Kinetics of Thermal Decomposition of Heterophasic Ethylene-Propylene Copolymers

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KINETICS OF THERMAL DECOMPOSITION OF HETEROPHASIC ETHYLENE–PROPYLENE COPOLYMERS†

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ABSTRACT

Kinetics of thermal decomposition of various heterophasic ethylene–propylene copolymers in the temperature range 215–432°C by thermogravimetry (TG) and 150–180°C by differential scanning calorimetry (DSC), where volatile formation was negligible, was investigated and compared with isotactic polypropylene. Under nitrogen flux the activation energy for decomposition was in the range of 71–89 kcal·mol^{-1} in TG and 42–64 kcal·mol^{-1} in DSC. The thermal stability depends on the copolymer composition. The effect of heating rate on DSC thermograms has been studied.

INTRODUCTION

Isotactic polypropylene is a stiff thermoplastic ($T_g = -9°C$) on account of its ability to crystallize. However, incorporation of ethylene as a comonomer in polypropylene causes a lowering of the glass-transition temperature (-9 to $-60°C$) depending upon the comonomer content. Heterophasic copolymers of ethylene and propylene are a family of commercially important materials containing <16 mol% of ethylene which shows superior low temperature impact properties with a negligible loss of stiffness compared to homopolymers. Structurally, they are a physical

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mixture [1] of a highly crystalline component (<16 mol% ethylene) and a more amorphous fraction (>35 mol% ethylene) formed during polymerization.

The thermal decomposition of polyethylene and polypropylene has been studied extensively [2–6]. Gan et al. [7] and Busico and coworkers [8] studied the ethylene–propylene rubber and random copolymer, respectively, by differential scanning calorimetry (DSC).

Less attention has been paid to aspects of thermal decomposition of ethylene–propylene heterophasic copolymers. The emerging commercial significance of heterophasic ethylene–propylene copolymers containing less than 16 mol% ethylene prompted us to examine this system. In the present paper we report the thermal decomposition of such copolymers and their comparison with isotactic polypropylene.

EXPERIMENTAL

Samples used in this study were commercial materials. Isotactic polypropylene (Koylene S 3030, MI = 3.0 sample I) was obtained from Indian Petrochemical Corporation, Baroda, India, and ethylene–propylene heterophasic copolymers (EPQ 30R, MI = 0.6–0.9 sample II and EPF 30R, MI = 13.0 sample III) were from Himont, Italy. The copolymers had a nominal ethylene content [9, 10] of 15.1 and 12.0 mol% for EPQ 30R and EPF 30R, respectively.

The pellets were purified to remove processing antioxidants by dissolving in xylene at 137°C under nitrogen atmosphere and precipitating with methanol. The polymer was dried under vacuum at 50°C. The copolymer was further heated for 1 hour at 137°C with xylene under nitrogen. The xylene solution was cooled to 30°C, and the xylene-insoluble portion (fraction A) was filtered and dried under vacuum. The xylene-soluble portion (fraction B) was recovered by precipitation with acetone and dried under vacuum. The ethylene content in the two fractions was cross-checked by ^{13}C-NMR spectroscopy [11]. Fractions A and B together generally accounted for more than 95.0% of the original weight of the polymer taken.

Thermal analysis of the polymer samples was carried out by using a Netzsch Thermal Analyser STA 409 and a differential scanning calorimetry (Perkin-Elmer DSC-2). Thermogravimetry (TG) was performed in the temperature range of 25–900°C at 10°C/min, and DSC was determined at different rates (5 to 40°C/min) from 50 to 250°C in a nitrogen atmosphere. The peak maximum from the DSC melting endotherm was considered to be the melting temperature (T_m).

RESULTS AND DISCUSSION

The thermal decomposition data were treated for kinetic parameters according to the method of Reich [2, 5] and Madorsky [12]. These methods are generally limited to processes involving a single decomposition rate wherein the primary products of decomposition are stable.

