Journal of Thermal Analysis, Vol. 36 (1990) 855-867

EFFECT OF MOLECULAR WEIGHT ON NON-ISOTHERMAL DECOMPOSITION KINETICS OF HYDROXYL TERMINATED POLYBUTADIENE

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(Received December 22, 1988; in revised form June 9, 1989)

Hydroxyl terminated polybutadiene prepared by free radical polymerization was fractionated by a solvent-nonsolvent precipitation method. The fractions were characterized by gel permeation chromatography for their molecular weight averages ($\overline{M}_n$, $\overline{M}_w$ and $\overline{M}_z$) and dispersities. The kinetic parameters, viz., energy of activation E and preexponential factor A for the thermal decomposition of the fractions were computed from their TG data, using four nonisothermal integral equations. Quantitative correlations between the kinetic constants and the molecular weight parameters were derived for the first time for HTPB as:
E (or $\ln A$) $= k_1 - k_2/\overline{M}_n$ (or $\overline{M}_w$ or $\overline{M}_z$) and the trend is explained on the basis of the kinetic compensation effect.

Hydroxyl terminated polybutadiene (HTPB) prepolymers have a wide range of applications and are used as polymeric fuel binders in modern composite solid propellants [1, 2] because of their excellent mechanical and ballistic properties. HTPB is generally prepared by anionic or free radical polymerization techniques. The latter method is associated with random transfer reactions resulting in distribution of molecular weights, functionality, branching, microstructure etc. [3].

Fractionation of HTPB has been reported by Chang *et al.* [4], Muenker and Hudson [5], R. D. Law [6] and Regan *et al.* [7]. The method adopted here is similar to the one reported by Regan and co-workers. An HTPB sample, prepared by free radical polymerization technique was fractionated by solvent-nonsolvent precipitation method. The fractions were characterized by gel permeation chromatography (GPC) which is a powerful technique for characterizing polymers in terms of their molecular weight averages and dispersities.

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Thermogravimetry has been extensively used for the evaluation of the thermal decomposition kinetics of polymers [8] and recently it has been applied in the study of HTPB binders [9]. The effect of $\overline{M}_n$ (number average molecular weight) on the energy of activation (E) for the decomposition of polystyrene has been reported earlier [10].

In this communication we present our studies on the correlation between the molecular weight parameters and the kinetic constants for the thermal decomposition of the fractions of the HTPB sample.

Experimental

Sample

Hydroxyl terminated polybutadiene (HTPB) prepared by free radical polymerization at the Vikram Sarabhai Space Centre was used in this study.

Fractionation

HTPB was fractionated by the solvent-nonsolvent precipitation method using toluene-methanol system. 10 g of the polymer was dissolved in 100 ml toluene at room temperature and methanol was added in small quantities with constant stirring till a permanent turbidity was observed. The solution was warmed and then cooled at 5 - 10° for 24 hours when a clear separation of the two liquid phases was observed. The lower layer containing the polymer was removed and the polymer recovered using a rotary evaporator. Methanol was then added to the upper layer to precipitate out the next fraction. This procedure was repeated to collect seven fractions. The last fraction (seventh) was obtained by evaporating off the solvent since further addition of methanol did not precipitate out the resin. No antioxidant was added and the GPC and TG studies of the fractions were carried out immediately after the removal of the solvent.

Gel Permeation Chromatography (GPC)

Unfractionated HTPB and the fractionated samples were analysed for their molecular weight averages and dispersities using a Waters Associates ALC/GPC 244 with four microstyragel columns of pore sizes 10^4 Å, 10^3 Å, 500 Å and 100 Å. (Column dimensions: 30 cm length, 0.78 cm i.d.). Tetrahydrofuran (THF, HPLC grade) at a flow rate of 2 ml/min was the eluent. The columns were calibrated with commercially available narrow disperse polystyrene standards (Waters Associates). Sample solutions of 1% concentration were prepared in THF and 100 μl injected in each case. A differential refractive index (DRI) detector R-401 was employed at a sensitivity 8x. Molecular weight averages (number average molecular weight $\overline{M}_n$, weight average molecular weight $\overline{M}_w$ and z-average molecular weight $\overline{M}_z$) and dispersities were calculated using the *M* 730 Data Module.

