> -Ph	1.55
$\left[ \text{NH}-\text{Ar}_2-\text{O}-(\text{CH}_2)_n-\text{O}-\text{Ar}_2-\text{NHOC}-\text{Ar}_1-\text{CO} \right]_x$				
MM5	<i>m</i> -Ph	5	<i>m</i> -Ph	0.80
PM5	<i>p</i> -Ph	5	<i>m</i> -Ph	0.80
MP5	<i>m</i> -Ph	5	<i>p</i> -Ph	1.85
PP5	<i>p</i> -Ph	5	<i>p</i> -Ph	— <sup>b</sup>
MM8	<i>m</i> -Ph	8	<i>m</i> -Ph	0.63
PM8	<i>p</i> -Ph	8	<i>m</i> -Ph	0.60
MP8	<i>m</i> -Ph	8	<i>p</i> -Ph	1.08
PP8	<i>p</i> -Ph	8	<i>p</i> -Ph	— <sup>b</sup>

<sup>a</sup> Determined at 25°C with a polymer concentration of 0.5 g/dL in trifluoroacetic acid/chloroform (1/1).

<sup>b</sup> Insoluble.

polymers containing bis-oxyethylene units, and the same effect is observed for octamethylene and trioxyethylene.

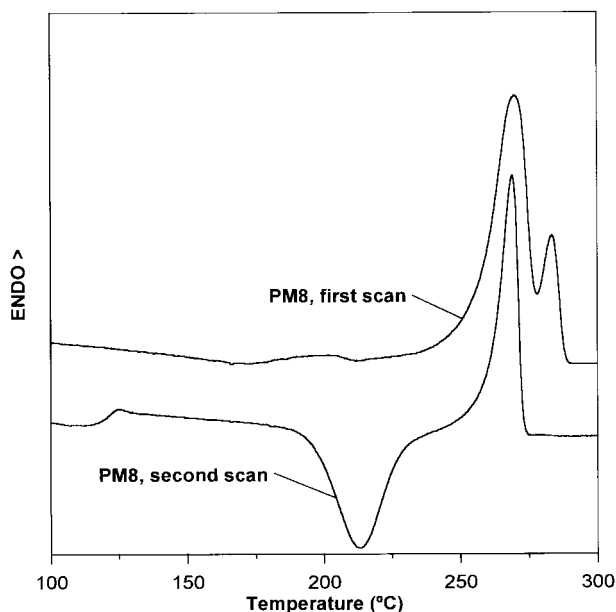
As might be expected, the most relevant effect on the  $T_g$  is the influence of the *m*- or *p*-orientation of the phenylene rings in the polymer chain. The presence of *p*-oriented rings increases the chain stiffness to an important extent relative to the *m*-oriented ones; and, therefore, an increase of the number of *p*-oriented rings in the polymer structure brings about a noticeable increase of the  $T_g$  (Table II).

As shown in Figure 1, melting endotherms were observed for all polymers; and several endotherms could be registered in many instances. Different crystalline forms or different crystallite sizes are responsible for this multiplicity. Data collected in Table II correspond to the peak of the highest temperature endotherm in the second run. The degree of crystallinity and the melting temperature are directly determined by the number of *p*-rings in the repeating unit (0, 1, 2, or 3), as can be observed in Table II. It is worth noting

the unexpectedly high  $T_m$ s found for some of these aliphatic-aromatic polyamides; thus, some  $T_m$ s were over 400°C for the structures containing all *para*-oriented phenylene rings, regardless of the nature or the length of the flexible spacer.

Admittedly, interchain hydrogen bonds are one of the most important factors that determine crystallinity in polyamides; so that upon increasing the distance between amide groups (hydrogen bonds), a decreasing of the  $T_m$  should be observed.<sup>1,2</sup> However, this effect was not observed in the current polyamides because the length of the flexible chain does not seem to play any important role in the melting temperature; and, unlike  $T_g$ s, polymers with five methylene linkages show  $T_m$  values very close to those of polyamides with eight methylene linkages. This evidence is actually not surprising if the well-known odd-even effect is considered; i.e., even numbered aliphatic spacers are known to provide higher melting temperatures than the odd numbered ones.