The thermogravimetric curves of the copolymer samples (i-PP = I; EPQ 30R = II, II$_A$, II$_B$; and EPF 30R = III, III$_A$, and III$_B$) are shown in Figs. 1 and 2. For copolymer II, weight loss begins at 200°C whereas it starts at 280°C for III. The
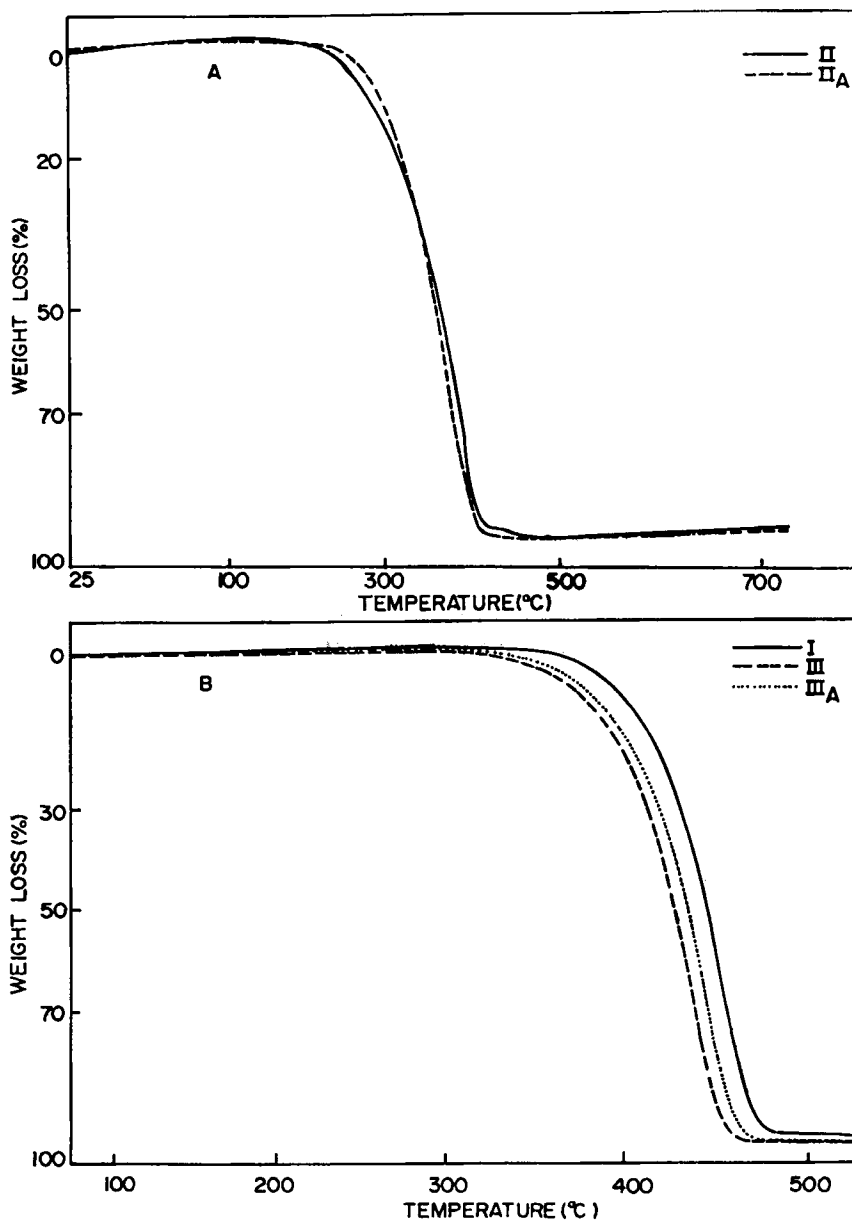
FIG. 1.   Thermogravimetry curves of E-P copolymers in air. A: EPQ 30R (II), EPQ 30R fraction A (II$_A$). B: i-PP (I), EPF 30R (III), EPF 30R fraction A (III$_A$).
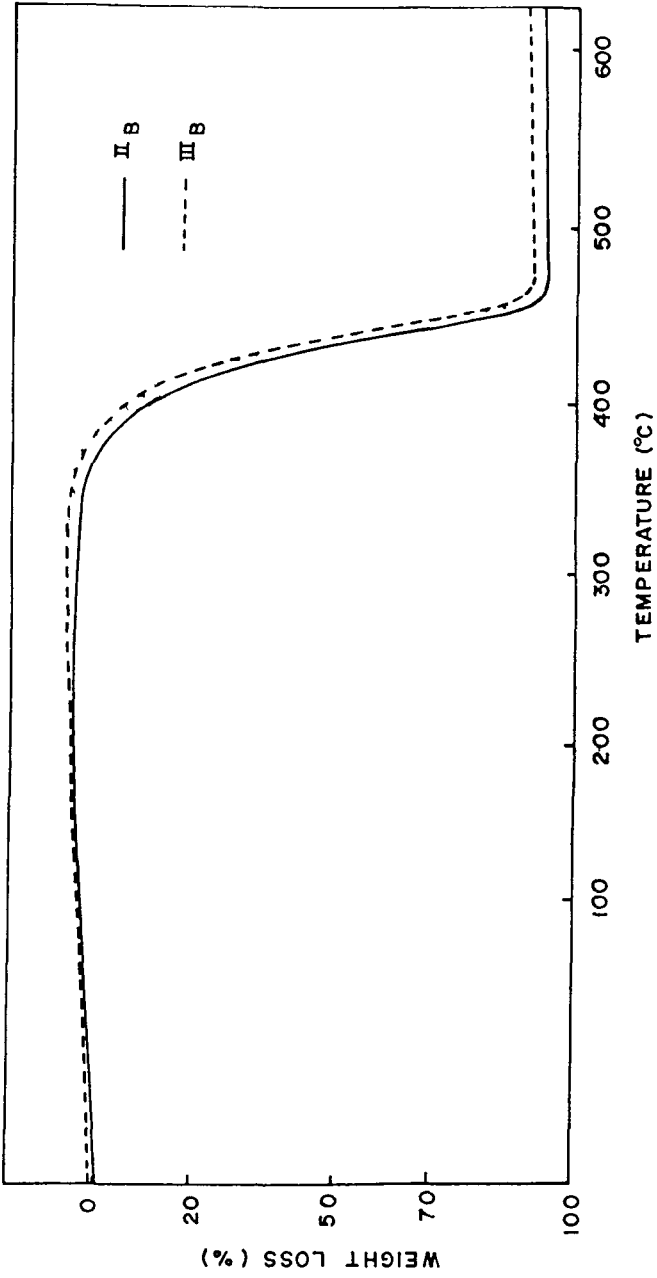
FIG. 2.   Thermogravimetric curves of E-P elastomeric fractions in air: EPQ 30R fraction B (II$_B$), EPF 30R fraction B (III$_B$).