Thermogravimetry

TG studies were conducted using a DuPont 990 thermal analyser in conjunction with 951 thermogravimetric analyser. The sample atmosphere was pure nitrogen, purged at a rate of 50 $cm^3\ min^{-1}$. A constant sample mass of 10 ± 0.1 mg and a heating rate of 10 $deg.min^{-1}$ were employed for the entire study. Computational work was done by a CDC computer using a FORTRAN IV program.

Results and discussion

Fractionation and GPC

Seven fractions of the polymer were obtained with a recovery of about 97% (Table 1). Loss of material during transfer of the fractions could have resulted in the slightly lower yield.

Table 1 Molecular weight parameters of fractionated and unfractionated HTPB

Fraction No.	Weight, %	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	Dispersity
1	10.15	8890	36000	79000	4.05
2	34.35	8420	26100	53100	3.10
3	15.49	6740	14000	26100	2.08
4	8.27	5370	9860	17100	1.84
5	5.43	4970	7700	12100	1.55
6	4.36	4500	6850	10100	1.52
7	21.95	2500	3860	4350	1.54
Unfrac. HTPB	–	4900	16700	49000	3.40

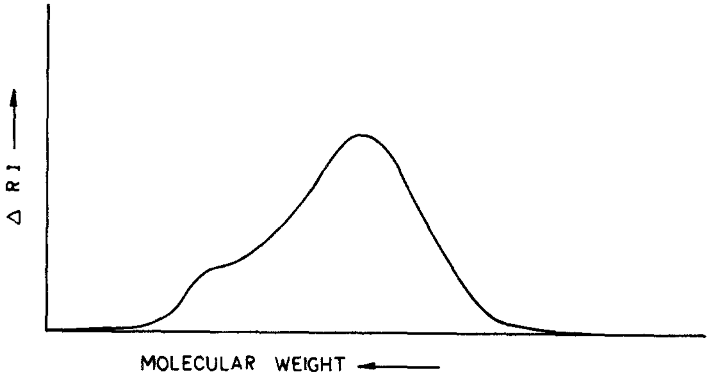

Fig. 1 GPC molecular weight distrubution curve of unfractionated HTPB

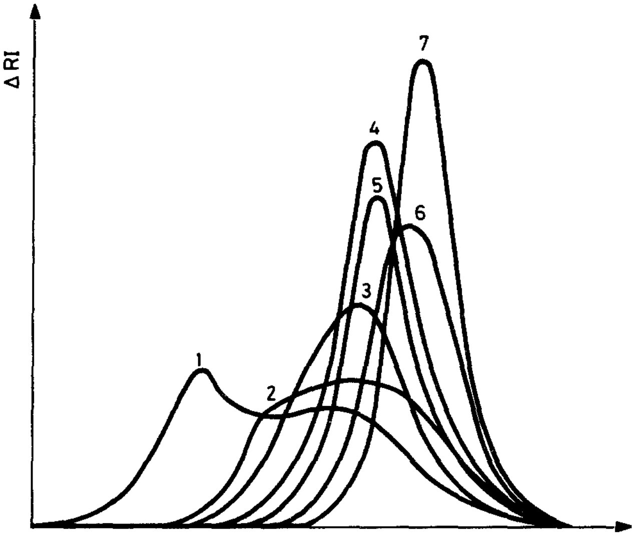

Fig. 2 GPC molecular weight distribution curves of HTPB fractions

The molecular weight averages of the fractions were determined by GPC whose accuracy and precision are comparable to the vapour pressure osmometer (VPO) results of number average molecular weight for HTPB [11]. Figures 1 and 2 show the GPC molecular weight distribution curves of unfractionated polymer and the seven fractions respectively. From the GPC results given in Table 1, it can be seen that the molecular weight decreases systematically for the fractions one to seven. Fractions one and two have a wide molecular weight distribution while fractions three to seven show a narrower distribution. Low molecular weight material was found to be present in all the fractions, which is a phenomenon associated with solvent-nonsolvent precipitation [12]. The dispersity values are not constant as reported earlier [7] but are found to decrease from fractions one to six. The number average molecular weight is found to decrease from 8890 to 2500, weight average molecular weight from 36000 to 3860 and z-average molecular weight from 79000 to 4350. A similar decrease in the values of dispersity is observed (D = 4.1 to 1.5) for the first fractions. The values of $\overline{M}_n$,$\overline{M}_w$ and $\overline{M}_z$ computed from the molecular weights and quantities of the seven fractions ($\overline{M}_n$ = 5020, $\overline{M}_w$ = 17160, $\overline{M}_z$ = 51700) are in close agreement with those of the unfractionated polymer ($\overline{M}_n$ = 4900, $\overline{M}_w$= 16700, $\overline{M}_z$= 49000) confirming the validity of the experimental procedures employed in this work.