Because the chains of these polyamides consist of an alternating sequence of aromatic rigid blocks



**Figure 1** DSC thermograms of polymer PM8.

and flexible spacers, it may be assumed that they could show the thermal behaviour of polymer liquid crystals, particularly the polymers of the series PP (Table I), that contain a rigid rod-like

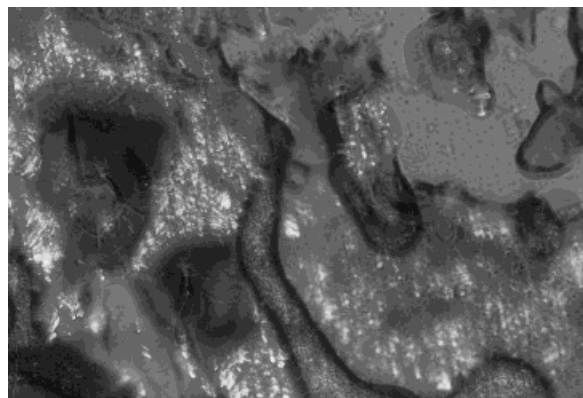
**Table II** Thermal Properties of Poly(ether-amide)s

Polymer	$T_g$	$T_m^a$	$T_d^b$	Residue % (700°C)
MM2O2	126	170	440	32
PM2O2	140	273	435	30
MP2O2	155	320	440	30
PP2O2	— <sup>c</sup>	416	450	30
MM2O2O2	111	207	440	28
PM2O2O2	116	265	435	33
MP2O2O2	129	292	435	29
PP2O2O2	— <sup>c</sup>	416	445	30
MM5	125	180	425	38
PM5	135	275	430	36
MP5	155	341	440	34
PP5	— <sup>c</sup>	434	450	29
MM8	117	201	445	30
PM8	122	284	435	38
MP8	128	320	435	32
PP8	— <sup>c</sup>	430	450	30
MPD-I	276	> 450	455	50

<sup>a</sup> Endothermic peak at highest temperature.

<sup>b</sup> Onset temperature of initial decomposition.

<sup>c</sup> Not observed.



**Figure 2** Cross-polarizing microscopy picture of PP202O2 at 395°C.

block of three *p*-phenylene rings linked by amide groups. The combination of this unit, 18.53 Å long in its most probable transconformation, with aliphatic and oxyethylene spacers in the repeating unit, produces polymers with  $T_m$  beyond the decomposition temperature in some cases. For polymer PP202O2, a  $T_m$  value of 386°C was observed, together with an endotherm above  $T_m$ . For this endotherm, an enthalpy of 8.8 J/g was measured, which could be indicative of a transition at high temperature ( $T_i$ ) from an anisotropic mesophase to an isotropic molten phase. The temperature interval between  $T_m$  and  $T_i$  was only 30°C, between 386 ( $T_m$ ) and 416 ( $T_i$ ). At these extreme temperatures, the polyamide PP202O2 decomposes rather rapidly, and the observation of a mobile mesophase by means of cross-polarizing microscopy is quite difficult. However, upon applying a high heating rate (20°C/min), pictures such as that reproduced in Figure 2 could be obtained at approximately 395°C. Although the picture does not allow for the assignment of the texture precisely, it is most probably a smectic mesophase.

This was confirmed by XRD; e.g., Figure 3 reproduces the X-ray diffractogram of polymer PP202O2. Reflection peaks can be observed at low angles, 3.3° and 6.7°, typical of first- and second-order reflexions of layer-ordered supramolecular structures of the type smectic-C.

