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Thermal analysis of polymers and copolymers derived from n-1-alkylitaconamic acids

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THERMAL ANALYSIS OF POLYMERS AND COPOLYMERS DERIVED FROM N-1-ALKYLITACONAMIC ACIDS

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Poly(N-1-alkylitaconamic acid) (PNAIA) containing ethyl, propyl, butyl, hexyl, octyl, decyl and dodecyl groups and random N-1-alkylitaconamic acid-co-styrene copolymers (NAIA-co-S) of three different compositions were selected and studied by dynamic thermogravimetric analysis (TGA). The thermal stability of homopolymers and copolymers depends on the structure of the NAIA and on the composition of the copolymer. The kinetic analysis of the degradation data shows that the thermal decomposition of the PNAIA can be described by zero order kinetic model. In the case of NAIA-co-S copolymers, the degradation process can be described by two different kinetic orders depending on the copolymer and on the composition. The thermal stability of the PNAIA in general increases as the length of the side chain increases. In the case of copolymers with styrene the relative thermal stability depends clearly on the composition and on the type of substituent in the side chain.

Keywords: N-1-alkylitaconamic acid-co-styrene, copolymers, thermal stability, degradation profiles, kinetic order, side chain structure

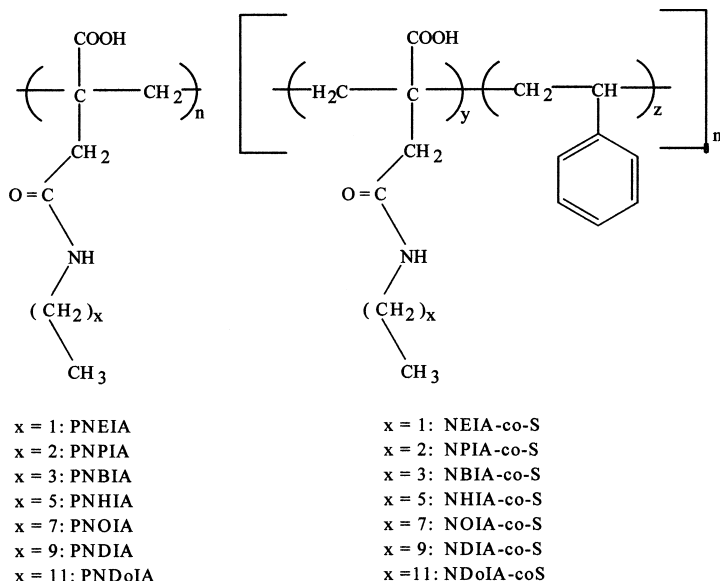
INTRODUCTION

Polymers derived from itaconic acid are of great interest from different points of view [1–4]. Mono and diesterification of itaconic acid can be

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SCHEME 1

carried out, obtaining monomers and polymers having either one or two of the carboxyl groups esterified in each repeating unit [5,6]. Poly(N-1-alkylitaconamic acids) are a family of functionalized polymers derived from itaconic acid, containing a free carboxylic group and an amide group per repeating unit with aliphatic side chains. This kind of polymers can be prepared with different length in the alkyl side chain, thus resulting in polymers with controlled hydrophobicity [7,8]. Because of the peculiar structure, with a free carboxylic group and an amide group, the autoassociation of these polymers is an effect to be taken into account, before any analysis [9]. This phenomenon could influence the thermal and mechanical behaviour. On the other hand, the outstanding thermal and mechanical properties of amido group containing polymers is a matter of current interest. Therefore, according to the polymer structure of poly(N-1-alkyl itaconamic acids) (PNAIA), it is possible to assume that these polymers may interact with themselves and with other polymers in polymer blends as well as in the case of copolymers containing this moiety [9,10]. For this reason, the thermal analysis of polymers and copolymers containing NAIA moiety should be of interest in order to get confidence about the particular behaviour of this kind of functionalized polymers.

The aim of this work is to analyze polymers and copolymers derived from NAIA in order to know the effect of the side chain structure on

the thermal stability of these systems. To reach this objective poly(N-1-alkylitaconamic acids) and copolymers with styrene, with different length of the side chain were synthesized *i.e.*, PNAIA containing ethyl (PNEIA), propyl (PNPIA), butyl (PNBIA), hexyl (PNHIA), octyl (PNOIA), decyl (PNDIA) and dodecyl (PND_oIA) and the corresponding copolymers of three different copolymer compositions with styrene (NAIA-co-S) (see Scheme 1).

