

Chemiluminescence from Amine Cured Epoxy Resins Modified with Halogenated Phenylglycidyl Ethers

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SYNOPSIS

Chemiluminescence from thermooxidized epoxide alone and that modified with phenyl glycidyl ethers has been investigated in isothermal and nonisothermal regime. Isothermal curves are characterized by a monotonous fall of chemiluminescence intensity from some initial value to very low levels of light emission. Nonisothermal curves show a maximum intensity at temperatures above 473 K. The luminescence intensity is influenced by both T_g and thermal stability of epoxide. The higher T_g or higher thermal stability brings about the higher intensity of light emission and vice versa. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polymers prepared from epoxy resins produce rather intense bursts of chemiluminescence when heated in oxygen at temperatures above 370 K.¹ The intensity of initial light uptake depends significantly on the temperature, curing catalyst, and the presence of coagents. Of interest is rather fast decay of the light emission from the initial value which can be related with the progress in the oxidation and coloration of the sample. As the process of oxidation of cured epoxide can occur via several alternatives of mechanisms,² no ultimate reaction pathway responsible for chemiluminescence appearance from epoxides was formulated until now. The similar uncertainty, however, exists also in interpretation of chemiluminescence accompanying the thermooxidation of other polymers.³⁻⁷ Although a concept of recombination of peroxy radicals as the main reaction route that provides the light emission appears to predominate now, the type of peroxy radicals and mechanism of how they are generated can differ from polymer to polymer. In spite of considerable progress brought by some papers^{8,9} new experiments are needed to throw more light on the problem.

The isothermal chemiluminescence (CL)-time

curves of crosslinked epoxies indicate¹ rather fast consumption of some reactive species, concentration of which exceeds that of equilibrium level corresponding to a certain rate of initiation. The similar patterns of CL-time decay were also observed for poly(2,6-dimethyl phenylene oxide) and high impact polystyrene blends.¹⁰ Their interpretation represents a challenge to the theoretical oxidation scheme because no induction period of CL uptake can be observed when the polymer is stabilized with common phenolic or amine thermooxidative inhibitors. The effect of such inhibitors is displayed here only in a decrease of intensity of light emission.¹⁰ The influence of several anhydrides as reactive coagents on chemiluminescence of cured epoxy resin has been investigated.¹

In the present article, we attempt to elucidate the effect of halogenated phenyl glycidyl ethers (PGE), which were used as reactive coagents during the epoxy hardening with an intention to lower the flammability of original epoxide.¹¹ We have found that the samples of epoxy cured with PGE differ considerably also in CL patterns, and the reasons for this might be of interest and add to the general knowledge on CL of polymers.

A method of evaluation of nonisothermal chemiluminescence data has been proposed that enables differentiation of several temperature-dependent processes, and results were compared with isothermal curves.

EXPERIMENTAL

Phenyl glycidyl ether (PGE) substituted by chlorine or bromine (XPGE, where X = 2-chloro, trichloro, pentachloro, tribromo, and pentabromo) on phenyl ring¹² was mixed with low molecular weight resin ChS Epoxy 15 of the DGEBA type, product of Chemical Works, Ústí/Labem, Czech republic (5.22 mol of epoxy units/kg) in weight ratio 1 : 9, 2 : 8, and 3 : 7, and cured by a stoichiometric amount of diaminodiphenyl methane. Halogenated phenyl glycidyl ethers were prepared by alkaline condensation of epichlorohydrine with corresponding chloro or bromophenol.¹² The samples were cured in degassed molds as plates of thickness 5 mm, subsequently 1 h at 363 K, 1 h at 373 K, and 5 h at 433 K.¹²

Chemiluminescence measurements were carried out on Biolumat RB 8501 spectrometer of the fy Berthold, Germany. The apparatus is equipped with an oven connected to a photomultiplier by the optical cable. The initial weight of sample was about 250 mg. The flow rate of oxygen above the surface of the sample was 6 L/h.

Nonisothermal thermogravimetry experiments were performed on Derivatograph MOM 1500 D of Hungariam production. The initial weight of sample was 100 mg, atmosphere of nitrogen (flow 6 L/h), the rate of sample heating 10 K/min.

Glass transition temperature T_g was measured on DSC-2, Perkin Elmer.

ESR spectra of carbon residues obtained from the polymer heated in nitrogen, the rate 10 deg/min up to 773 K, were measured on a spectrometer Varian E 4 working in 3 cm band (9.5 GHz). ESR spectra were measured at room temperature.

The concentration c of paramagnetic particles was expressed in relative units. As the ESR signal of carbon residue is a singlet line, the relative unit is defined by the ratio

$$c = \frac{L * (\Delta H)^2}{w * S},$$

where L is the height of this singlet line in cm, H is the width in mT, w is the weight of sample in g, and S is the sensitivity of ESR spectrometer.