TABLE 1. Thermal Properties of Polypropylene Homo- and Copolymers

Sample code	Ethylene content, mol%	IDT, °C	T_{max}, °C	IPDT, °C	Weight loss				
					10°C	20°C	30°C	40° C	50°C
I	—	320	425	454	403	412	421	429	434
II	15.1	200	424	396	288	318	345	355	366
II$_A$	7.7	217	428	398	307	376	353	361	371
II$_B$	40.9	328	440	466	402	410	418	424	429
III	12.0	280	435	447	387	403	410	416	421
III$_A$	6.2	290	438	449	392	403	410	419	424
III$_B$	55.7	343	445	472	408	419	429	426	432

same pattern of weight loss is followed in II$_A$, II$_B$, III$_A$, and III$_B$. However, the residue at 435°C is similar in all cases (4–6%). The initial decomposition temperature (IDT), the maximum decomposition temperature (T_{max}), and the 10 to 50 wt% (weight loss in percent) decomposition temperature (T_{10}–T_{50}) were read from the TG curves. The integral procedural decomposition temperatures (IPDT) were calculated from the normalized curves (with respect to residual weight) using Doyle's equation [13]:

$$T^* = 875A^* + 25 \tag{1}$$

where T^* represents IPDT and A^* is the total area under the normalized curves from 25 to 900°C. The values are given in Table 1. In case of copolymers, the values of IDT, T_{max}, IPDT, and T_{50} for xylene insoluble (II$_A$ and III$_A$) and soluble (II$_B$ and III$_B$) fractions are uniformly higher than for the neat copolymers (II and III). This implies that incorporation of larger proportions of ethylene in lower ethylene content (<16 mol%) copolymers decreases marginally thermal stability (i.e., II, II$_A$, III, and III$_B$), but in higher ethylene content (40 mol%) copolymers (II$_B$ and III$_B$) the stability increases with ethylene content.