Thermal decomposition kinetics

The kinetic parameters viz., energy of activation E and pre-exponential factor A of the seven fractions were calculated from their TG curves. Four non-isothermal integral equations were used for the computation of the kinetic parameters. The equations employed are:

1) Coats-Redfern (CR) equation [13]

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right] = \ln\left[\frac{AR}{\Phi E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT}$$

2) MacCallum-Tanner (MT) equation [14]

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)}\right] = \log\frac{AE}{\Phi R} - 0.483E^{0.435} - \frac{(0.449+0.217E)\,\mathrm{x}\,10^3}{T}$$

3) Horowitz-Metzger (HM) equation [15]

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)}\right] = \ln\frac{ART_s^2}{\Phi E} - \frac{E}{RT_s} + \frac{E\theta}{RT_s^2}$$

4) Madhusudanan-Krishnan-Ninan (MKN) equation [16]

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^{1.9215}}\right] =$$

$$= \ln\frac{AE}{\Phi R} + 3.7721 - 1.9215\ln E - \frac{0.12039E}{T}$$

where α = the fraction decomposed
n = order parameter
T = temperature (K)
R = gas constant
T_s = DTG peak temperature
Φ = heating rate
$\theta = T - T_s$

The order parameter n was evaluated using the Coats-Redfern and the MKN equations by an iteration method described earlier [9]. Using a computer, linear plots of LHS *vs.* $1/T$ were drawn by the method of least squares for different values of n in the range of 0 to 2 and the order parameter was selected for the best fit curves. The value of n calculated using both the equations was found to be zero for all the TG curves. This is in agreement with our earlier observations [9]. By substituting the value of $n=0$ in the four kinetic equations, E and A were calculated for all the eight samples (Table 2). The correlation coefficients r for the plots were also determined in each case, and found to be near unity for all the twenty eight plots, indicating the linearity of the curves.

From Table 2, it can be seen that the values of E and A show a regular decrease with decrease in the molecular weights of all the fractions. Thus for the Coats-Redfern equation, value of E decreases from 125 to 92 kJ mole^{-1} and A from 2.8×10^6 to 9.1×10^3 s^{-1}. The values are in the same range as what we have earlier reported for HTPB [9]. The MKN and MacCallum Tanner equations also give very close values of E and A. However higher values of the kinetic parameters were obtained from the Horowitz-Metzger equation because of the approximation method employed in the derivation of the equation [17].

Treatment of the GPC and kinetic data

Table 2 Kinetic parameters for the thermal decomposition of HTPB fractions

Fraction	Kinetic Equations					
No.	Coats–Redfern			MacCallum–Tanner		
	E	*A*	*r*	*E*	*A*	*r*
1	125.4	2.832×10^{6}	0.9900	129.5	5.686×10^{6}	0.9901
2	117.5	8.582×10^{5}	0.9936	121.5	1.554×10^{6}	0.9946
3	117.1	7.212×10^{5}	0.9930	121.0	1.416×10^{6}	0.9937
4	112.7	3.578×10^{5}	0.9926	116.6	6.966×10^{5}	0.9947
5	111.9	3.143×10^{5}	0.9937	115.8	6.099×10^{5}	0.9933
6	110.0	2.263×10^{5}	0.9921	113.9	4.378×10^{5}	0.9925
7	91.5	9.014×10^{3}	0.9815	95.1	1.683×10^{4}	0.9948