RESULTS AND DISCUSSION

The chemiluminescence intensity-temperature runs recorded at the rate of heating 2 deg/min from 373 K to 523 K for samples of epoxide cured with 10,

20, and 30% w. of PGE are shown in Figure 1. It may be seen that the maximum intensity decreases with the increasing content of PGE while the temperature of this maximum is shifted to higher values. Chloro or bromo derivatives of PGE give to further reduction of maximum CL intensity (I_{\max}).

The values of I_{\max} and T_{\max} are summarized in Table I. Nonisothermal chemiluminescence experiments were evaluated assuming first-order kinetics of CL decay. An equation used for this purpose contains the assumption that chemiluminescence process is the sum of several independent first-order reactions as follows:

$$I = \sum_{i=1}^n M_i A_i * \exp(-E_i/RT) \times \exp \int_T (-A_i/\beta \exp(-E_i/RT) dT) \quad (1)$$

where I is the intensity of CL in counts/s/g; A_i and E_i are preexponential factor and activation energy of the i th independent step of the light release; β is the rate of heating in deg/min; M_i is the proportionality constant that stands for the surface below the i th peak.

Number of processes composing the resulting CL intensity-temperature run depends on the quality of the fit with an experiment; usually one or two first-order processes were considered as being responsible for the measured record. The fit with experiment was searched by nonlinear regression analysis and the results for $k = 2$ are summarized in Table II.

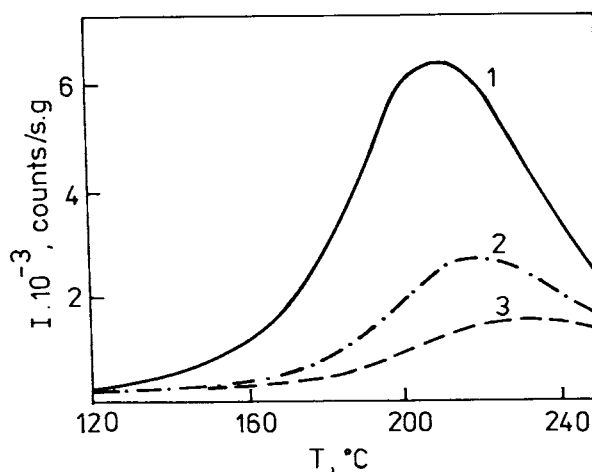


Figure 1 Nonisothermal chemiluminescence runs for epoxy cured with 10 (1), 20 (2), and 30 (3) % wt of PGE. The rate of heating 2 deg/min, oxygen atmosphere.

Table I Maximum Chemiluminescence Intensity I_{\max} and Temperatures T_{\max} Related to This Maximum for Samples of Epoxy Cured Along with Phenylglycidyl Ethers

Sample Epoxy +	I_{\max} Counts/g/s	T_{\max} K	$-\ln(k_{T_{\max}} \cdot \text{min})$
—	6353	484	18.9
10% wt PGE	6277	481	15.1
20% wt PGE	2761	492	9.7
30% wt PGE	1576	506	9.1
10% wt o-Cl PGE	5490	486	12.4
20% wt o-Cl PGE	1977	502	8.6
30% wt o-Cl PGE	1415	512	6.8
10% wt triCl PGE	2057	496	7.0
20% wt triCl PGE	909	516	4.8
30% wt triCl PGE	699	507	4.3
10% wt pentaCl PGE	619	492	—
20% wt pentaCl PGE	374	494	—
30% wt pentaCl PGE	121	494	—
10% wt triBr PGE	1333	494	6.6
20% wt triBr PGE	577	506	4.6
10% wt pentaBr PGE	670	493	—
30% wt pentaBr PGE	203	523	—

It may be seen that two processes can be found in the case of pure epoxide only or epoxide cured with 10% wt of PGE, 10% wt of o-chloro PGE, or 10% wt of tribromo PGE.

The position of the two peaks representing the first-order processes on the temperature axis is

rather close and experimental data of chemiluminescence-temperature give the impression of a one-peak process. The temperature of the maximum of the first peak for pure epoxide lies at 483 K while that of the second peak is at 509 K. The subsequent suppression of the first peak by modification of ep-

Table II Parameters of Two-Peak Fit of Chemiluminescence Temperature Records for Epoxy + PGE Polymers