These observations were not possible for the other PP polyamides. Polymers PP5 and PP2O2 have spacers too short to develop a LC (liquid crystal) mesophase, and polymer PP8 has a  $T_m$  even higher than PP202O2, which means that it decomposes before the mesophase can stabilize.

It is worth emphasizing that these poly(ether-

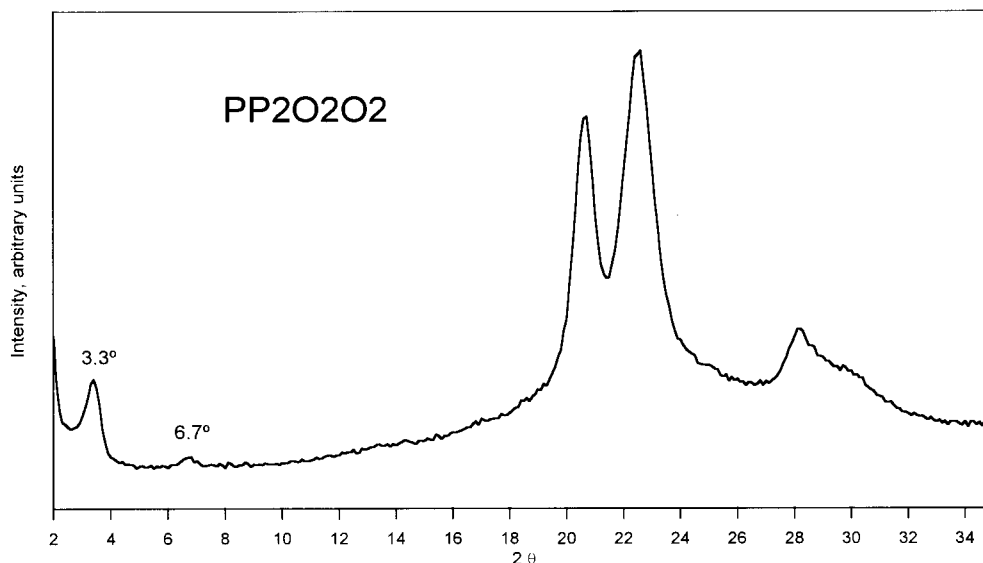


Figure 3 X-ray diffractogram of polymer PP20202.

amide)s can develop high crystallinity, as can be deduced from the X-ray diffractogram of Figure 3. It should be kept in mind that the sample did not undergo any thermal annealing, and it can be presumed that a suitable thermal treatment could still improve the degree of crystallinity. At any rate, the role that crystallinity plays in the thermal behavior has not been quantified in the present work.

The thermal analysis data obtained by dynamic TGA are summarized in Table II, and a typical TGA curve is presented in Figure 4. Initial decomposition temperatures ( $T_d$ s) in the range of 430–450°C were observed, which compare fairly well with those of traditional aromatic polyamides,<sup>1,2</sup>

