

Photochemical Degradation of *N*-Substituted Polyethylenimines

Dedicated to the Memory of the late Professor Ichiro Sakurada

Georges SMETS and Leo RAEYMAEKERS

Laboratory of Macromolecular and Organic Chemistry,
K. Universiteit Leuven, B-3030 Leuven, Belgium

(Received January 16, 1987)

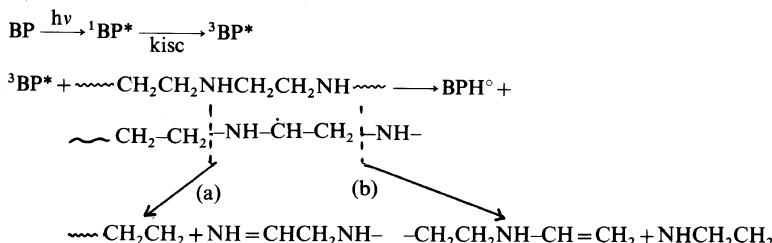
ABSTRACT: The degradation of *N*-substituted polyethylenimines (PEI) in the presence of benzophenone (BzPh) as photoinitiator has been studied in function of the branching of PEI and of the *N*-substitution by methoxycarbonylmethyl $\text{CH}_3\text{OCOCH}_2-$ and by phenyl groups. The reaction kinetics were followed by viscometry of the polymer solutions in dimethylsulfoxide and expressed in terms of S , the number of main chain scission, and, in the cases of copolymers, in terms of L , number average of linkages. The rate constants of chain scissions of branched PEI are one-third higher than those of linear PEI. Copolymers of EI and *N*-methoxycarbonylmethylethylenimine prepared by substitution of 1-PEI with methyl chloroacetate have apparent rate constants k_{app} , which decrease with the degree of substitution x and can be expressed by $k_{app} = (1-x)k_d + xk_a$ where k_d and k_a are the rate constants of chain scission and chain addition respectively. In the case of copolymers of *N*-phenyl EI (M_1) and *N*-methoxy-carbonylmethylpropylenimine (M_2), k_{app} depend on the composition of the copolymers ($r_1 = 0.86$; $r_2 = 0.53$) and on the monomer dyad distribution.

KEY WORDS Photochemical Degradation / Kinetics / Substituted Polyethylenimines /

The degradation of polyethylenimine (PEI) in the presence of benzophenone (BzPh) as photoinitiator results from the abstraction by the triplet excited state BzPh of α -hydrogen atoms with respect to the amino nitrogen, and subsequent β -chain scission of the polymeric

radicals (Scheme a).

In linear PEI (*l*-PEI) all the hydrogen atoms are equivalent and the resulting main chain scission proceeds uniformly following paths (a) and (b) with decrease of molecular weight.



Some data about that degradation were already reported previously.¹ In the present paper the influence of chain branching of PEI on this degradation will be first considered in

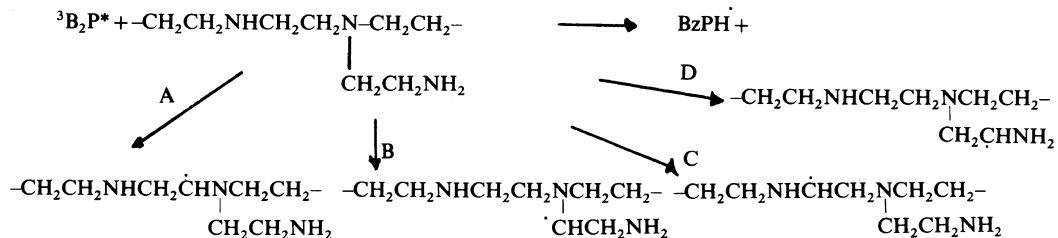
comparison with *l*-PEI; afterwards the influence of the nitrogen substitution in *l*-PEI by methoxycarbonylmethyl groups $\text{CH}_3\text{O}-\text{CO}-\text{CH}_2-$ and by phenyl groups will be examined.

It is indeed assumed that the differentiation between the hydrogen atoms may not only affect the rate of reaction but also modify fundamentally its course.

LINEAR AND BRANCHED PEI

Branched PEI (*b*-PEI), as obtained by cationic polymerization of ethylenimine, is already a typical example of *N*-substituted PEI.