Sample Epoxy with wt %	$M_1 \cdot 10^{-6}$ Counts/g	A_1 min^{-1}	E_1 kJ/mol	k_1 (473 K) $\cdot 10^2, \text{min}^{-1}$	$M_2 \cdot 10^{-6}$ Counts/g	A_2 min^{-1}	E_2 kJ/mol	k_2 (473 K) $\cdot 10^2, \text{min}^{-1}$
—	5.2	$2.6 \cdot 10^{12}$	123	6.8	5.6	$2.2 \cdot 10^9$	101	1.5
10 PGE	3.0	$1.1 \cdot 10^{12}$	119	7.9	9.8	$1.5 \cdot 10^6$	70	2.8
20 PGE	—	—	—	—	5.3	$2.0 \cdot 10^7$	80	2.9
30 PGE	—	—	—	—	3.7	$6.0 \cdot 10^5$	68	1.9
10 o-Cl PGE	2.6	$1.5 \cdot 10^{13}$	131	5.1	7.9	$2.8 \cdot 10^6$	73	2.4
20 o-Cl PGE	—	—	—	—	2.8	$2.7 \cdot 10^7$	83	1.8
30 o-Cl PGE	—	—	—	—	3.7	$4.8 \cdot 10^7$	85	1.9
10 triCl PGE	—	—	—	—	4.1	$1.0 \cdot 10^7$	78	2.4
20 triCl PGE	—	—	—	—	1.9	$5.4 \cdot 10^6$	79	1.0
30 triCl PGE	—	—	—	—	1.2	$3.6 \cdot 10^8$	93	1.9
10 pentaCl PGE	—	—	—	—	1.3	$1.8 \cdot 10^6$	70	3.3
20 pentaCl PGE	—	—	—	—	0.8	$2.8 \cdot 10^6$	72	3.1
30 pentaCl PGE	—	—	—	—	0.2	$1.6 \cdot 10^9$	97	3.1
10 triBr PGE	0.6	$6.1 \cdot 10^{11}$	117	7.3	1.9	$8.6 \cdot 10^7$	87	2.1
10 pentaBr PGE	—	—	—	—	1.3	$2.0 \cdot 10^6$	71	2.9
30 pentaBr PGE	—	—	—	—	0.2	$3.4 \cdot 10^4$	53	3.6

The rate of temperature increase 2 deg/min, initial weight of samples 250 mg, oxygen atmosphere.

Table III Constants k_1 and k_2 Determined from Nonisothermal (a) and Isothermal (b) Chemiluminescence of Epoxide in Oxygen and Constants k for the First-Order Decay of Chemiluminescence of Epoxide in ref. 1

Temperature, K	$k_1 \cdot 10^2$ min ⁻¹	$k_2 \cdot 10^2$ min ⁻¹	$k \cdot 10^2$ min ⁻¹
(a)			
453	1.7	0.5	4.26
473	6.8	1.5	9.1
493	24.1	4.4	13.15
513	77.7	11.4	7.2
(b)			
393	4.6	—	
413	40.8	0.5	
433	57.5	1.1	
453	4.2	1.8	
463	9.3, ^a 13.8 ^b	2.8, ^a 2.9 ^b	
473	9.6	2.2	
483	13.6	1.2	
493	23.4	4.7	
503	29.2	4.1	
513	36.2	4.4	

Chemiluminescence decay is assumed to be composed of two first-order processes.

^a 90 mg of sample.

^b 160 mg of sample.

oxide by larger amount of PGE leads then to the shift of the temperature T_{\max} corresponding to I_{\max} to higher values (Table I).

Comparison of rate constants of the first order determined from A_1 , E_1 , and A_2 , E_2 for 473 K indicates that the first process is faster than the sec-

ond. The rate constants k_1 and k_2 for pure epoxide for different temperatures approach those derived from isothermal experiments published by Tchar-khtchi et al.¹ for chemiluminescence of epoxy cured with methyltetrahydrophthalic anhydride (Table IIIa).

The nature of the faster step and the mechanism of its suppression by PGE remains unclear. It may quite well reflect the decay of structural defects generated and trapped in a polymer matrix during the curing process.

Isothermal chemiluminescence-time records for some samples of epoxide are shown in the Figure 2. In the case of epoxide alone, the experimental lines were again observed to be composed of two first-order processes. Below T_g temperature of the polymer, the rate constants k_1 of the first process are rather high. Above T_g , the process has obviously other character because the values of k_1 fall initially but increase with further increase of temperature (Table IIIb). The values k_2 increase up to 463 K, then decrease and start to increase slowly again (Table IIIb).

Quite a good correspondence has been found between nonisothermal and isothermal measurements.

This can be seen in the Table IV, where the values of initial intensity I_0 obtained for respective samples at different temperatures are compared with I'_0 values calculated from corresponding preexponential factor and activation energy determined from nonisothermal records assuming single or two-peak process.