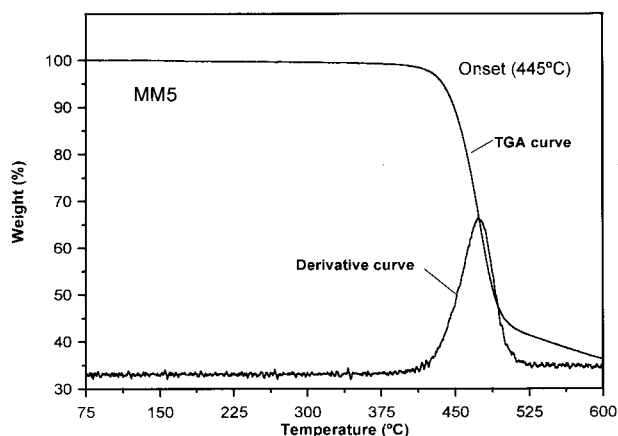


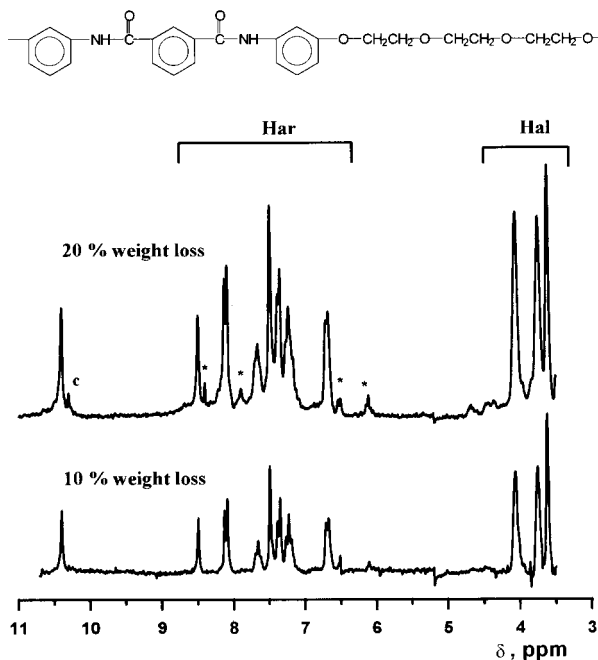
Figure 4 TGA curve of polymer MM8.

like MPD-I, which shows a decomposition onset at 455°C. The narrow range of  $T_d$ s did not allow for finding any trend based on the molecular structures of the set of samples investigated.

Although the current polymers presented initial decomposition onsets near the range of conventional aromatic polyamides with similar rigid structures, the presence of aliphatic moieties lead to smaller weight residues at high temperatures. Thus, MM5 showed a 38% residue at 700°C; whereas MPD-I, a wholly aromatic, all *meta*-oriented polyamide had a 50% weight residue at that temperature; MM8, MM202, and MM20202 showed still less weight residue than MM5. The length of the flexible spacer played the expected role: the longer the aliphatic moiety, the lower the weight residue at high temperature.

Higher weight loss at high temperatures in aliphatic polyamides compared to aromatic ones is a consequence of the easy production of volatile molecules upon the cleavage of the aliphatic bonds,<sup>9</sup> while the cleavage of aromatic bonds produces heavier and less volatile products that can recombine with other degradation products, with an overall slower rate of weight loss.<sup>10,11</sup>

In a degradation study made by <sup>1</sup>H-NMR combined with TGA on polymers MM8 and MM20202 at 10 and 20% weight loss (see Fig. 5 and Table III), an increase of the ratio  $H_{\text{aromatic}}/H_{\text{aliphatic}}$  during degradation could be observed. Although the thermal degradation is faster and more complete in the aliphatic moiety, a general degradation



**Figure 5**  $^1\text{H-NMR}$  curves of polymer MM20202 at 10 and 20% weight loss.

mechanism is observed in the spectra, with emerging  $H_{\text{amidic}}$  signals of increasing intensity as the degradation proceeds, and with new aromatic signals due to aromatic fragments containing amines, acids, nitriles, etc.<sup>9</sup> This overall degradation mechanism, involving virtually all the linkages of the macromolecule, can be confirmed by an unique decomposition step observed on the TGA thermograms (see derivative curve of Fig. 4). A kinetic study of the isothermal decomposition has also been made, with the method described by MacCallum.<sup>12,13</sup> For isothermal experiments performed over a range of temperatures, eq. (1) is followed, where  $E_a$  is the activation energy and  $\ln[F(1 - \alpha)]$  has the same value for a given conversion.  $E_a$  can be calculated for a range of temperatures by plotting the logarithm of the time taken to reach a fixed conversion  $\alpha$  against the reciprocal temperature of the experiment.

$$\ln t = \frac{E_a}{RT} + \ln[F(1 - \alpha)] \quad (1)$$

The kinetic data for the set of polyamides of the present work are represented in Figure 6. Although the data obtained by this method have no real mechanistic significance, the use of them is justified when some kind of structure-thermal