TABLE 2. Kinetic Parameters ΔE and n from TG Curves in Nitrogen

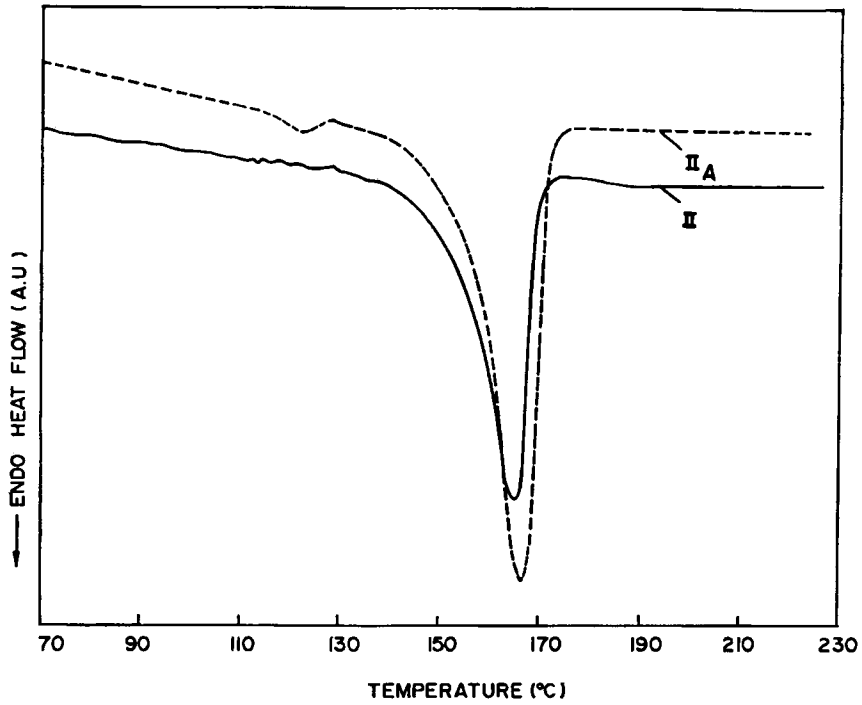| Sample	1–10% Conversion range		10–50% Conversion range	
	ΔE, kcal·mol^{-1}	n	ΔE, kcal·mol^{-1}	n
I	61	0.72	83	1.03
II	42	0.94	71	1.14
II$_A$	48	0.88	73	1.11
II$_B$	63	0.76	86	1.00
III	51	0.78	76	1.08
III$_A$	53	0.74	80	1.06
III$_B$	65	0.68	89	0.98

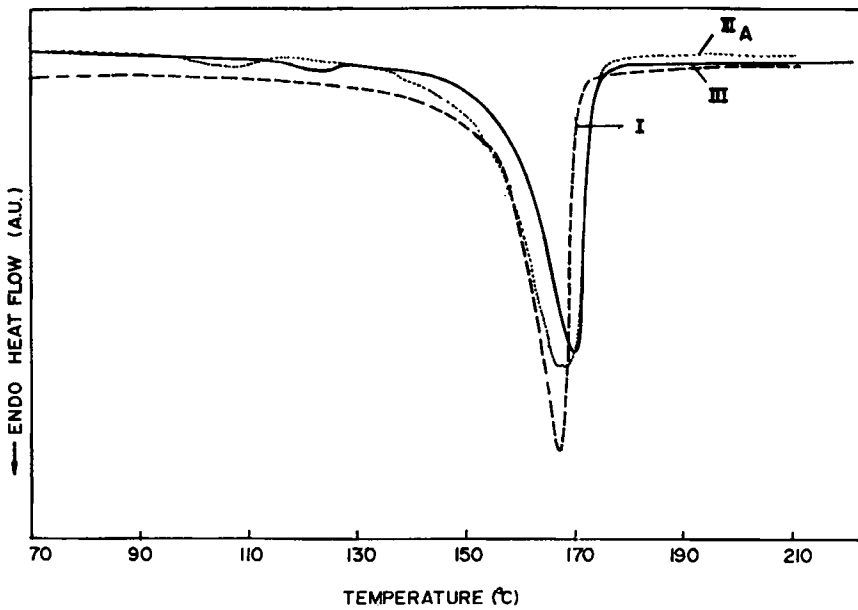FIG. 3.   DSC thermograms of II and II$_A$.
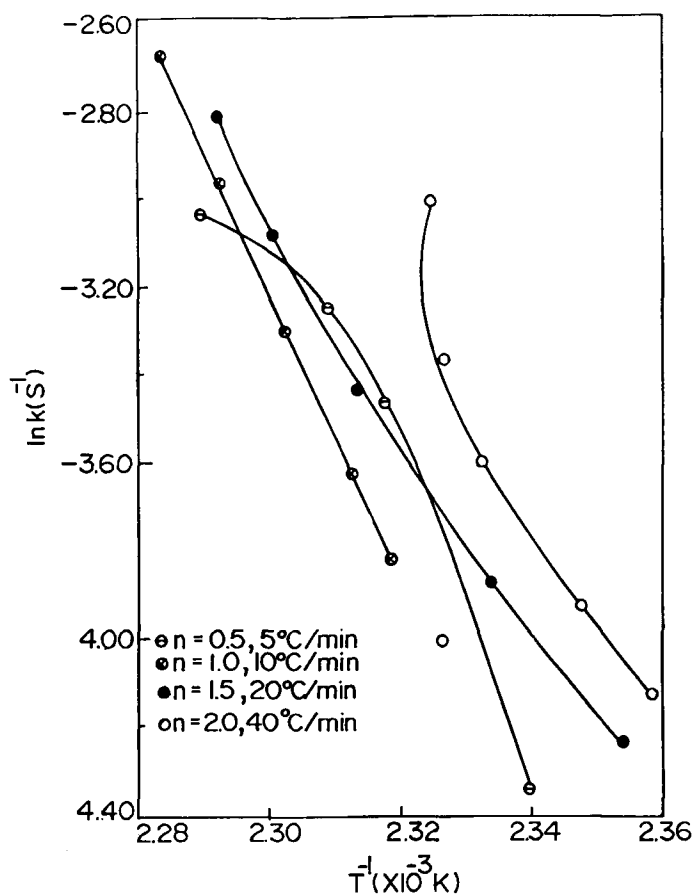