Fraction No.	Horowitz–Metzger			Madhusudanan–Krishnan–Ninan		
	E	*A*	*r*	*E*	*A*	*r*
1	150.1	1.789×10^{8}	0.9918	125.8	2.964×10^{7}	0.9900
2	142.1	4.920×10^{7}	0.9971	117.6	7.804×10^{6}	0.9937
3	141.6	4.495×10^{7}	0.9968	117.4	7.498×10^{6}	0.9945
4	137.0	2.166×10^{7}	0.9975	113.0	3.718×10^{6}	0.9934
5	136.8	2.113×10^{7}	0.9966	112.3	3.265×10^{6}	0.9915
6	134.3	1.363×10^{7}	0.9970	108.4	1.654×10^{6}	0.9910
7	116.7	6.579×10^{5}	0.9915	91.9	9.281×10^{4}	0.9850

(E in kJ mol^{-1} and A in s^{-1})

GPC analysis showed a decreasing trend of molecular weights of the fractions. A similar decreasing trend was observed in the case of the Arrhenius parameters also. The regular trend in the kinetic parameters relative to the GPC molecular weights of $\overline{M}_n$,$\overline{M}_w$ and $\overline{M}_z$ makes the data amenable for statistical treatment. It was found that E and $\ln A$ from all the four equations could be reasonably plotted against the molecular weights and Figs 3-5 show the curves obtained. Using computer different curve fits such as linear, exponential, parabola, rectangular hyperbola, etc. were worked out with the data. It was found that for all the four equations the energy of activation *vs.* $\overline{M}_n$ could be best represented as

$$E=a_1 - a_2/\overline{M}_n$$

where a_1 and a_2 are empirical constants whose numerical values are different for the four equations.

Similar curves were obtained in the case of $\overline{M}_w$ and $\overline{M}_z$ also.

$$E = b_1 - b_2/\overline{M}_w$$
$$E = c_1 - c_2/\overline{M}_z$$

where b_1, b_2, c_1 and c_2 are empirical constants for the four equations. The values of the empirical constants along with the corresponding correlation coefficients for the curves are given in Table 3.

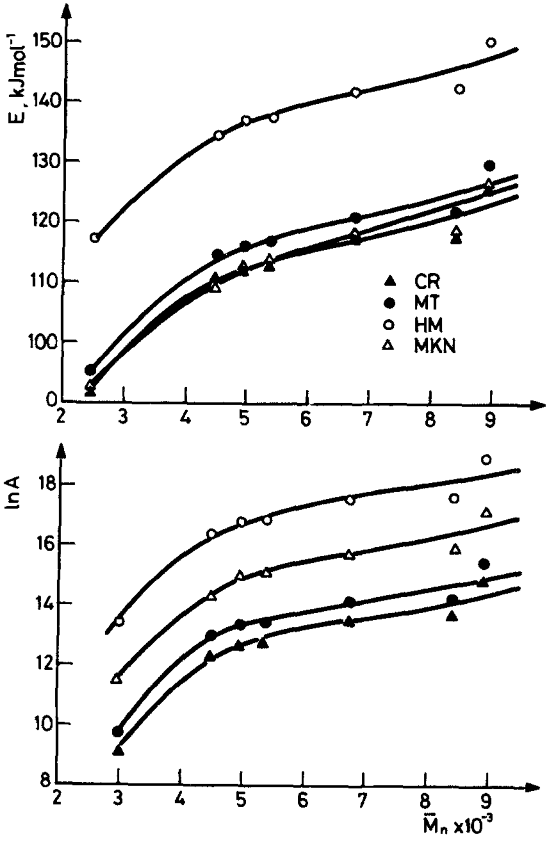

Fig. 3 Variation of kinetic parameters (E and $\ln A$) with $\overline{M}_n$

Table 3 Curve fit constants for activation energy *vs.* molecular weights curves

Kinetic	E *vs.* $\frac{1}{\overline{M}_n}$			E *vs.* $\frac{1}{\overline{M}_w}$			E *vs.* $\frac{1}{\overline{M}_z}$		
Equations	a_1	a_2	r	b_1	b_2	r	c_1	c_2	r
CR	133.1	$1.048\text{x}10^5$	0.9787	126.6	$1.293\text{x}10^5$	0.9736	122.8	$1.373\text{x}10^5$	0.9750
MT	137.3	$1.063\text{x}10^5$	0.9787	130.7	$1.311\text{x}110^5$	0.9735	126.9	$1.392\text{x}10^5$	0.9749
HM	157.3	$1.028\text{x}10^5$	0.9763	151.0	$1.271\text{x}10^5$	0.9721	147.2	$1.345\text{x}10^5$	0.9719
MKN	133.2	$1.051\text{x}10^5$	0.9755	126.8	$1.305\text{x}10^5$	0.9754	122.9	$1.379\text{x}10^5$	0.9735

