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Non-Isothermal Kinetics and Thermodynamics of Solid State Decomposition of Polyethylene

P. VARSHNEY* and V. KUMAR
Department of Chemistry, Govind Ballabh Pant University of
Agriculture and Technology, Pantnagar-263 145, India
E-mail: bsv1952@yahoo.co.in

Non-isothermal kinetics and thermodynamics of solid-state decomposition of low density polyethylene (LDPE) and high density polyethylene (HDPE) has been investigated through simultaneous thermogravimetric-differential thermal analysis-differential thermo gravimetric [TG-DTG-DSC] under nitrogen atmosphere. Thermal data deduced was used for calculations of thermodynamic parameters through Horowitz-Metzger and Coats-Redfern methods along with kinetics and mechanism of degradations according to the method of Sestak, Berggren and Satava.

Key Words: Polyethylene, Non-isothermal kinetics, Thermodynamics, TG-DTG-DSC.

INTRODUCTION

The studies on kinetics and thermodynamics of solid state decomposition of polymers play integral role in their quality control and assessment[1,2]. Among a variety of thermoanalytical methods, the application of thermogravimetric-differential thermal analysis and differential scanning caloriemetry has recently emerged as a rapid and cost effective substitute over other analytical methods with reproducible results[3,4]. Most of the modern chemical and metallurgical industries employ process involving solid-state gas-solid interface reactions. A detailed knowledge of the thermodynamics, kinetics and reaction mechanisms of these thermally induced processes is of immense help to optimize and control the operating parameters leading to design of proper process equipment. Thermal analysis techniques like thermogravimetry (TG), differential scanning colorimetry (DSC) *etc.*, where the property of a substance measured, as a function of temperature is extremely useful in this context[5]. In addition, if real time analysis of the product gases evolved during a thermally induced reaction will greatly enhance the possibility of correctly interpreting the kinetic data and arriving at most appropriate mechanism governing the process. Thus, knowledge of single particle kinetics becomes a pre-requisite for studying interface transport phenomena between moving gas stream and porous of solid materials[6]. Such single particle kinetics can be easily studied through simultaneous TG-DTG-DSC, The technique TG-DTG-DSC is frequently used as a means of assessing the thermal stability and conveniently provide valuable information about kinetics and thermodynamics of the solid state decompositions of polymers and related heat resistant materials[5,6].

EXPERIMENTAL

The thermoplastic materials such as low density polyethylene (LDPE) and high density polyethylene (HDPE) were purchased from Sigma-Aldrich, USA. Their physical characteristics have been summarized in Table-1.

TABLE-1
PHYSICAL PROPERTIES OF LOW AND HIGH DENSITY POLYETHYLENE

Compound	Molecular weight (mw)g/mol	Density	Melt index	T_m (°C)	T_g (°C)	DTG peak (°C)
LDPE	–	0.9229g/mL at 25 °C	[(ASTMD 1238, 190 °C/2.16 kg) 1.5g/10 min)]	115	-125	413
HDPE	*ca.* 1,25,000	0.95 g/mL at 25 °C	[(ASTMD 1238, 190 °C/2.16 kg) 2.2g/10 min)]	120	-30	406

Thermal analysis: A simultaneous thermogravimetric (TG) differential thermo gravimetric (DTG) differential scanning calorimetry (DSC) of each of the polyethylene samples has been performed over Perkin Elmer (Pyris Diamond) thermal analyzer model STA 409. The sample amount ranged from 11.8 to 12.79 mg. The samples were allowed to decompose in air at heating rate of 10 °C/min. using alumina as a reference. All such thermoanalytical procedure were executed at Analytical Section, Institute Instrumentation Centre, Indian Institute of Technology, Roorkee.

Interpretation of thermal data: Thermogravimetric (TG) data of each of the polymers were evaluated for their weight loss (%) with reference to temperature. The decomposition stages involved and kinetic parameters with reference to their order (n) and energy of activation of thermal degradation (E), entropy change (ΔS) was evaluated through a series of calculation procedures such as Horowitz-Metzger method[7] and Coats-Redfern method[8] [Table-3(a-b)]. Thermal properties and thermodynamic data of solid state decomposition of polymers evaluated are summarized [Table-2(a-b)]. DSC data were used to evaluate a series of temperature profile of the polymers during their decomposition. The selected DSC data were assigned as glass transition temperature (T_g), oxidation temperature (T_{ox}), crystallization temperature (T_c) and decomposition temperature (T_d), respectively [Table-2(c)].