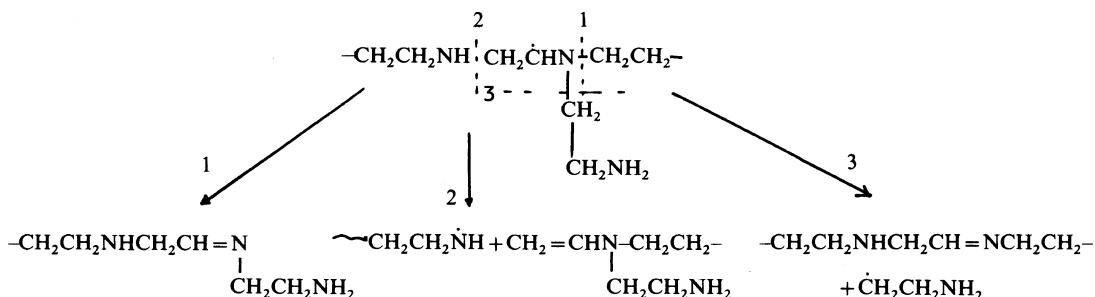
It is well known that it contains only 40% secondary amino groups, (of which 25% belong to the main chain and 15% are present in the side chain), besides 30% primary and 30% tertiary amino groups. For *b*-PEI the degradation may proceed through several pathways depending on the nature of H-atoms which are abstracted and the structure of the resulting macroradical



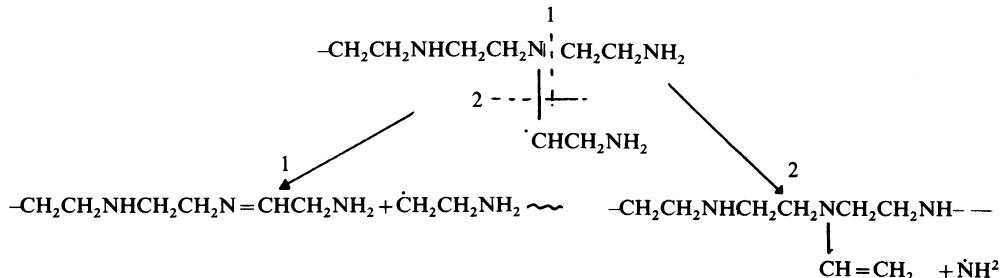
Considering the overall structure of *b*-PEI, and taking into account that the rates of H-abstraction in aliphatic amines follow the order tertiary > secondary > primary amines¹ paths A, B, C have to be considered, while

path D is of secondary importance. On dismutation the corresponding macroradicals undergo main chain scission, except when the side chain is broken off (reactions A₃ and B₂).

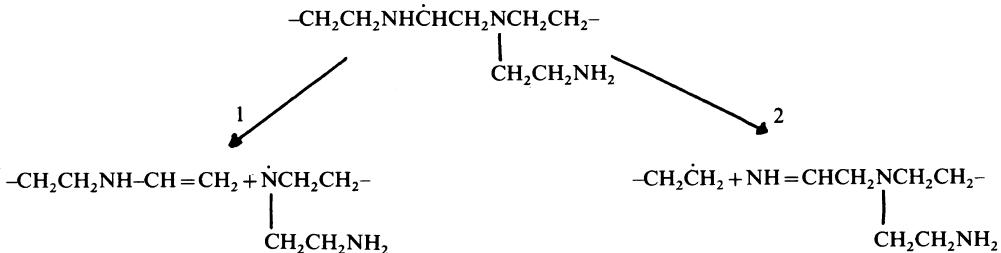
Following path A



Following path B



Along path C



Path D would only be responsible for cut off side chains. The degradation kinetics have been followed viscometrically by measuring the change of solution viscosities during the irradiation; they are expressed in terms of number average chain scissions

$$S = \frac{\bar{X}_{n_0}}{\bar{X}_n} - 1 \equiv \frac{\bar{M}_{n_0}}{\bar{M}_n} - 1 = \frac{(\eta)_0^{1/a}}{(\eta)^{1/a}} - 1 \quad (1)$$

