

A Kinetic Study of the Polymerization of Aliphatic Imides

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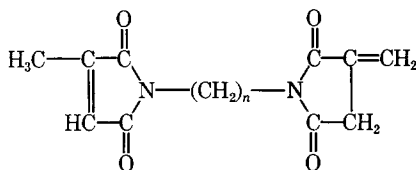
Synopsis

Thermal polymerization of a homologous series of aliphatic poly(methylene) citra-itaconimides was investigated by differential scanning calorimetry. Enthalpic analysis indicated that, at least to a major extent, the conversion reactions followed pseudo-first-order kinetics. A reasonably linear correlation between the number of sequential methylene groups (6, 8, 10, and 12), between the imide ring structures of the monomers, and the activation energy was observed. Reaction rates and initial temperatures of polymerization as well as thermal stability are compared to those of related poly(methylene)-biscitraconimides and -bismaleimides.

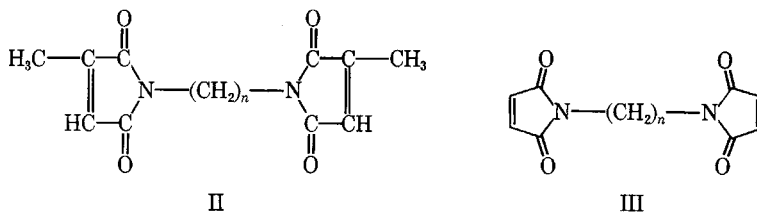
INTRODUCTION

Extensive research effort has been directed toward the development of easily processible and void-free polymeric systems that exhibit exceptional end-use thermal-mechanical properties. To date, some compromise has been required to achieve the best combination of these polymer characteristics. For example, the fully aromatic polyimides prepared by condensation from dianhydrides and diamines possess outstanding mechanical properties at elevated temperatures. However, these polyimides suffer from instability of the intermediate polyamic acid, and, more seriously, evolution of volatiles upon curing which causes voids in the finish product. Alternatively, significant work¹⁻⁶ has been devoted to addition-type imide monomers terminated with maleic derivatives that polymerize without gaseous byproducts. However, since the vinyl groups of maleimides, in general, are not especially reactive, our research has focused upon fully aliphatic addition-type polyimides based upon an itaconic functionality that more readily homopolymerizes. Although some degree of thermal stability is sacrificed, the aliphatic nature of the monomers was selected to enhance the moisture resistance of these polyimides.

Three series of isomeric aliphatic imides have been prepared^{7,8} from the reaction between itaconic anhydride and a homologous group of diamino-alkanes with the general formula $H_2N(CH_2)_nNH_2$, where $n = 6, 8, 10,$ and 12 . This article presents a kinetic study on the polymerization of one series of these compounds, the citra-itaconimides, which have the following general structure:



The structures of two related classes of poly(methylene) monomers, biscitraconimides (II) and bismaleimides (III), are also noted here to permit convenient comparisons:



EXPERIMENTAL

The homologous series of the citra-itaconimide monomers used in this study was prepared as described^{7,8} earlier. The samples were analyzed on a Perkin-Elmer DSC II which was calibrated from 50°C to 160°C with the melting points of high purity indium and naphthalene standards at a heating rate of 10°C/min. The DSC recorder chart area was calibrated in energy units using standard samples weighed to ± 0.0001 mg. Thermogravimetric analysis was conducted on a DuPont 951 Thermogravimetric Analyzer.

The calorimetric data were analyzed using the differential enthalpic method described by Barrett.⁹ At a given temperature, the rate of heat evolved during polymerization is directly related to the rate of polymerization and the reaction in order. For a first-order reaction, the rate expression reduces to

$$k_{(T)} = \frac{dH}{cT} \left(\frac{1}{A - a} \right)_T K$$

where k is the rate constant (s^{-1}), dH/dT is the rate of heat evolution (J/s), $(A - a)$ represents the difference between the total area (A) and the partial area (a) under the enthalpic curve up to a specific temperature (T), and K is the calibration constant with units of area per joule.

RESULTS AND DISCUSSION

Figure 1 presents a typical DSC curve that shows the endothermic melting followed by an exothermic region which represents the total heat of polymerization. The polymerization DSC exotherms for each citra-itaconimide monomer started immediately after the sharp melting endotherm was completed. This behavior of initial polymerization just above the melting point was similarly observed⁷ for the series of the biscitraconimide isomers (II) and has been also reported¹ for bismaleimide monomers (III) as well. The melting points of these related imides shown in Table I reflect the significant differences in initial temperatures of polymerization for the corresponding polymers.

From a structural viewpoint, the conjugation of the exomethylene group outside the ring would be expected to impart the lowest monomer stability for class I monomers as observed. The reactivity difference between classes II and III is attributed to polarity and/or resonance effects upon the radical caused by the electron-donating methyl groups in II relative to the highly electron poor environment of the double bonds in III. Similar effects of methyl substituents

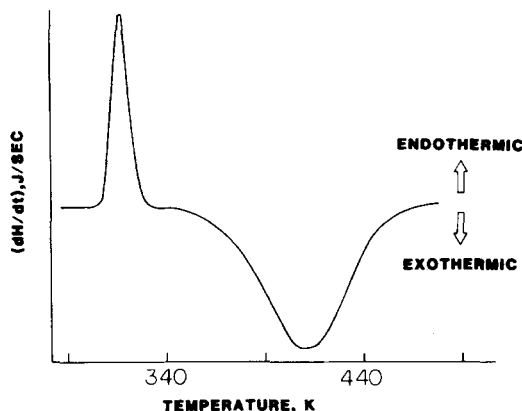


Fig. 1. Typical differential scanning calorimetric curve for $n = 6$ citra-itaconimide.

on vinyl-type monomers with aromatic moieties have been recently noted.³

For the class I monomers studied in this work, the peak temperatures of all the DSC exotherms ranged from 132°C to 152°C, while the temperatures at the end of the exotherms occurred at 183–187°C.