Non-isothermal kinetics of solid-state decomposition of samples has been calculated from TG data to ascertain the rate controlling process according to the procedure reported by Sestak and Berggren and Satava[9]. Non-isothermal kinetics of solid-state decompositions of the selected polymers were evaluated from different integral forms of kinetic expressions and the declaring rate equation based on diffusion was studied in terms of parabolic law satisfied to one dimensional transport (D_1), two dimensional diffusion (D_2), three dimensional diffusion according to Jander equation (D_3) and three dimensional diffusion according to Ginstling-Brounshtein equation (D_4) and the rate laws at one dimensional, zero order, two dimensional; cylindrical symmetry (R_2) and three dimensional spherical symmetry (R_3) [Table-4].

TABLE-2
THERMAL PROPERTIES OF LDPE AND HDPE

(a) TG Profile

Thermal properties	Temperature (°C)	Weight residue (°C/%)	
		LDPE	HDPE
TG [Weight residue (%)/°C]	200	99.80	99.70
	300	95.80	98.70
	400	45.80	48.54
	500	3.120	1.130
	600	0.000	1.360

(b) DTG Profile

Thermal properties	Peak	LDPE	HDPE
DTG[°C/ %/ min]	Broad	382 (20)	–
	Sharp	413 (23)	406 (29)

(c) DSC Profile

Thermal properties	LDPE	HDPE
T_g (°C) [ΔH/mJ/mg]	109 [31.3]	129 [125]
T_m (°C) [ΔH/mJ/mg]	–	256 [–260]
T_{ox} (°C)	385	408
T_d (°C) [ΔH/mJ/mg]	416 [–2795]	422 [–2539], 490 [–239]

TABLE-3(a)
KINETIC AND THERMODYNAMIC DATA OF SOLID STATE DECOMPOSITION OF LDPE

Reaction order (n)	Method	E (kg/mol × 10^3)	Z (min^{-1})	ΔS(JK^{-1}/min)
0	Coats-Redfern	49.70	6.83	-14.54
	Horowitz and Metzger	83.86	7.17	-13.77
1	Coats-Redfern	58.40	3.36	-22.49
	Horowitz and Metzger	105.61	8.92	-9.720
2	Coats-Redfern	81.74	6.16	-16.05
	Horowitz and Metzger	149.22	12.40	-1.720

TABLE-3(b)
KINETIC AND THERMODYNAMIC DATA OF SOLID STATE DECOMPOSITION OF HDPE

Reaction order (n)	Method	E (kg/mol × 10^3)	Z (min^{-1})	ΔS(JK^{-1}/min)
0	Coats-Redfern	62.71	3.63	-21.89
	Horowitz and Metzger	84.85	7.32	-13.40
1	Coats-Redfern	79.63	4.22	-20.54
	Horowitz and Metzger	109.81	9.36	-8.720
2	Coats-Redfern	116.04	8.86	-9.730
	Horowitz and Metzger	160.75	13.44	-1.690

TABLE-4
MECHANISM OF SOLID STATE DECOMPOSITION VERIFIED FOR LDPE/HDPE

D_1	$\alpha^2 = kt$	1-Dimensional diffusion (Parabolic law)
D_2	$(1 - \alpha)[-\ln(1 - \alpha)] + \alpha = kt$	2-Dimensional diffusion, cylindrical symmetry
D_3	$[1 - (1 - \alpha)^{1/3}]^2 = kt$	3-Dimensional diffusion, spherical symmetry (Jander equation)
D_4	$(1 - 2 - \alpha/3 - (1 - \alpha)^{2/3} = kt$	3-Dimensional diffusion, spherical symmetry (Giastiling Brownshtein equation)
F_1	$-\ln(1 - \alpha) = kt$	Random nucleation; One nucleus on each particle (Mampel equation)
A_2	$[-\ln(1 - \alpha)]^{1/2} = kt$	Random nucleation (Avrami equation I)
A_3	$[-\ln(1-\alpha)]^{1/3} = kt$	Random nucleation (Avrami equation II)
R_2	$1 - (1 - \alpha)^{1/2} = kt$	Phase boundary reaction; cylindrical symmetry
R_3	$1 - (1 - \alpha)^{1/3} = kt$	Phase boundary reaction; spherical symmetry