In this equation \bar{X}_{n_0} , \bar{M}_{n_0} , and $(\eta)_0$ are respectively the number-average degree of polymerization and molecular weight, and the intrinsic viscosity at time 0, while \bar{X}_n , \bar{M}_n , and (η) are the same after time t of irradiation, a is the exponent in the Kuhn–Mark–Houwink equation; it was determined experimentally for both *l*- and *b*-PEI (see Experimental). Assuming a random degradation, one has equation 2² which on combination with equa-

$$\frac{1}{\bar{X}_n} = \frac{1}{\bar{X}_{n_0}} + kt \quad (2)$$

tion 1 gives

$$S = \bar{X}_{n_0} kt \quad (3)$$

By plotting the number of chain scissions against time, one obtains a linear diagram going through the origin. The slope divided by \bar{X}_{n_0} gives an “apparent” rate constant. Figure 1 illustrates such plots of S in function of the time in the presence of the same concentration of benzophenone ($4.28 \times 10^{-3} \text{ mol l}^{-1}$) at different PEI concentrations of both *l*-PEI and *b*-PEI; the temperature of irradiation was 50°C . In both cases the k -values decrease with increasing polymer concentration on account of

the large excess of PEI (from 0.1 to 0.6 M) as compared to the benzophenone concentration (2 to $4 \times 10^{-3} \text{ M}$). The variation of k_{app} can be represented by a very simple linear equation $k = k_0 - K(\text{PEI})$ where k_0 is the extrapolated degradation rate constant at $\text{PEI} \approx 0$. As expected these k_0 -values depend from the absorbed light intensity I_a as can be seen from Table I. As can be seen from this table, the experimental rate constants of chain scission of *b*-PEI are about one-third higher than those of *l*-PEI. Their energy of activation is respectively

$$Ea_1 = 12.1 \text{ kJ mol}^{-1}$$

$$\text{and } Ea_b = 18.8 \text{ kJ mol}^{-1}$$

The quantum yields of chain scission

$$\varphi_{\text{cs}} = \frac{C_2}{\bar{M}_{n_0}} \frac{dS}{dt} \frac{I}{I_a}$$

vary parallelly to dS/dt and is also function of the PEI concentration. Their values are represented in Figure 3.

In conclusion of this comparison between linear and branched PEI it must be stated that the differences although relatively small, are nevertheless significant, especially if one considers that in *b*-PEI only the amino groups of the main chain contribute to chain degradation.

N-SUBSTITUTED LINEAR PEI

Linear polyethylenimine has been substituted by reaction with methyl chloroacetate.

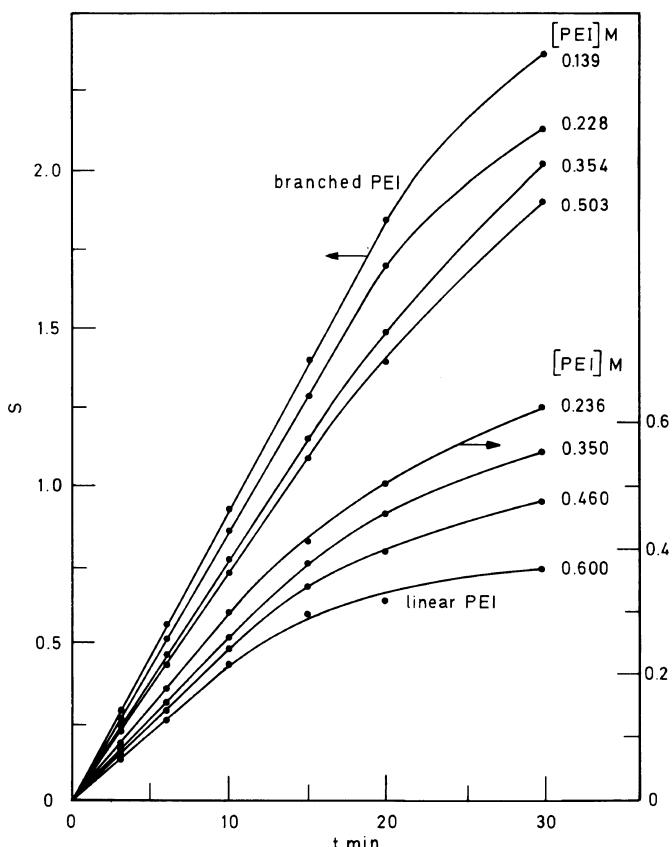
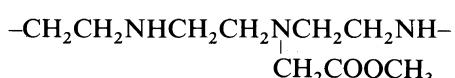


Figure 1. Degradation of linear and branched PEI. Variation of number of chain scission S with time of irradiation; dependence on PEI-concentration. $\bar{X}_{n_0} = 120$ for linear PEI; 245 for branched PEI.