Table 4 Curve fit constants for pre-exponential factor *vs.* molecular weights curves

Kinetic	In A *vs.* $1/\overline{M}_n$			In A *vs.* $1/\overline{M}_w$			In A *vs.* $1/\overline{M}_z$		
Equations	a_1'	a_2'	r	b_1'	b_2'	r	c_1'	c_2'	r
CR	16.27	$1.799\text{x}10^4$	0.9836	15.15	$2.214\text{x}10^4$	0.9753	14.51	$2.356\text{x}10^4$	0.9787
MT	16.94	$1.809\text{x}10^4$	0.9811	15.81	$2.226\text{x}10^4$	0.9722	15.17	$2.370\text{x}10^4$	0.9775
HM	20.29	$1.734\text{x}10^4$	0.9786	19.21	$2.135\text{x}10^4$	0.9717	18.59	$2.268\text{x}10^4$	0.9739
MKN	18.54	$1.799\text{x}10^4$	0.9785	17.43	$2.227\text{x}10^4$	0.9756	16.78	$2.361\text{x}10^4$	0.9769

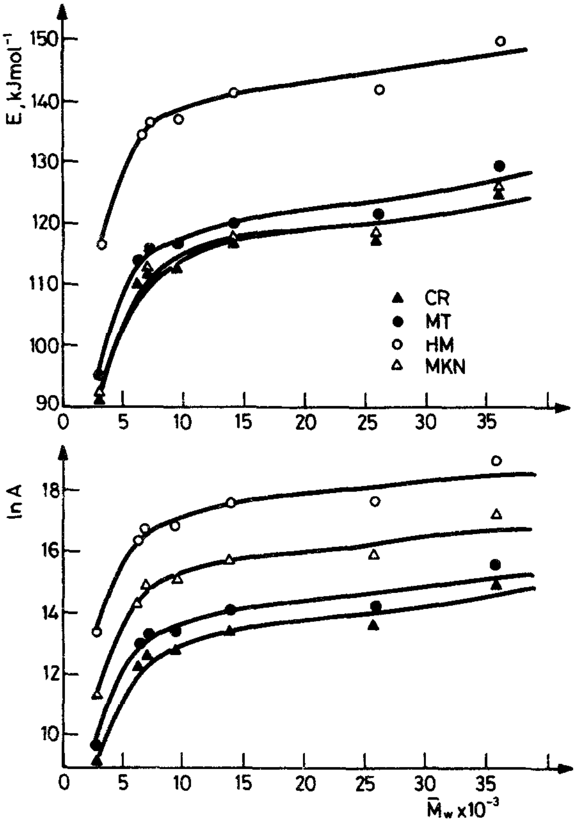

Fig. 4 Variation of kinetic parameters (E and $\ln A$) with $\bar{M}_w$

In the case of pre-exponential factor the best fit curves are obtained for the curves of $\ln A$ *vs.* molecular weight and the equations for the curves are:

$$\ln A = a'_1 - a'_2/\bar{M}_n$$
$$\ln A = b'_1 - b'_2/\bar{M}_w$$
and $$\ln A = c'_1 - c'_2/\bar{M}_z$$

where a'_1, a'_2, b'_1, b'_2, c'_1, and c'_2 are empirical constants for the different equations. Their values along with the correlation coefficients for the graphs are given in Table 4.