RESULTS AND DISCUSSION

The study of non-isothermal kinetics and thermodynamics of solid state decomposition has recently played significant role in the evaluation of quality control and thermal properties of a wide range of materials including pharmaceuticals and polymers. In this context, study of the non-isothermal kinetics and thermodynamics of degradation of polymers has been of great interest since past few years. Realizing the need of investigation of appropriate kinetic profiles, the nature of thermal degradation and related thermodynamic parameters, the present investigation has been made and directed towards the study of polyethylene and its selected derivatives of great commercial potentials with particular emphasis to LDPE and HDPE. The non-isothermal kinetic, thermodynamic parameters and various models related to the mechanism of thermal degradation of the thermoplastic materials have been investigated through evaluating their thermal data from simultaneous TG-DTG-DSC and the data were compared.

Thermogravimetry: Thermogravimetric data of the investigated polymers are summarized in [Table-2(a)]. A significant variation in thermal profiles of all the polymers was observed in their respective TG with particular emphasis to their initial decomposition temperature, final decomposition temperature, char yields and the number of steps involved in thermal decomposition.

Low density polyethylene has shown two step decompositions. Each of the decomposition steps in LDPE was associated with broad range of weight losses. The initial decomposition of LDPE was observed at 234 ºC with 99.65 % weight residue. A slight weight loss (0.35 %) associated at this temperature may be due to the residual moisture content and binders added during the processing of the polymer. Low density polyethylene has started decomposition corresponding to first stage at 356 ºC with weight residue 89.9 %. This polymer has shown subsequent decomposition corresponding to second stage at 391 ºC with weight residue 53.09 %. This polymer has shown a weak TG profile at 409 ºC with weight residue 31.68 % and final decomposition at 427 ºC with char yield 8.51 % and complete volatilization at 543 ºC. [Fig. 1 (a)].

High density polyethylene has shown decomposition in two different stages. Initial decomposition of HDPE was started at 242 ºC with weight residue 99.68 %. Before this temperature a slight weight loss shown by HDPE may be due to moisture and binder content. The decomposition steps of HDPE were associated with broad range of weight loss. The first stage decomposition of HDPE was observed at 366 ºC with weight residue 87.12 %. This polymer has shown a weak TG profile at 399 ºC with weight residue 66.73 % and has shown a subsequent decomposition corresponding to second stage at 412 ºC with weight residue 39.28 %. This polymer has shown final decomposition at 428 ºC with char yield 7.80 % and complete volatilization at 505 ºC [Fig. 1(b)].

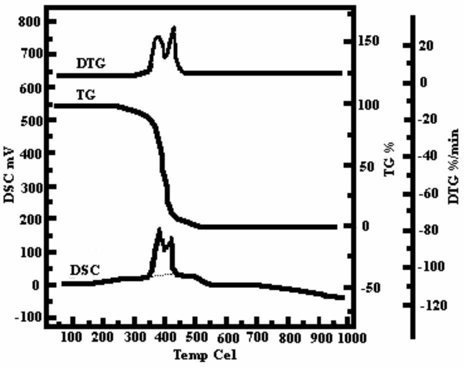

Fig. 1(a). DSC-DTG-TG scan of LDPE

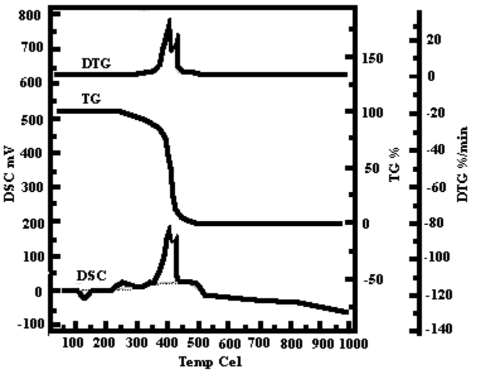

Fig. 1(b). DSC-DTG-TG scan of HDPE

Thermal decomposition of polymers was further investigated at selected temperatures and the data are summarized in [Table-2(a)]. All such polymers have shown weight residue (%) ranging 99.8-100 indicating their resistance against thermal decomposition at 200 ºC. A comparative account of thermal data at 300 ºC, indicate that LDPE has shown highest decomposition rate followed by HDPE.