EXPERIMENTAL

Monomer and Polymer Preparation

N-1-alkylitaconamic acids (NAIA) were synthesized by reaction of itaconic anhydride with the corresponding 1-alkylamine in chloroform, following procedures previously reported [8,11] and improved by us. Polymers, PNEIA, PNPIA, PNBIA, PNHIA, PNOIA, PNDIA and PND_oIA were obtained by radical polymerization in bulk at 343–393 K (depending on the N-1-alkylitaconamic acid used) under nitrogen, using α,α' -azobisisobutyronitrile (AIBN) (0.6% mol) as initiator. Purification of the polymers was achieved by reprecipitation with methanol in THF solution, before vacuum drying.

Copolymerization of the monomers with styrene was carried out in bulk at 354–388 K (depending on the N-1-alkylitaconamic acid used) under nitrogen using α,α' -azobisisobutyronitrile (AIBN) (0.6 mol%) as initiator. The conversion of most of the copolymers were rather low (>10%). Purification of the copolymers was achieved by reprecipitation with methanol in THF solution, before vacuum drying.

Thermogravimetric Measurements

Dynamic thermogravimetric measurements were 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 thermogravimetric results were processed by the Mettler 821 calorimetric system using the STAR^e program. The samples were heated on Al₂O₃ pans. Measurements were carried out between 300 and 1000 K at 20°min⁻¹ under N₂.

RESULTS AND DISCUSSION

Figure 1 shows the thermogravimetric profiles corresponding to PNEIA, PNPIA, PNBIA, PNHIA, PNOIA, PNDIA and PND_oIA of

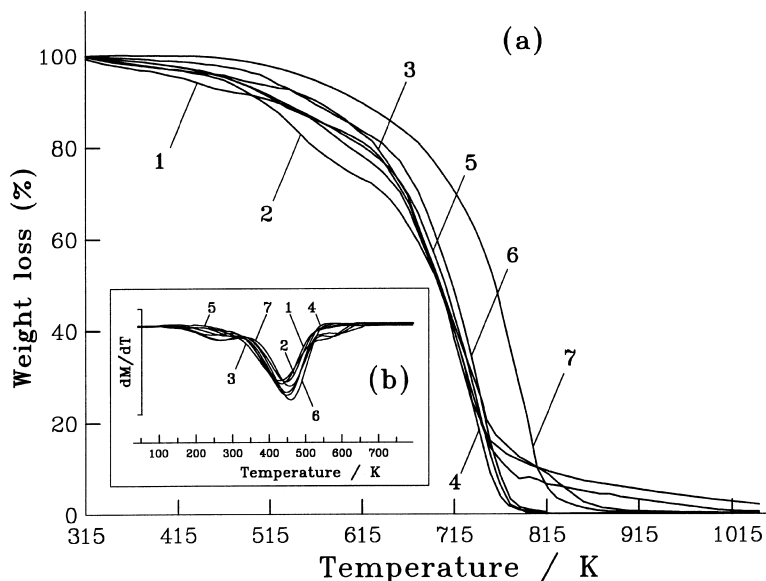


FIGURE 1 (a) Thermogravimetric profile for poly(N-1-alkylitaconamic acids): (1) PNEIA, (2) PNPIA, (3) PNBIA, (4) PNHIA, (5) PNOIA, (6) PNDIA, (7) PND_oI_A. (b) First derivative of the weight loss thermogravimetric profiles dM/dT against temperature for: (1) PNEIA, (2) PNPIA, (3) PNBIA, (4) PNHIA, (5) PNOIA, (6) PNDIA, (7) PND_oI_A.

similar weight average molecular weight \overline{M}_w in order to compare the degradation behaviour of the homopolymers. These curves represent the dependence of the loss of weight on temperature between 315 and 1000 K. All polymers begin to degrade about 500 K and apparently follow a single one stage decomposition process (see Figure 1a). Nevertheless, if the first derivative of the loss weight with temperature is represented, a two stage decomposition can be observed in all the polymers and a three stage decomposition profile is observed in the case of PND_oI_A (Figure 1b). This result indicates a complex degradation process in these systems. Table 1 summarizes the decomposition results obtained from Figure 1. The relative thermal stability of these polymers can be appreciated by comparing the decomposition temperature for the different polymers which is dependent on the length of the alkyl side chain. According to the results compiled in Table 1, $TD^{50\%}$ follows the order: PND_oI_A \geq PNDIA $>$ PNOIA $>$ PNHIA \geq PNBIA \geq PNPIA $>$ PNEIA.