The sum of both I_{01} and I_{02} values calculated from the parameters of nonisothermal chemilumines-

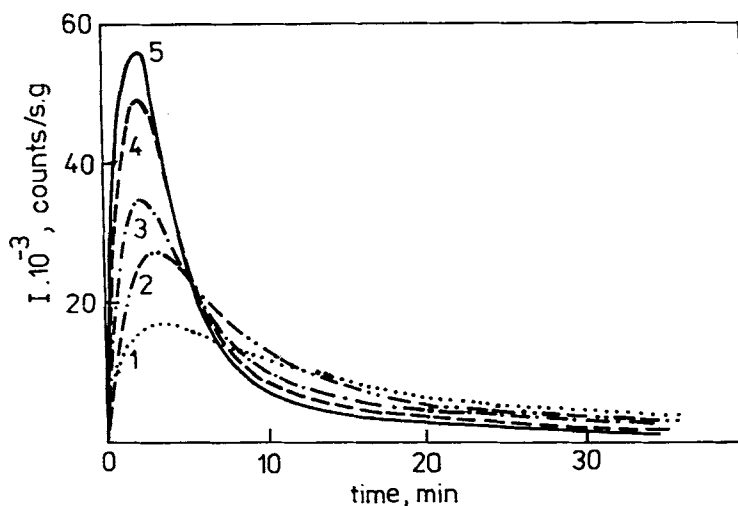


Figure 2 Isothermal chemiluminescence-time records of pure epoxide polymer in oxygen atmosphere at: 200 (1), 210 (2), 220 (3), 230 (4), and 240 (5) °C.

Table IV Comparison of Initial Values I_0 of Chemiluminescence Intensity Obtained in Isothermal Experiments with Those Calculated from Preexponential Factor and Activation Energy of Nonisothermal Curves I_0 (I_{01} , and I_{02} in the case of two-peak fit)

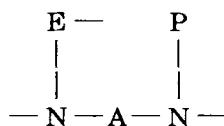
Sample	Temperature K	I_0	I_{01}	I_{02}	I_0^a	
			Counts/g/s			
Epoxide without PGE	393	147	10	8	18	
	413	911	62	34	96	
	433	2642	326	134	460	
	453	6137	1477	463	1940	
	463	10947	2990	826	3816	
	473	17014	5876	1439	7315	
	483	26242	11229	2450	13679	
	503	49016	37953	6662	44615	
	513	55703	67340	10667	78017	
Epoxide						
	+10% PGE	463	8221	2063	3101	5164
	+20% PGE	463	2765		1664	
	+30% PGE	463	1095		787	
	+ 10% triCl PGE	463	3556		1082	
	+20% triCl PGE	463	547		209	
	+30% triCl PGE	463	500		232	
	+10% triBr PGE	463	2790	384	416	800
	+10% pentaBr PGE	463	1066		423	

$$^a I_0 = I_{01} + I_{02}$$

cence experiments is lower than the value of I_0 —initial value of chemiluminescence intensity determined under isothermal conditions. This indicates again that the isothermal light emission involves some reaction of highly reactive particles trapped in a polymer and released abruptly when fast heating of the sample to a given temperature of isothermal experiment takes place.

The Crosslink Density, T_g and Chemiluminescence Intensity

Theoretical values of crosslink density were calculated assuming the following fundamental structural units of epoxide network,



where E denotes the structure of original epoxy, P is substituted phenyl glycidyl ether and N—A—N is diphenyldiaminomethane moiety.

If the degree of substitution by monofunctional P units is α and N linked with E represents the

junction of a polymer network, the density of crosslinks can be expressed as

$$d = \frac{2 - \alpha}{(2 - \alpha)M_E + \alpha M_P + M_A} \text{ mol/kg}$$

If introducing $x = \alpha M_P / (2 - \alpha) M_E$, where x stands for the initial mass ratio of P and E units, M_E is molecular mass of the epoxy units, M_A is molecular mass of N—A—N moiety, and M_P is molecular mass of substituted PGE units, we can express the crosslink density d as follows:

$$d = \frac{2}{2M_E + M_A + x(2M_E + M_A M_E / M_P)} \text{ mol/kg}$$

The values of d together with T_g of individual samples are given in the Table V and graphically illustrated by the Figure 3. The general tendency can be seen from the Figure 3, namely the denser network, the higher T_g values. Although a linear plot can be drawn for all samples, regardless of the initial concentration of PGE and its substitution (Fig. 3)

$$T_g = 90.5d + 240.2$$

Table V The Values of Crosslinking Density (in mol kg⁻¹, and T_g (in K) of Epoxies Cured Together with Substituted Phenyl Glycidyl Ether (PGE)