Typical Arrhenius plots are displayed in Figure 2 for the citra-itaconimide monomers with $n = 6, 8, 10,$ and 12 . The linearity of the data indicates that the polymerization reactions follow a pseudo-first-order rate law in accordance with eq. (1). In all the plots, the data represent at least 75% monomer conversion. Depending upon the value of n , the computed rate constants of the compounds varied from 0.011 s^{-1} to 0.082 s^{-1} over the temperature range of 401–449°K. The specific values of the rate constants for the citra-itaconimides are shown in Table II. (Also shown are comparative kinetic data for two bismaleimides with $n = 6$ and $n = 12$ taken from the literature.¹)

The plots in Figure 2 show that the polymerization rates of the monomers decrease as the number of sequential methylene units between the imide rings increases. This behavior may be attributed, in part, to the differences in concentration of the vinyl double bonds as n varies. Higher concentrations of these reactive groups per unit volume would be expected to influence the rate of crosslinking in a positive sense, as was observed. In addition, the number of methylene units in the monomer may also exert a role upon the reaction rates through viscosity and mobility effects within the polymerizing system.²

In comparison with similar aliphatic bismaleimides the rate constants for the analogous ($n = 6$ and $n = 12$) citra-itaconimides are larger by a factor of about 10. Equally important, especially from a standpoint of ease of processing, these

TABLE I
Melting Points of Related Vinyl-Containing Aliphatic Imide Monomers (°C)

p	Citra-itaconimide ⁸ (I)	Biscitraconimide ⁸ (II)	Bismaleimide ¹ (III)
6	72	109	137
8	45	81	—
10	45	61	—
12	40	68	111

TABLE II
Comparative Values of Rate Constants (s^{-1}) for the Polymerization of Various Aliphatic Citra-Itaconimides and Bismaleimides

Temp ($^{\circ}$ K)	401	403	405	409	411	423	425	429	431	435	444	449
<u>Citra-itaconimide</u>												
$n = 6$				0.018				0.045				0.082
$n = 8$	0.017				0.023				0.042			
$n = 10$		0.011				0.020					0.030	
$n = 12$			0.012				0.017			0.021		
<u>Bismaleimide</u>												
$n = 6$	508	513	528	533	548	563						
$n = 12$	0.0022	0.0028	0.0063	0.0053	0.017	0.014						

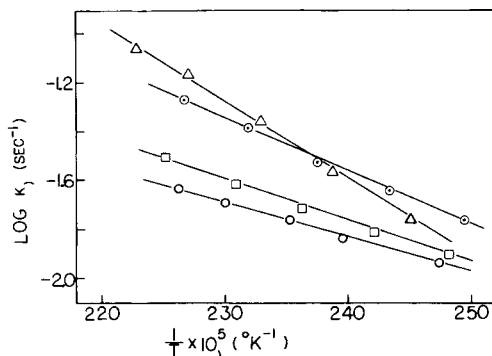


Fig. 2. Arrhenius plots for polymerization at 10°C/min of citra-itaconimides with varying number of methylene groups (n) between the imide rings: (Δ) $n = 6$; (\odot) $n = 8$; (\square) $n = 10$; (\circ) $n = 12$.

higher rates were attained at much lower temperatures than those required to thermally polymerize the bismaleimides.

Activation energies for the thermal polymerization of the aliphatic citra-itaconimides are presented as a function of the number of sequential methylene groups between the imide rings in Figure 3. The collision frequency factor A was computed for each monomer as (s^{-1}) 2.4×10^6 , 6.0×10^4 , 1.1×10^3 , and 1.0×10^2 for compounds where $n = 6, 8, 10$, and 12 , respectively. The values of the activation energies are within the expected order of magnitude (about 80 kJ/mol) while the frequency factors are of reasonable magnitudes for thermally initiated polymerizations especially for the lower n compounds.¹⁰

Samples of the various monomers were cured into polymer films by heating at 175°C for 1 h. In appearance, the films were transparent yellow in color; physically, the films ranged from rigid to flexible as n in the monomeric unit was varied from 6 to 12. The fairly good thermal stability of the polymers was demonstrated by thermogravimetric analysis which showed that the TGA-to-

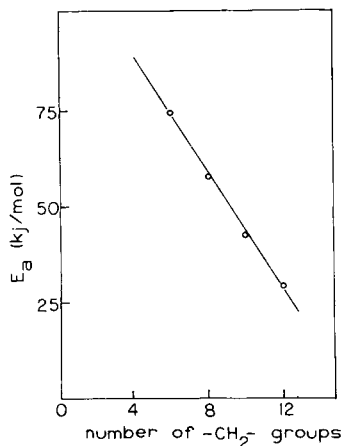


Fig. 3. Activation energy of thermal polymerization of several citra-itaconimides as a function of the number of methylene groups between the imide rings.

break points for these imides were comparable to the 420°C and 455°C reported¹ for $n = 6$ and $n = 12$ bismaleimides:

Citra-itaconimide:	$n = 6$	$n = 8$	$n = 10$	$n = 12$
TGA to break (°C):	430	425	475	440

Weight losses of less than 10% were observed for all the samples at temperatures up to 400°C.

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Received March 11, 1983

Accepted October 12, 1983