FIG. 4.   DSC thermograms of I, III, and III$_A$.

FIG. 5. Plot of log k_1 as a function of $1/T$ in I.

The thermal decomposition of E-P copolymers follows a complex process in which the maximum weight loss occurs between 215 and 450°C. All the volatiles are evolved after a prolonged heating of ~3 hours at 215°C, where the weight loss is ~1%. Subsequent to the evolution of volatile products (>150°C), the thermal methods of analysis are limited to kinetically simple processes with respect to a single process occurring at one time over a temperature range from 215 to 450°C, and the decomposition [14, 15] is only revealed by a decrease in molecular weight. Above this temperature range the polyolefins become a residue and the decomposition products are stable. Hence, the possibility of consecutive reactions is eliminated and thermal studies remain uncomplicated. In order to understand the mechanism of decomposition, the kinetic parameters have been evolved using the method of Anderson and Freeman [16]:

$$\log \ (-dw/dt) \ = \ n\Delta\log \ W_r \ - \ (\Delta E/2.303R)\Delta(1/T) \tag{2}$$

where dw/dt is the rate of reaction, n is the order of reaction, ΔE is the activation energy, R is the gas constant, T is the absolute temperature, and $W_r \ = \ \Delta W_c \ -$
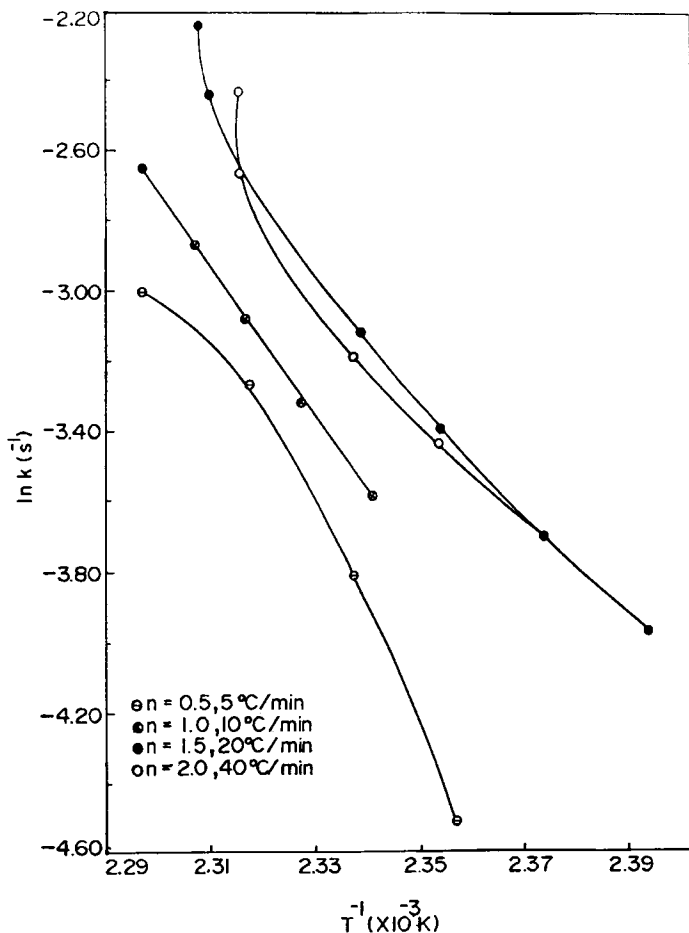
FIG. 6.   Plot of log k_1 as a function of $1/T$ in II.