Initial Amount of PGE % wt	Type of PGE	PGE	o-Chl PGE	tri Chl PGE	penta Cl PGE	tri Br PGE	penta Br PGE
10	d	1.83	1.85	1.87	1.89	1.89	1.90
	T_g	396	396	405	415	415	417
20	d	1.63	1.66	1.70	1.72	1.73	1.75
	T_g	379	381	392	402	405	413
30	d	1.48	1.51	1.56	1.58	1.60	1.62
	T_g	365	369	379	393	—	407
0	d	2.08					
	T_g	424					

from the scatter of points it can be noticed that each concentration as well as each kind of substitution behave independently, giving a straight line of its own. For instance:

$$\text{triBr PGE } T_g = 54.0d + 311.9$$

$$\text{pentaBr PGE } T_g = 35.9d + 349.3$$

(lines 1, 2, 3, 4, 5, and 6 of Fig. 3)

$$\text{PGE } T_g = 97.5d + 219.8$$

$$\text{o-Cl PGE } T_g = 95.7d + 222.7$$

$$\text{triCl PGE } T_g = 85.6d + 245.8$$

$$\text{pentaCl PGE } T_g = 63.2d + 293.6$$

Maximum chemiluminescence intensity I_{\max} measured for respective samples in oxygen under nonisothermal conditions (the rate of heating 2 deg/min) correlates with d , as shown in Figure 4. It is seen that I_{\max} increases with increasing density of

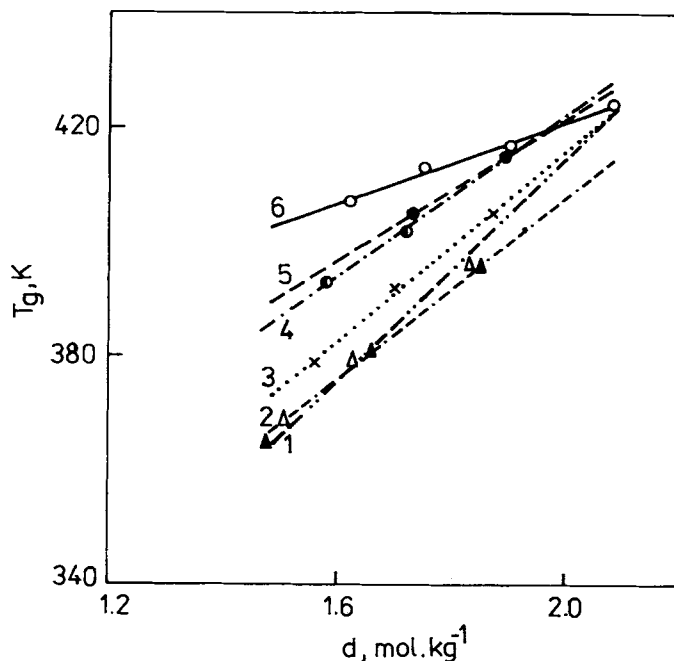


Figure 3 The plot of glass transition temperature T_g on crosslink densities d for samples of epoxides from Table VI. 1 (PGE), 2 (o-Cl PGE), 3 (triCl PGE), 4 (penta ClPGE), 5 (triBr PGE), 6 (pentaBr PGE).

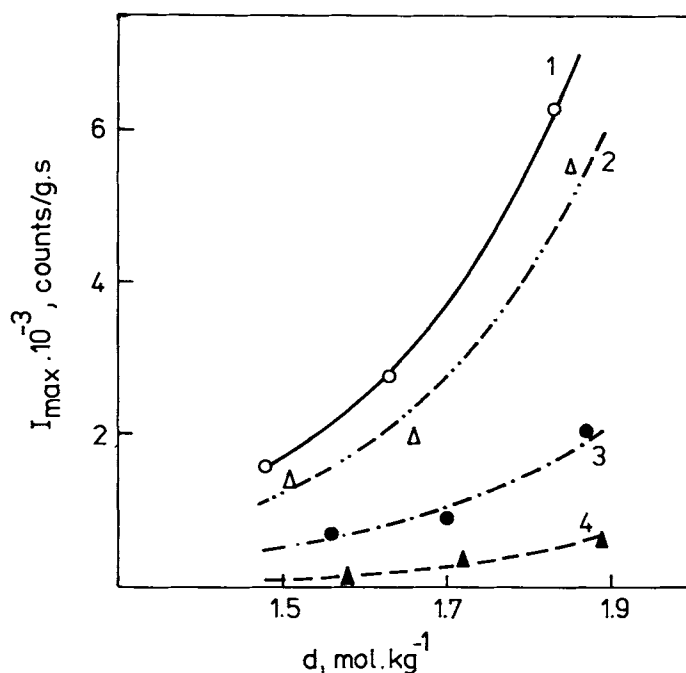


Figure 4 Maximum chemiluminescence intensity I_{\max} from nonisothermal chemiluminescence experiments plotted against the crosslink density d for epoxide polymers modified with phenylglycidyl ether (PGE)—1, *o*-chloroPGE—2, trichloroPGE—3, pentachloroPGE—4.

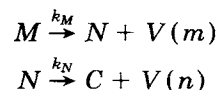
epoxide network (line 1 of Fig. 4). On the other hand, for a certain concentration of X-PGE, I_{\max} decreases from higher values typical for PGE additions to low values in the order PGE > *o*-chloro PGE > trichloro PGE > pentachloro PGE > tribromo PGE > pentabromo PGE.