**Table III**  $^1\text{H-NMR}$  Signal Ratio ( $H_{\text{aromatic}} : H_{\text{aliphatic}}$ ) of MM8 and MM20202

Polymer	Integral Ratio ( $H_{\text{aromatic}} : H_{\text{aliphatic}}$ )		
	Original	10% Weight Lost	20% Weight Lost
MM20202	1	1.3	1.5
MM8	0.75	0.8	0.9

stability trend is to be outlined for structurally related polymers, a trend that could not be found by dynamic measurements. As was expected, the results indicate that as the reaction progresses, the apparent activation energy increases, which means that several reactions are involved at advanced decomposition stages.

The most important information provided by this analysis is the  $E_a$  order in each polymer series. Thus, higher values of  $E_a$  could be measured for the polymers containing *para*-oriented rings. Also in this case, no significant differences could be observed when the aliphatic and the oxyethylene series were compared.

## CONCLUSIONS

This work has shown that aliphatic-aromatic poly(ether-amide)s have  $T_g$ s and  $T_m$ s between those of aliphatic polyamides and aromatic polyamides.

Although chain flexibility clearly increases with the frequency of ether linkages in the molecular backbone, this fact was not translated into any substantial  $T_g$  or  $T_m$  difference between oxyethylene and polymethylene spacers.

The thermal degradation temperatures of the present polymers are high, slightly lower than those of aromatic polyamides; and a predominant cleavage of aliphatic linkages is observed in the first conversion steps. In this respect, not only the aromatic moieties but also the length of the aliphatic ones play an important role in the thermal stability.

The combination of rigid and flexible sequences can bring about thermotropic properties for poly(ether-amide)s containing only *p*-phenylene rings. Polymers of the series PP contain a potential mesogenic unit, and, based on the thermal behavior of polymer PP20202, they will be predict-

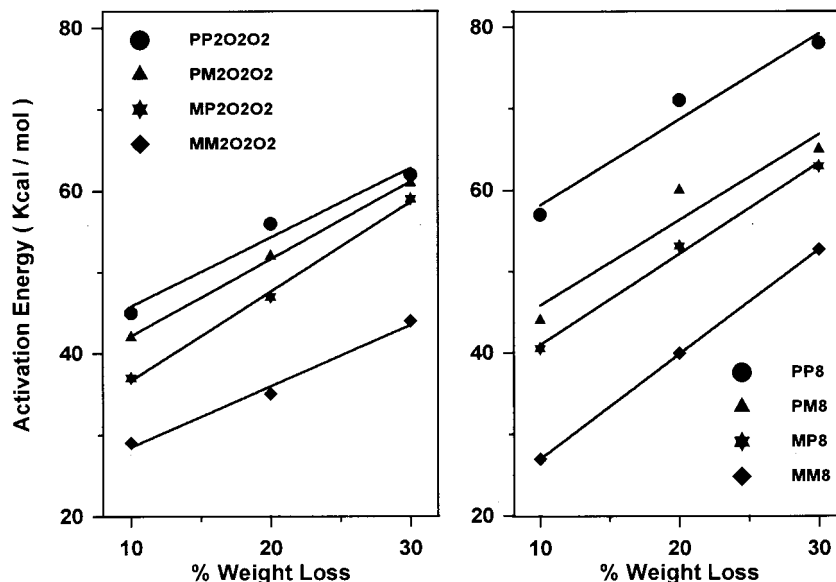


Figure 6 Activation energy of poly(ether-amide)s thermal decomposition.

ably thermotropic if they contain a longer spacer, either polymethylene or poly(oxyethylene).

The poly(ether-amide)s with a favorable ratio of *meta*- and *para*-phenylene rings ( $T_m$ s in the range 260–320°C) offer a satisfactory combination of properties and processability as technical materials.

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