Differential thermogravimetry: Differential thermogravimetric data of the investigated polymers are summarized in [Table-2(b)]. Low density polyethylene has shown three DTG profiles at 382 ºC with decomposition rate 20 %/min. With further increase in temperature, this polymer has shown a sharp profile at 413 ºC with decomposition rate 23 %/min and a weak profile at 501 ºC with decomposition rate 1.0 %/min. These observations indicate that decomposition of LDPE was at maximum rates at second stage decomposition in TG.

Effect of density on thermal stability of polyethylene was investigated through studying the thermal profiles of HDPE and LDPE. High density polyethylene has shown three DTG profiles supported with TG. This polymer has shown a sharp DTG profile at 406 ºC with decomposition rate 29 %/min and relatively weak profile at 420 ºC with decomposition rate 18 %/min. With further increase in temperature, a weak DTG profile was shown by HDPE at 487 ºC at the decomposition rate 1 %/min. These observations indicate that HDPE was decomposed with maximum rate at first stage decomposition, followed by second stage decomposition in TG.

Differential scanning calorimetry: A regular variation in DSC profiles of the polymers has been observed with variation in density of samples. Low density polyethylene has shown lowest T_g (109 ºC), followed by HDPE . These observations clearly indicate that the gas transition temperature of the polymers investigated was greatly influenced by their density. In general, T_g was increased with density of polymers.

Due to the high amorphous character of LDPE, this has rendered no sharp DSC endotherm corresponding to their melting points. Increase in density of LDPE to HDPE, the later has rendered a sharp melting point at 256 ºC with heat of melting -260 mJ/mg.

Low density polyethylene has shown a broad DSC exotherm corresponding to oxidation and decomposition at 385 and 416 ºC, respectively. The DSC profiles have shown common heat of decomposition at -2795 mJ/mg. High density polyethylene has shown DSC exotherm at 408 and 422 ºC with corresponding heat of transition at -2539 mJ/mg. High density polyethylene has also shown a weak DSC profile at 490 ºC with heat of decomposition -239 mJ/mg. 676 mJ/mg [Table-2(c)].

Order of decomposition: Thermogravimetric thermograms of thermoplastic polymers such LDPE and HDPE have been evaluated to investigate their non-isothermal kinetic of solid-state decomposition. The kinetic of each of the materials has been investigated as the variation of T^{-1} (K) with log g(α) functions. Each of evaluations were made at the orders of n = 0, 1 and 2, respectively. These data were deduced by applying Coats-Redfern method and Horowitz-Metzger method, respectively.

Coats-Redfern method: Coats-Redfern data of the various polymers under investigation in terms of their log g(α) were obtained from the respective kinetic equations for permissible order of decompositions and studied graphically [Figs. 2(a-b)]. In this context, the degradation temperature for LDPE under investigation was in the range of [$1/T \times 10^{-3}$] 2.445 to 1.226. This has shown corresponding Coats and Redfern data ranging -4.201 to -0.988 for n = 0, -8.909 to -5.033 for n = 1 and -9.543 to -4.009 for n = 2. High density polyethylene was investigated at ($1/T \times 10^{-3}$) ranging 1.942-1.285. This has provided log g(α) ranging -7.726 to -5.463 for n = 0, -7.896 to -4.988 for n = 1 and -8.278 to -4.088 for n = 2.

Horowitz and Metzger method: The kinetics and thermodynamics of solid state decomposition under non-isothermal condition was further investigated through Horowitz-Metzger method. The data evaluated from Horowitz-Metzger equation at various reaction order of decomposition in terms of their log g(α) against T^{-1}(K) and studied graphically [Figs. 3(a)-3(b)].

In this context, the degradation temperature for LDPE was in the range of [$1/T \times 10^{-3}$] 2.445 to 1.225. The permissibility of log (α) at n = 0 was found to be –3.046 to 0.742, at n = 1. It was -3.287 to 1.332 and at n = 2 it was -4.008 to 2.786. Data evaluated from Horowitz-Metzger method for HDPE having at reaction order of n = 0, 1 and 2, respectively and T^{-1} (K) in the range of 1.941 to 1.285×10^{-3}. This has provided log g(α) ranging -2.117 to 0.448 for n = 0, -2.281 to 0.099 for n = 1 and -2.669 to 0.057 for n = 2.