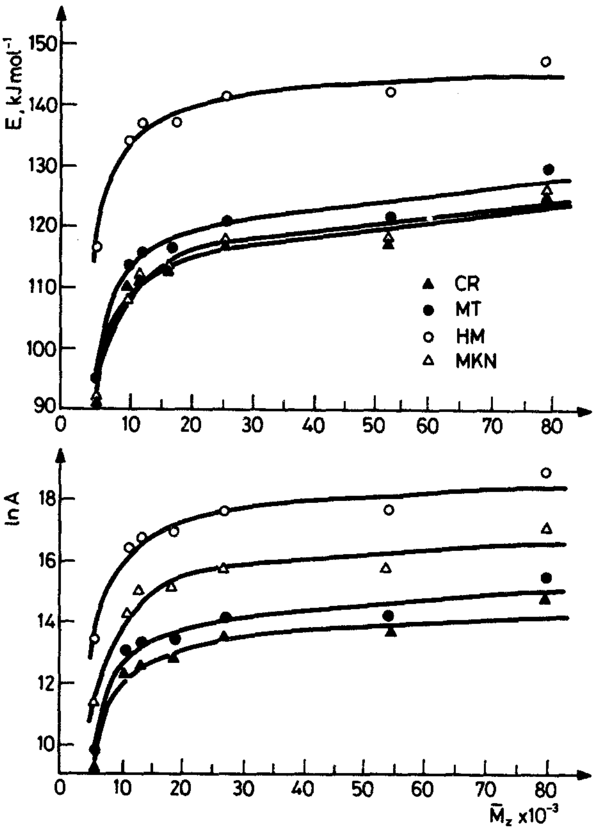

Fig. 5 Variation of kinetic parameters (E and $\ln A$) with $\bar{M}_z$

The correlation coefficients for all the twenty four curves are reasonably good (>0.97) confirming the validity of our assumption regarding the correlation between molecular weight and the kinetic parameters for the thermal decomposition of HTPB resin. Another interesting observation is that for the best fit curves molecular weights are correlated with E, whereas in the case of pre-exponential factor it is $\ln A$ that is correlated to the molecular weights. This can be explained on the basis of the kinetic compensation effect [18] postulating linear correlation between E and $\ln A$. A closer examination of the data given in Table 2 shows that for all the four kinetic equations E *vs.* $\ln A$ can be fitted as perfect straight lines following the equations:

1) Coats-Redfern equation

$$\ln A = -6.4790 + 0.1708\,E \quad (r = 0.9996)$$

2) MacCallum-Tanner equation

$$\ln A = -6.3775 + 0.1698\,E \quad (r = 0.9998)$$

3) Horowitz-Metzger equation

$$\ln A = -6.1937 + 0.1682\,E \quad (r = 0.9997)$$

4) MKN equation

$$\ln A = -4.2005 + 0.1701\,E \quad (r = 0.9998)$$

Conclusions

HTPB has been fractionated by using toluene as solvent and methanol as non-solvent. GPC analysis of the fractions showed a regular decrease in $\overline{M}_n$, $\overline{M}_w$ and $\overline{M}_z$. Low molecular weight material was found to be present in all the fractions.

The kinetic parameters (E, A and n) for the thermal decomposition of the fractions were evaluated from their TG data using four integral equations. The values of activation energy and pre-exponential factor calculated using all the four equations showed a systematic decrease with decrease in molecular weight averages ($\overline{M}_n$, $\overline{M}_w$ and $\overline{M}_z$). Quantitative correlation between kinetic constants and molecular weight parameters have been derived and the best fit correlations can be expressed as hyperbolae of the type E (or $\ln A$) $= k_1 - k_2/\overline{M}_n$ (or $\overline{M}_w$ or $\overline{M}_z$) for the range of our results.

* * *

We thank Dr. K. V. C. Rao, Mr. M. R. Kurup and Director, VSSC for their kind permission to publish this paper.

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Zusammenfassung — Mittels eines Löser-Nichtlöserverfahrens wurde ein durch Radikalpolymerisation hergestelltes, Hydroxyl-endständiges Polybutadien fraktioniert. Das mittlere Molekulargewicht ($\bar{M}_n$,$\bar{M}_w$ and $\bar{M}_z$z) und der Dispersionsgrad der einzelnen Fraktionen wurden durch Gelchromatograpie charakterisiert. Die kinetischen Parameter, d.h. die Aktivierungsenergie E und der präexponentielle Faktor A wurden auf der Basis der TG Daten unter Zuhilfenahme von vier nichtisothermen Integralgleichungen berechnet. Zum ersten Male konnte für HTPB ein quantitativer Zusammenhang zwischen den kinetischen Konstanten und den Molekulargewichtparametern gefunden werden: E (order $\ln A$) $= k_1 - k_2/\bar{M}_n$ (order $\bar{M}_w$ order $\bar{M}_z$). Diese Tendenz wurde auf der Basis des kinetischen Kompensationseffektes gedeutet.