These results indicate that PND_oI_A and PNDIA have similar thermal stability which is higher than that of PNHIA and PNOIA and

TABLE 1 Temperature Range of the Decomposition Profile (T_i = Initial Temperature, T_{max} = Maximum Temperature), Initial Decomposition Temperature TD^i (Taken at 10% Weight Loss) and Temperature of 50% Weight Loss $TD^{50\%}$ for Poly(*N*-1-Alkylitaconamic Acids)

Polymer	$T_i - T_{max}$ (K)	TD^i (K)	$TD^{50\%}$ (K)
PNEIA	(a) 535–605	515	700
	(b) 635–745		
PNPIA	(a) 450–580	520	702
	(b) 645–780		
PNBIA	(a) 610–770	575	703
	(b) 780–880		
PNHIA	(a) 465–565	530	705
	(b) 645–790		
PNOIA	(a) 620–780	535	710
	(b) 840–900		
PNDIA	(a) 515–595	570	725
	(b) 655–800		
PNDoIA	(a) 450–580	610	730
	(b) 650–800		
	(c) 815–890		

these are more stable than PNEIA and PNPIA. The effect of the side chain length on the thermal stability of this family of polymers can be explained in terms of the higher molar volume of the monomer unit as the alkyl chain increases which should increase the rigidity of the chain. On the other hand the degree of packing of the side chains is larger as the number of carbon atoms in the side chain increases. Figure 2 shows the thermogravimetric profiles for some copolymers of three compositions 20/80, 50/50 and 80/20% (NAIA/Styrene). This figure shows only the thermograms for copolymers containing NEIA, NHIA, and NDIA as an example of the general behaviour. The other thermograms are not included for sake of clarity. Table 2 compiles the thermogravimetric results for copolymers of NEIA-co-S, NPIA-co-S, NPIA-co-S, NPIA-co-S, NHIA-co-S, NOIA-co-S, NDIA-co-S and NDoIA-co-S at the three different compositions studied. According to the results summarized in Table 2, as a general observation it can be concluded that TD^i increases as the styrene content increases. On the other hand, it is interesting to note that in the case of copolymers the degradation process takes place at lower temperatures than that corresponding to the NAIA homopolymers. The only exception in this case is the hexyl