It appears that the light absorption increases in the same order of PGE substitution and accordingly, the more halogenated samples produce less intense light emission. This explanation could be accepted for halogenated PGE, but it does not correspond with the reduction of chemiluminescence intensity due to modification by unsubstituted PGE. Here, it appears that the process of light emission is localized to the neighborhood of junction points.

Nonisothermal Thermogravimetry of Cured Epoxies Together with Substituted PGE

Curing of epoxy with substituted PGE leads to the destabilization of resulting polymer and to an easier formation of volatile products, which becomes rather distinct in the case of pentachloro, tribromo, and pentabromo PGE.¹² The formation of volatiles from the polymer is accompanied by the formation of a solid carbon residue. The nonisothermal curves of

decomposition of epoxide into volatile products were interpreted by the scheme of subsequent reactions in which the volatiles V are released in each step of the reaction scheme:



In this scheme, k_M and k_N are the rate constants of individual reaction steps dependent on temperature by Arrhenius equation:

$$k_{M,N} = A_{M,N} \cdot \exp(-E_{M,N}/RT)$$

M is original crosslinked epoxide, N is an intermediate product and C is a carbon residue; m and n indicate the fractional amount of volatiles released in a respective reaction step.

The optimum values of parameters A_M , A_N , E_M , E_N , m , and n for nonisothermal thermogravimetry curves are presented in the Table VI. The highest temperature coefficient (≈ 320 kJ/mol) was obtained for the first step (20 wt % of volatiles) of decomposition of epoxide alone. It leaves about 30% of carbon residue at 773 K; the formation of volatiles in the second step (about 50 wt %) has very low

Table VI Parameters of the Model Describing the Decomposition of Epoxide + PGE Polymers into Volatile Products

Sample (xx)	$\ln(A_M \cdot \text{min})$	E_M kJ/mol	$\ln(A_N \cdot \text{min})$	E_N kJ/mol	m	n	${}^b c \cdot 10^{-2}$ rel. u.
Epoxy +							
—	61.8	324	2.7	22	0.20	0.50	3.3
10% wt PGE (2)	44.3	235	8.7	55	0.30	0.32	2.8
20% wt PGE (3)	31.3	164	20.8	126	0.48	0.16	2.7
3% wt PGE (4)	38.2	171	^a	^a	0.54	0.09	2.4
10% wt o-Cl PGE (5)	39.8	212	9.4	60	0.37	0.29	2.7
20% wt o-Cl PGE (6)	29.4	159	29.1	172	0.51	0.14	3.6
30% wt o-Cl PGE (7)	23.1	127	^a	^a	0.60	0.07	2.2
10% wt triCl PGE (8)	20.7	114	^a	^a	0.55	0.08	3.1
20% wt triCl PGE (9)	17.7	97	15.7	96	0.52	0.17	2.7
30% wt triCl PGE (10)	17.6	93	8.1	52	0.40	0.29	3.7
10% wt triBr PGE (11)	38.0	183	4.2	28	0.18	0.50	2.8
20% wt triBr PGE (12)	37.8	179	^a	0	0.38	0.40	4.4
30% wt trBr PGE	53.2	245	^a	0	0.40	0.46	4.8

Data from nonisothermal thermogravimetry, atmosphere of nitrogen, initial amount of sample 50 mg, the rate of heating 10 deg/min.

^a Cannot be determined reliably.

^b c is concentration of paramagnetic particles in carbon residue formed in nonisothermal thermogravimetry measurements carried out to 773 K at the rate of heating 10 deg/min; ESR spectra were measured at room temperature in air. (xx) = The sequence number of sample in Figure 6.

temperature coefficient. Introduction of PGE segments into the polymer network leads to considerable reduction of activation energy of the first step (to 170 kJ/mol for 30% wt of PGE). More significant reduction occurs with o-chloro PGE and trichloro PGE, where activation energy of the first step falls to 90 kJ/mol. It is of interest that the introduction of tribromo PGE gives an increase of activation energy (up to 240 kJ/mol for 30% wt of tribromo PGE), but the second step takes place spontaneously (zero temperature coefficient). Typical nonisothermal thermogravimetry curves for epoxide alone and that cured with 30% wt of PGE, o-chloro PGE, trichloro PGE and tribromo PGE are shown in Figure 5.

If I_{\max} from nonisothermal chemiluminescence experiments were plotted against $(-\ln k_{T_{\max}})$, where

$k_{T_{\max}}$ is the rate constant of the release of volatile products corresponding to the first nonisothermal thermogravimetry step and T_{\max} is temperature of the maximum of nonisothermal chemiluminescence record, a surprisingly good correlation was obtained (Fig. 6). Approximation of I_{\max} to zero gives the value of $k_{T_{\max}} = 2.4 \cdot 10^{-2} \text{ min}^{-1}$. Above this rate constant of formation of volatile products no chemiluminescence could be observed at all because of counterstream of volatiles being formed in degradation reaction. This finding can be of significance in localization of the site of chemiluminescence process.