ΔW. ΔW is the weight loss at the point where dw/dt is taken, and ΔW_c is the total weight loss associated with a given reaction. The slope of the plot $\Delta \log (dw/dt)$ versus $\Delta \log W_r$ gives n, and the intercept on the ordinate gives ΔE when $\Delta 1/T$ is kept constant.

In order to overcome the shortcomings of overall decomposition, we estimated these parameters at 1–10% and 10–50% conversion to separate the overall decomposition into initiation and main chain decomposition. In 1–10% conversion the reaction order is 0.68 to 0.94 with a ΔE in the range of 42 to 65 kcal·mol^{-1} (Table 2). The initial decomposition (1–10%) with a low ΔE may be due to scission of branched chains or end chain cleavage since these require less energy for bond rupture. Thus, the initial degradation would have less effect on the molecular weight of the polymers. In the region of 10 to 50% conversion (temperature range 350–429°C), there appears a transition in the order from fractional to first order. The
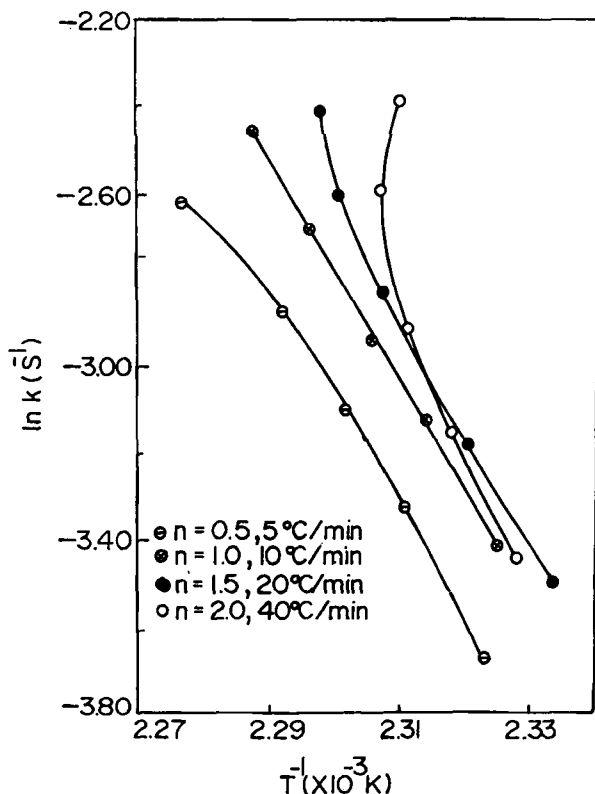
FIG. 7.   Plot of log k_1 as a function of $1/T$ in II_A.

weight loss is observed to be faster in this region, showing that large carbon chain molecules are being decomposed. The conversion from 10–50% is first order ($n =$ 0.98 to 1.14) with ΔE in the range of 71 to 89 kcal·mol^{-1} (Table 2), which may be attributed to random scission of $C-C$ bonds. Moreover, the general shapes of the TG traces are sigmoid, typically quite characteristic of a chain-branching process.

The kinetic parameters depend on the copolymer composition. For copolymers II, II_A, III, and III_A, which have a low ethylene content, higher values of ΔE were obtained. However, in the cases of II_B and III_B, ΔE increases with higher ethylene content. This trend is similar to that observed for IPDT results.