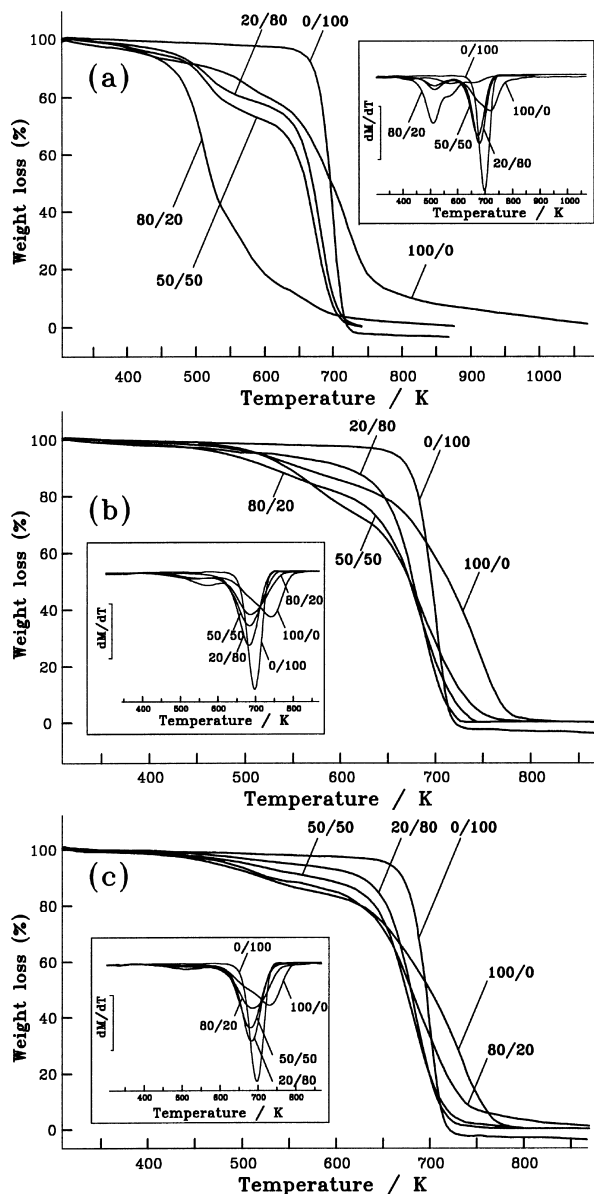


FIGURE 2 Thermogravimetric profiles and first derivative of the weight loss thermogravimetric profiles dM/dT against temperature for: (a) NEIA-co-S, (b) NHIA-co-S, and (c) NDIA-co-S at three different compositions: 20/80; 50/50, and 80/20 w/w% (NAIA/S) and the corresponding pure polymers.

TABLE 2 Copolymer Composition (w/w), Temperature Range of the Decomposition Profile (T_i = Initial Temperature, T_{max} = Maximum Temperature), Initial Decomposition Temperature TD^i (Taken at 10% Weight Loss) and Temperature of 50% Weight Loss $TD^{50\%}$ for (*N*-1-Alkylitaconamic Acids-co-Styrene) Copolymers

Copolymer	Composition (w/w)	$T_i - T_{max}$ (K)	TD^i (K)	$TD^{50\%}$ (K)
NEIA-co-S	20/80	(a) 485–565	520	680
		(b) 655–715		
	50/50	(a) 495–545	510	670
		(b) 635–705		
	80/20	(a) 465–525	470	530
		(b) 545–605		
(c) 625–705		470	530	
NPiA-co-S	20/80	645–695	530	700
		(a) 475–565	570	677
	80/20	(b) 635–725	600	685
		615–745		
NBiA-co-S	20/80	635–715	540	680
	50/50	(a) 505–545	500	675
		(b) 625–735		
	80/20	665–745	470	685
NHIA-co-S	20/80	635–715	640	680
	50/50	605–755	610	675
	80/20	(a) 465–525	560	685
		(b) 635–755		
		465–525		
NOiA-co-S	20/80	635–705	620	685
	50/50	(a) 515–575	590	680
		(b) 635–715		
	80/20	(a) 475–545	540	700
		(b) 635–755		
	NDiA-co-S	20/80	635–715	560
50/50		(a) 515–575	540	675
		(b) 625–715		
80/20		(a) 545–605	555	675
80/20		(b) 635–745		
NDoiA-co-S		20/80	635–700	590
	50/50	(a) 510–605	530	685
		610–700		
	80/20	(a) 505–600	520	650
		(b) 625–705		

derivative which decomposes at an intermediate temperature than that to the corresponding homopolymer. The effect of the alkyl side chain of the N-alkylitaconamic acid moiety is very interesting because as a general feature the degradation temperature increases as the length of the side chain of the NAIA moiety increases, which would be in agreement with the behaviour of the corresponding PNAIA. On the other hand, these temperatures are higher than in pure polystyrene. Therefore, the insertion of styrene segments on the PNAIA increases the thermal stability of the polymer. In order to get confidence about the degradation process of the polymers studied a kinetic analysis was performed. For this purposes we may consider the decomposition reaction to be irreversible, therefore the degradation rate $d\alpha/dt$ can be expressed as function of the degree of conversion α , according to:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

where k is the specific rate constant and $f(\alpha)$ is a function of the degree of conversion for a single reaction of the type: $A \rightarrow P$ and $f(\alpha)$ can be expressed in the form $f(\alpha) = (1 - \alpha)^n$ where n is the order of the reaction, therefore,