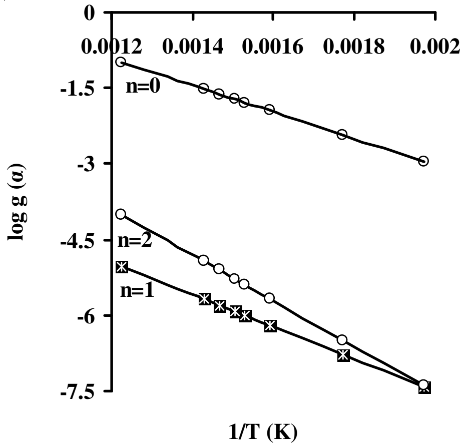

Fig. 2(a). CR Thermogram of LDPE

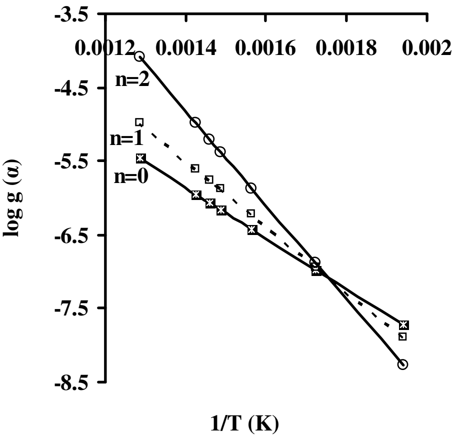

Fig. 2(b). CR Thermogram of HDPE

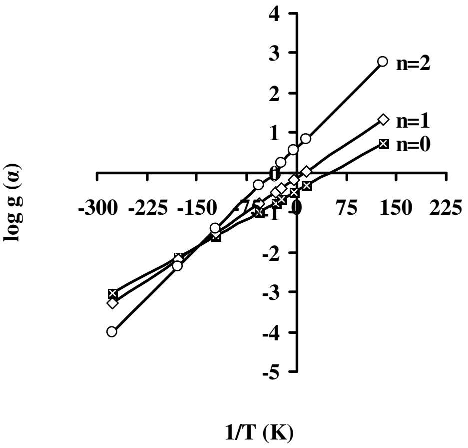

Fig. 3(a). HM Thermogram of LDPE

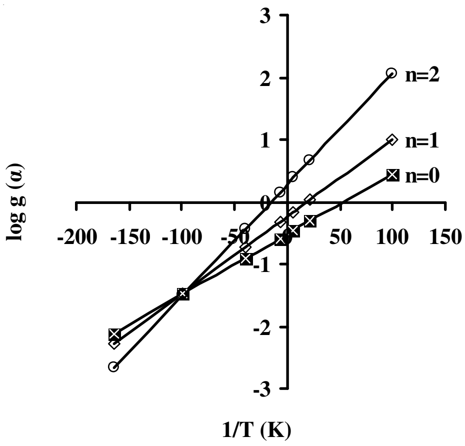

Fig. 3(b). HM Thermogram of HDPE

Kinetics and thermodynamics of solid state decomposition: Non-isothermal decomposition of LDPE and HDPE has been evaluated for investigation of thermodynamic and kinetic data of the reaction. Energy of activation E_a (KJ/mol), frequency factor Z (/min) were selected as a kinetic data and entropy change ΔS (JK^{-1}/min) as thermodynamic data.

Based on the variations in log g(α) against 1/T × 10^{-3} the kinetic and thermodynamic parameters of the polymers were investigated in terms of energy of activation, frequency factor and entropy change in thermal degradation from Coats-Redfern and Horowitz-Metzger method [Tables-3(a-b)]. Large differences in the energy of activation and frequency factors were observed for LDPE for all the reaction orders ranging n = 0 to n = 2. Whereas for n = o, both of the Coats-Redfern and Horowitz-Metzger method have shown almost identical changes in entropy with increase in the value of reaction order the discrepancy in entropy change was found to be higher [Table-3(a)]. For HDPE, similarly, a wide range of discrepancy was observed in the value of energy of activation of thermal degradation frequency factor and order of reaction [Figs. 2(b), 3(b)].