An attempt has been made to find some correlation of concentration of paramagnetic particles that appear in each carbon residue formed below 550°C. As it is seen in Figure 7, a pure correlation

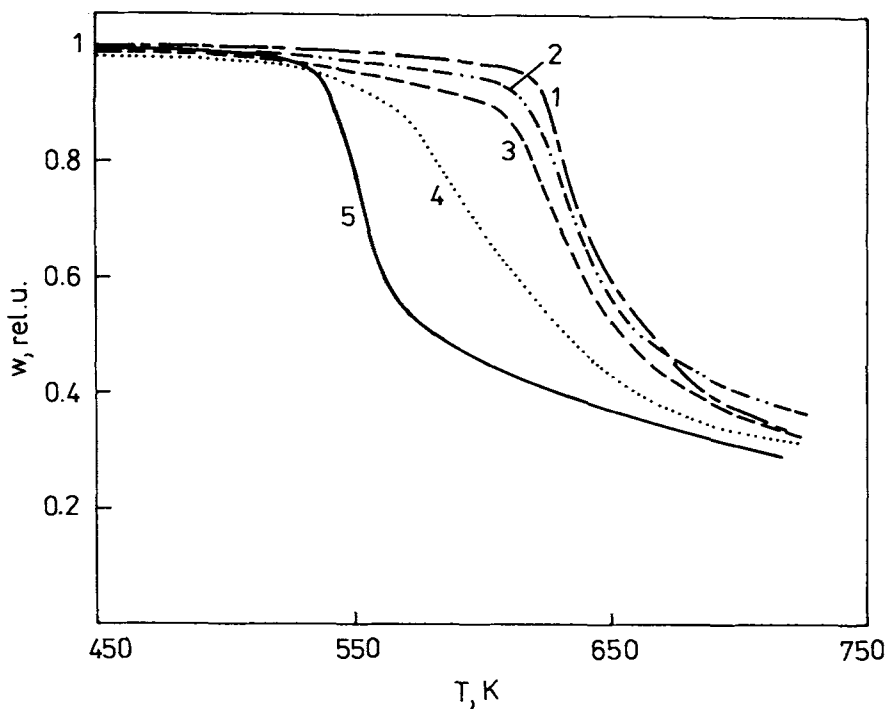


Figure 5 Nonisothermal thermogravimetry runs for epoxide (1) modified with 30% wt of phenylglycidyl ether (2), 30% wt of *o*-chlorophenylglycidyl ether (3), 30% wt of trichlorophenylglycidyl ether (4), and 30% wt of tribromophenylglycidyl ether (5). The initial weight of sample 100 mg, the rate of heating 10 deg/min, nitrogen atmosphere (6 L/h).

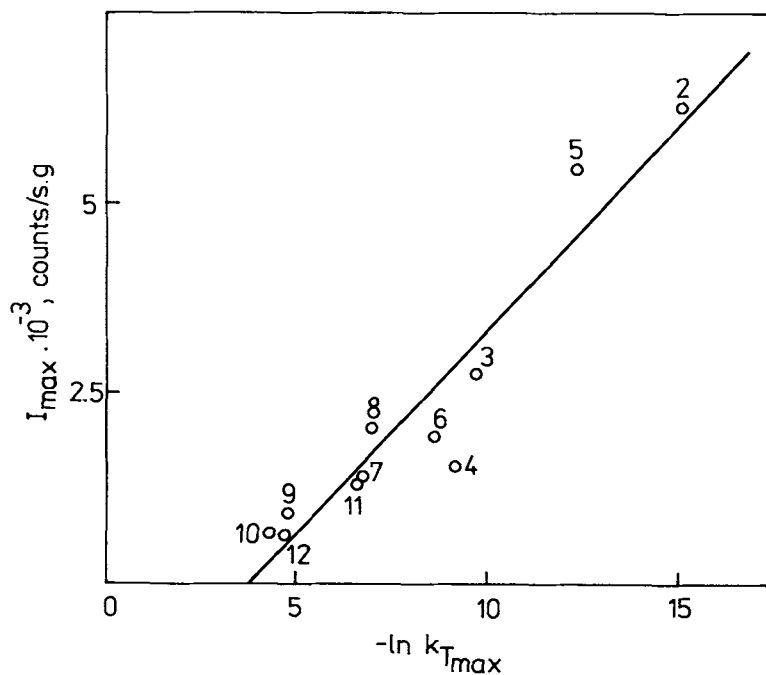


Figure 6 Correlation of maximum chemiluminescence intensity determined from nonisothermal experiments and the rate constants (in logarithmic scale) $k_{T_{\max}}$ determined for the first step of decomposition of epoxide into volatile products. T_{\max} is the temperature of the maximum of nonisothermal chemiluminescence record (Table I). The numbers of samples are given in the Table VI.