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

where α is the fraction of the sample weight reacted at time t . The specific rate constant is obtained from the Arrhenius relation

$$k = Ze^{-(E_a/RT)} \quad (3)$$

where Z is the frequency factor, E_a the energy of activation, T is the absolute temperature and R the gas constant. From equations (2) and (3) we obtain:

$$\ln \left[\frac{-(d\alpha/dt)}{(1 - \alpha)^n} \right] = \ln Z - \frac{E_a}{RT} = \beta \quad (4)$$

By this way and using a linear multiple regression program it is possible to calculate E_a and Z from a linear least-square fit of the data in a semilogarithmic plot of β against $1/T$. Following this procedure and applying it to PNAI and NAIA-co-S the kinetic parameters for the degradation process were determined. Figure 3 shows as an example the Arrhenius type plots for PNOIA and some copolymers with styrene. Tables 3 and 4 summarize the kinetic parameters values for PNAIA and NAIA-co-S copolymers. It can be observed that two n values are mainly obtained *i.e.*, 0 and 0.5 which are n values frequently found for the degradation process in analogous systems [12,13]. What is noteworthy is the 0.5 order found for the degradation

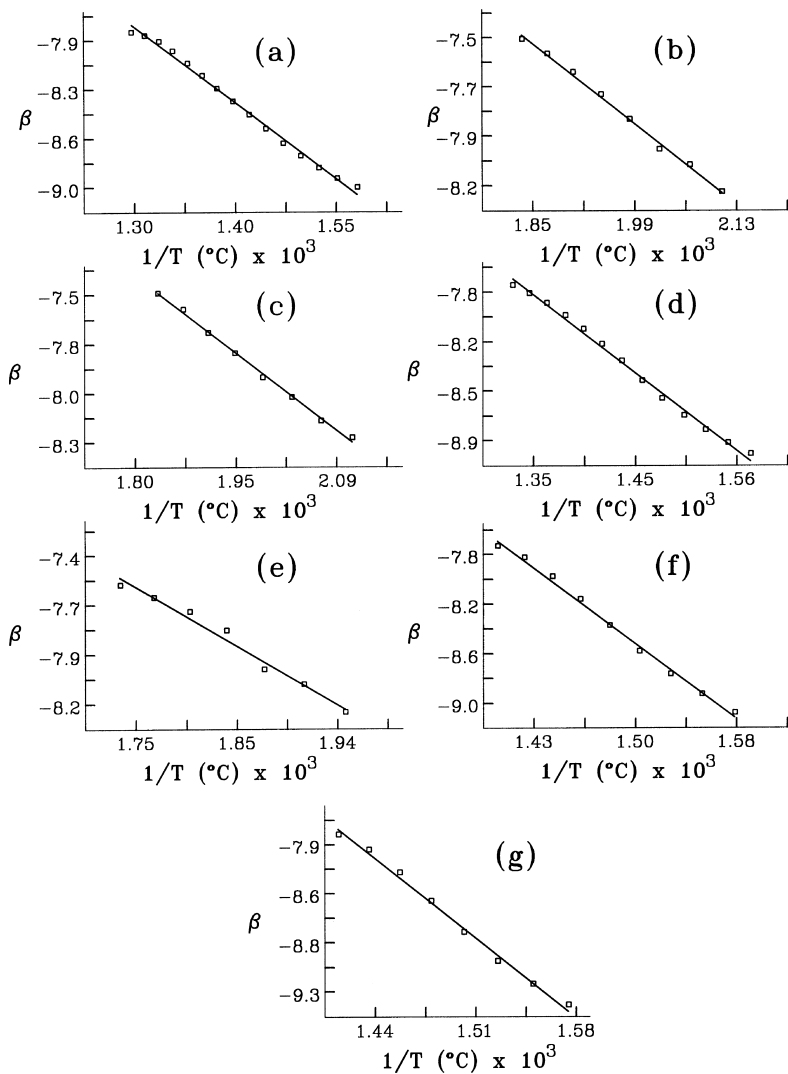


FIGURE 3 Plots of β vs. $1/T$ for PNOIA (a) first step, (b) second step, NOIA-co-S, (c) 80/20 w/w% first step, (d) second step, NOIA-co-S 50/50 w/w%, (e) first step, (f) second step, NOIA-co-S 20/80 w/w%.

process, because this value represents a kind of complex process. On the other hand it is necessary to take into account that all these systems decompose in at least two stages which should be considered as another aspect dealing with the complexity of the process. However,