In the determination of activation energies and frequency factor for the individual steps it was found that Horowitz and Metzger method equation gave somewhat higher values relative to Coats-Redfern equation in all cases. The entropy of activation values are negatives in all steps indicating more ordered structure of the activated complex than the reactants. It is also evident that the values of E_a and A increase in the order.

Mechanism of thermal decomposition: Mechanism of thermal decomposition of selected polymers was studied under non-isothermal conditions at definite intervals of temperature. The respective variations in log g(α) with $1/T \times 10^{-3}$ at various reaction orders ranging n = 0 to 3. This has been deduced by solving the thermogram for a series of diffusion, nucleation and phase boundary equations. at respective reaction orders. A comparative account has been made all the samples towards their thermal decomposition reaction and related non-isothermal relative parameters studies conducted and indicated that the calculation involved, was found to be more suitable for HDPE [Fig. 4(b)]. The rest of polymers have shown non- linear variations in their log g(α) against temperature. Various patterns of mechanism of polymers were studied by plotting the values of log g(α) against T (K). It has been observed that except F_1 mechanism that is random nucleation law for one nucleus on each particle (Mampel Equation) all patterns were progressed almost according to same trends.

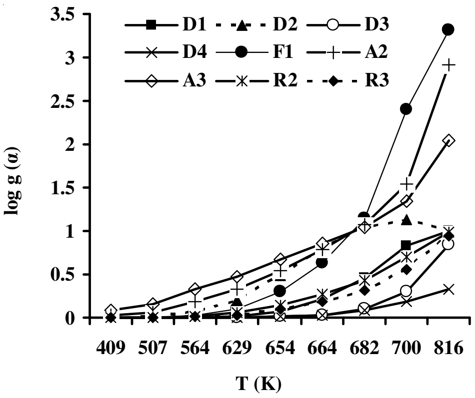

Fig. 4(a). Mechanism of thermal decomposition of LDPE

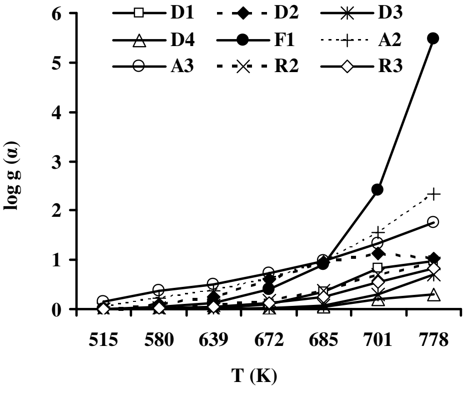

Fig. 4(b). Mechanism of thermal decomposition of HDPE

These observations indicate that at higher temperature these polymers indicated almost same behavior towards various log g(α) functions. Among all such mechanism, the most linear plot were observed at D4 indicating that mechanism of decomposition of theses polymers were satisfied according to D4 which is spherical symmetry according to Giastiling Brownshtein equation and variation of log g(α) against T (K).

Conclusion

Non-isothermal kinetics of solid state decomposition of LDPE and HDPE has been investigated through simultaneous TG-DTG-DSC under air. Both of the polymers have shown two step decompositions. Based on the variations in log g(α) against [$1/T \times 10^{-3}$] evaluated through Coats-Redfern and Horowitz-Metzger methods. The kinetic and thermodynamic parameters of the polymers were investigated in terms of energy of activation, frequency factor and entropy change in thermal degradation from Coats-Redfern and Horowitz-Metzger methods. Thermal data were used to evaluate log g(α) functions and its variation was studied with reference to temperature. The variations were investigated for a variety of decomposition mechanisms. In general all polymers display same mechanism of thermal decomposition at higher temperatures, except Mampel mechanism indicating random nucleation law. Due to the high amorphous character of LDPE this polymer has rendered no sharp DSC endotherm corresponding to their melting points. Both LDPE and HDPE polymers have shown weight residue ranging 99.8-100 % indicating their resistance against thermal decomposition at 200 ºC. A large discrepancies were observed in the entropy change, frequency factor and energy of activation of thermal decomposition of the selected polymers evaluated through Coats-Redfern and Horowitz-Metzger methods. At higher temperatures, these polymers indicated almost same behaviour towards various log g(α) functions. The most linear plot was observed for all polymers corresponding to Giastiling Brownshtein mechanism.

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