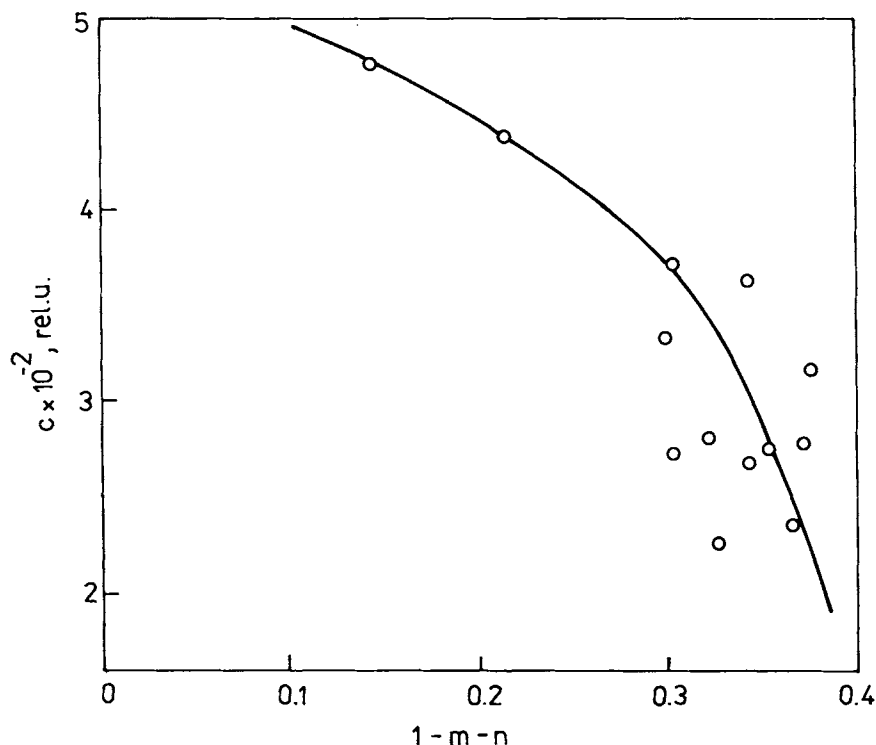


Figure 7 Correlation of relative concentration of paramagnetic particles in carbon residues from epoxides modified with phenylglycidyl ethers and relative amount of residual char $1 - m - n$ (Table VI).

exists only with the amount of residual char following the nonisothermal thermogravimetry run up to 500°C at the rate of heating 10 deg/min; the lower amount of carbon residue formed in epoxide degradation, the higher is the concentration of paramagnetic particles.

CONCLUSIONS

Chemiluminescence-time records of epoxide alone and that modified with phenyl glycidyl ethers revealed that the light emission falls from initial value monotonously to low levels of intensity. The luminescence intensity is influenced by both T_g and thermal stability of epoxide, so that the higher T_g or higher thermal stability brings about higher intensity of light emission and vice versa.

The method of nonisothermal chemiluminescence appears to bring the supplementary information on the mechanism of the light production during the oxidation of polymers.

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REFERENCES

1. A. Tcharkhtchi, L. Audouin, and J. Verdu, *J. Polym. Sci.*, **31**, 683 (1993).
2. B. L. Burton, *J. Appl. Polym. Sci.*, **47**, 184 (1993).
3. L. Audouin-Jiráčková and J. Verdu, *J. Polym. Sci., Polym. Chem. Ed.*, **25**, 1205 (1987).
4. L. Zlatkevich, in *Chemiluminescence Techniques in Solid State Polymer Research*, L. Zlatkevich, Ed., Marcel Dekker, New York 1989, p. 135.
5. N. C. Billingham and G. A. George, *J. Polym. Sci., Polym. Phys. Ed.*, **28**, 257 (1990).
6. G. A. George, *Dev. Polym. Degrad.*, **3**, 173 (1981).
7. L. Matisová-Rychlá, Z. Fodor, J. Rychlý, and M. Iring, *Polym. Degrad. Stab.*, **3**, 371 (1981).
8. N. C. Billingham, E. T. H. Then, and P. J. Gijsman, *Polym. Degrad. Stab.*, **34**, 263 (1991).
9. M. Celina and G. A. George, *Polym. Degrad. Stab.*, **40**, 323 (1993).
10. L. Rychlá, I. Chodák, J. Rychlý, and J. Bussink, *J. Appl. Polym. Sci.*, **49**, 1887 (1993).
11. O. Horák, J. Eichler, J. Dufek, and J. Melichárek, *Angewandte Makromol. Sci.*, **165**, 79 (1989).
12. J. Melichárek and O. Horák, *Plasty a kaučuk* (in Czech) **26**, 110 (1989).

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