TABLE 3 Thermogravimetric Kinetic Parameters of the Decomposition Process: Activation Energy E_a , Frequency Factor Z , and Reaction Order n for Poly(N-1-Alkylitaconamic Acids) (PNAIA)

Polymer	E_a (Kcal mol ⁻¹)	Z (s ⁻¹)	n
PNEIA	4.6	2.3×10^{-2}	0
	9.2	2.2×10^{-2}	0
PNPIA	10.6	10.7	0.5
	7.7	7.42×10^{-2}	0
PNBIA	9.9	0.4	0
	12.5	2.9	0.5
PNHIA	5.3	7.0×10^{-2}	0
	9.9	3.1×10^{-1}	0
PNOIA	9.5	0.2	0
	5.2	7.1×10^{-2}	0
PNDIA	6.4	0.1	0
	11.5	0.8	0
PNDoIA	7.8	0.8	0
	12.0	1.9	0

the most common value for n in these systems is 0 which is the most frequently found value for poly(methacrylates) and poly(itaconates) [8,11–13]. The activation energy values found for the degradation process are similar to those reported for other systems [13–18] but no linear correlation with the structure of the repeating unit is observed. Table 4 compiles the thermogravimetric kinetic parameters for copolymers of NAIA-co-S. The activation energy values for the copolymers increases with the increasing of styrene content. The value of E_a for pure poly(styrene) is 44.22 Kcal mol⁻¹ obtained by the same way. This is an expected result because is in agreement with the fact that E_a diminishes as the NAIA content increases because there is a larger probability of degradation, according to the thermogravimetric curves obtained for PNAIA.

CONCLUSIONS

The thermogravimetric behaviour of PNAIA and the copolymers with styrene shows that the thermal stability of the copolymers depends on the structure of the NAIA segment and on the composition of the copolymer. The thermal stability of the homopolymers in general increases as the length of the side chain of the itaconamic acid moiety increases. In the case of copolymers with styrene the relative thermal stability depends on the composition and on the type of substituent in the side chain. The kinetic analysis of the degradation data shows that

TABLE 4 Thermogravimetric Kinetic Parameters of the Decomposition Process: Activation Energy E_a , Frequency Factor Z , and Reaction Order n for Poly(*N*-1-Alkylitaconamic Acids-co-Styrene) Copolymers (NAIA-co-S)

Copolymer	Composition	E_a (Kcal mol ⁻¹)	Z (s ⁻¹)	n
NEIA-co-S	20/80	15.1	1.5×10^{-3}	0.5
		41.4	1.3×10^{10}	0.5
	50/50	19.3	1.0×10^{-5}	0.5
		12.7	4.24	0
	80/20	24.2	1.54	0
		2.2	3.4×10^{-3}	0
7.4	0.46	0.5		
NPIA-co-S	20/80	22.1	4.1×10^{-3}	0
	50/50	9.5	8.1	0.5
		12.5	3.0	0
	80/20	22.3	6.0×10^{-3}	0.5
NBIA-co-S	20/80	18.4	2.3×10^{-2}	0
	50/50	19.0	7.5×10^4	0.5
		25.0	5.2×10^4	0.5
	80/20	8.4	0.13	0
NHIA-co-S	20/80	33.5	8.1×10^{-3}	0
	50/50	27.0	$2. \times 10^5$	0.5
		12.5	1.4×10^2	0.5
	24.7	3.7×10^4	0.5	
NOIA-co-S	20/80	22.1	3.3×10^{-3}	0
	50/50	7.1	0.3	0
		16.0	35.8	0
		5.6	9.6×10^{-2}	0
	80/20	10.0	0.35	0
NDIA-co-S	20/80	20.4	8.9×10^2	0
	50/50	5.0	4.4×10^{-2}	0
		12.8	3.8	0
		4.6	0.7	0
	80/20	8.2	0.1	0
NDoIA-co-S	20/80	20.0	7.2×10^2	0
	50/50	8.0	6.2×10^2	0
		12.0	2.9	0
		4.0	1.2	0
	80/20	8.0	0.7	0

the thermal decomposition of the homopolymers can be described by zero order kinetic model. Copolymers can be described by two different kinetic orders depending on the copolymer and on the composition.

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