DSC thermograms of II, III, and their fractions II_A and III_A in nitrogen are shown in Figs. 3 and 4. The thermogram of i-PP is also given in Fig. 4. A sharp endotherm was observed at 167°C, the melting temperature of the respective samples in all cases. The rate constant for the overall decomposition in DSC was calculated from the equation [17]

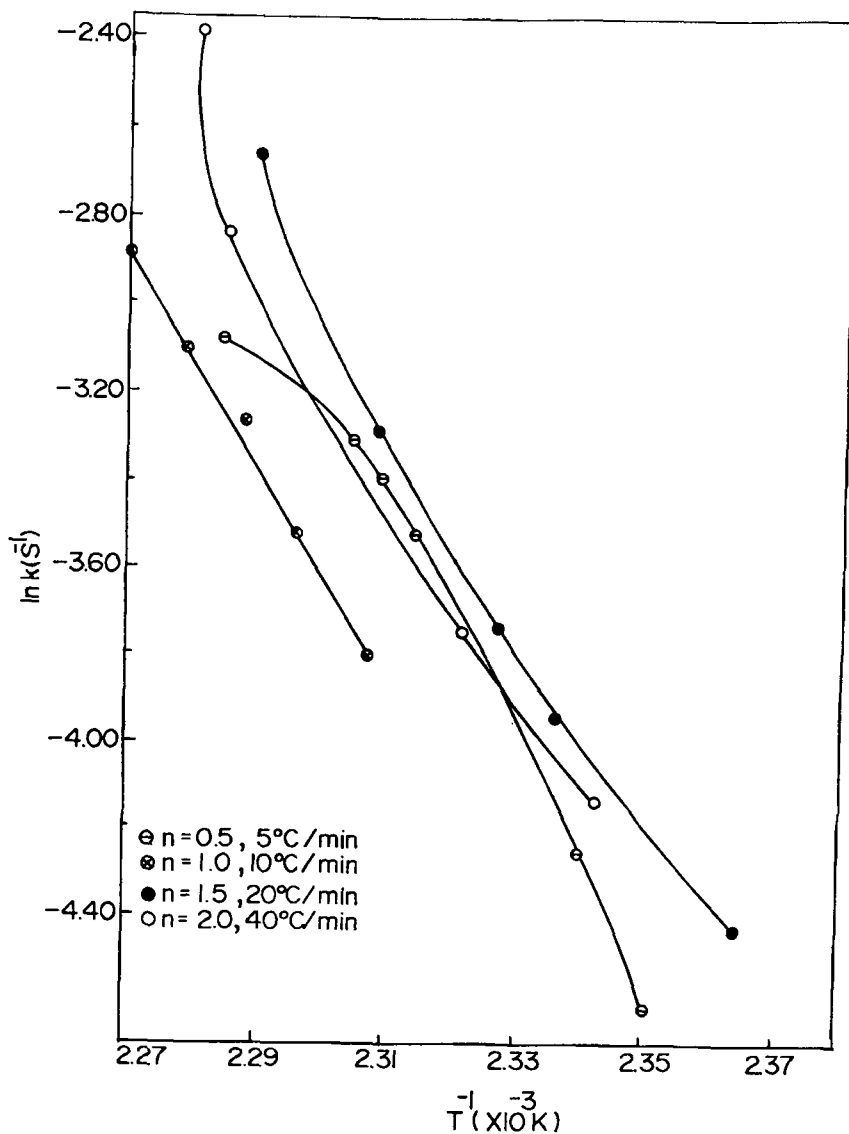$$R = \frac{H^{n-1}dH/dt}{(\Delta H - H_p)^n} \tag{3}$$

FIG. 8.   Plot of log k_l as a function of $1/T$ in III.

where R = rate constant which represents the fraction of reactant decomposed
per unit time at constant concentration

dH/dt = height of ordinate at a given temperature

H_p = partial heat change

ΔH = net heat change

n = order of reaction which gives the number of atoms or molecules whose
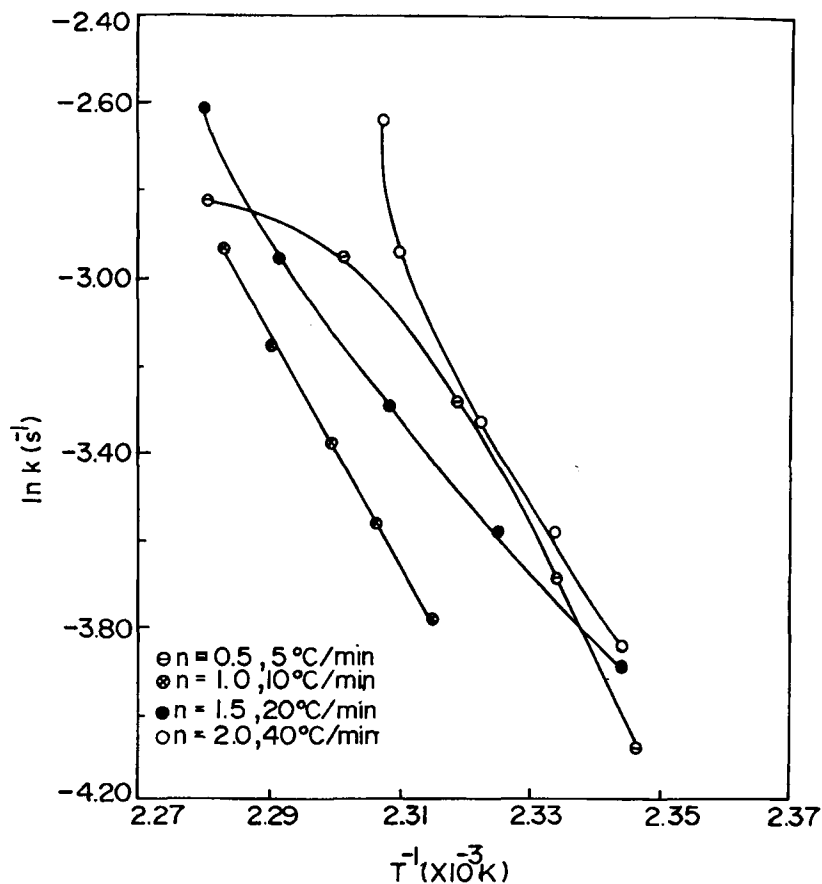concentration changes during the chemical change

FIG. 9. Plot of log k_1 as a function of $1/T$ in III_A.

Conversions at the peak maxima varied with the heating range. To overcome this difficulty, various values of n from 0.5 to 2.0 for heating rates from 5 to 40°C/min were substituted, and the best linear regression fits for the experimental data were obtained (Figs. 5–9). In all cases the best fit of log k versus $1/T$ for the experimental data was observed at a heating rate of 10°C/min for $n = 1.0$. This indicates that the reaction is first order and the conversion depends upon the concentration of only a single reactant. Such a treatment has been widely applied to analyze the random decomposition of high polymers [18].

The rate of heating determines the reaction order. In the DSC thermograms the reaction order varies from 0.5 to 2.0 for a heating rate from 5 to 40°C/min, respectively. The values of n for different heating rates are given in Figs. 5–9, while values of entropy (ΔS), enthalpy (ΔH_m), and ΔE of decomposition for a heating rate of 10°C/min are listed in Table 3, The value of ΔH_m is almost constant, suggesting that the mechanism of decomposition is similar in all cases.

The low ΔE values (42.7–64.2 kcal/mol) for DSC curves are due to the low temperature range (melting range 150–180°C). Moreover, these observations depend very much on the method and technique of measurements [19].

TABLE 3.   Changes in Activation Energies (ΔE), entropies (ΔS_m), and Enthalpies (ΔH_m) in DSC Thermograms of E-P Copolymers at 10°C/minute in a Nitrogen Atmosphere

Sample	T_m, °C	ΔE, kcal/mol	ΔS_m, cal/deg/mol	ΔH_m, kcal/mol
I	166.5	64.2	6.57	1.09
II	165.6	42.7	5.06	0.84
II$_A$	166.7	49.7	6.04	1.01
III	169.4	51.7	6.32	1.06
III$_A$	168.8	53.7	6.02	1.02

Finally, these methods yield kinetic parameters that, in a strict sense, are only apparent activation energies because the data are not derived from changes in the concentrations of reactants and products. This information is generally obtained in parallel studies where volatile products are monitored quantitatively by gas chromatography and mass spectroscopy [20, 21].

Differences in thermal stabilities among the E-P copolymers and their fractions are apparent from Tables 1-3. Based on TG and DSC results, the following thermal stability order can be perceived for the polymers studied:

$$III_B > II_B > I > III_A > III > II_A > II$$

The superior thermal stabilities of III$_B$ and II$_B$ may be attributed to the lower propylene content in the polymer. They are elastomeric copolymers having low degrees of crystallinity (3 to 5%). Polymer fractions III$_A$ and II$_A$, which have low ethylene contents (and hence higher degrees of crystallinity), show marginally better thermal stabilities than do the corresponding whole, unextracted polymers III and II. The lower thermal stabilities of the whole polymers (fractions A and B) are somewhat puzzling in view of the observation that fraction B has a higher thermal stability than fraction A. This could be due either to some transition metal catalyst residues or low molecular weight oligomers present in the whole polymer which were eliminated during the extraction step.

ACKNOWLEDGMENTS

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