Different degrees of substitution have been obtained, and the resulting polymers are actually copolymers of ethylenimine and *N*-methyloxycarbonylmethyl ethylenimine (MOCM-EI) with following structure



As for the preceding case, the degradation was followed by viscometry of the dilute solution in the course of irradiation. In the present case the molecular weights were calculated assuming $K = 6.7 \times 10^{-5}$ (as for *l*-PEI) but a equal to the unity, taking account of the more extended chain than for *l*-PEI by introduction of the bulky substituent. The four

copolymers were obtained starting from the same *l*-PEI ($\bar{M}_n = 4700$) and consequently have all the same degree of polymerization ($\bar{X}_{n_0} = 110$). The irradiations of the copolymers were carried out at 40°C in dimethylsulfoxide solution in the presence of 4.28×10^{-3} mol l⁻¹ benzophenone. The amine concentration was kept constant and equal to 0.246 mol l⁻¹. It was found quite surprisingly that the viscometric behavior of the copolymers differs considerably. At low degree of substitution x , the copolymer still degrades but to a much lower extent than pure *l*-PEI. At high values of x (0.43 and 0.63), the solution viscosities increase with the time of irradiation (Figure 4).

Therefore the variation of viscosity was

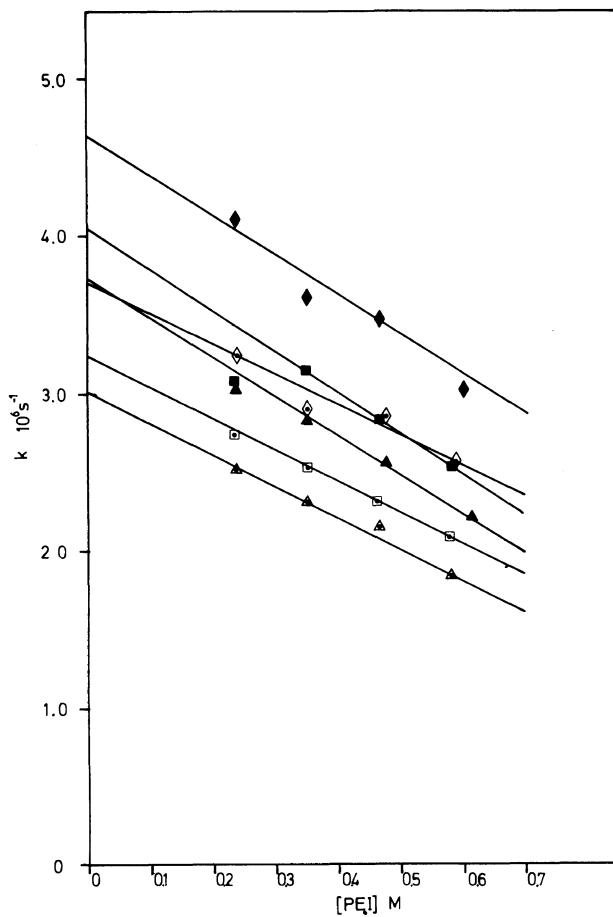


Figure 2. Variation of k_{app} with the *l*-PEI concentration. Determination of k_o : \triangle , 30°C; \square , 40°C; \diamond , 50°C. Open symbol, $[BzPh] = 2.14 \times 10^{-3}$ M; black symbol, $[BzPh] = 4.28 \times 10^{-3}$ M.

Table I. Determination of the kinetic parameters of degradation of linear and branched polyethylenimines

I_a $\text{mol l}^{-1} \text{s}^{-1}$	T $^\circ\text{C}$	k		k_o/I_a	
		10^6 s^{-1}		Linear	Branched
		Linear	Branched		
3.42×10^{-5}	30	3.00	3.46	8.8	10.2
	40	3.24	4.45	9.4	13
	50	3.70	5.36	10.8	15.7
4.23×10^{-5}	30	3.62	4.34	8.6	10.3
	40	4.06	5.64	9.6	13.3
	50	4.64	6.62	11	15.5

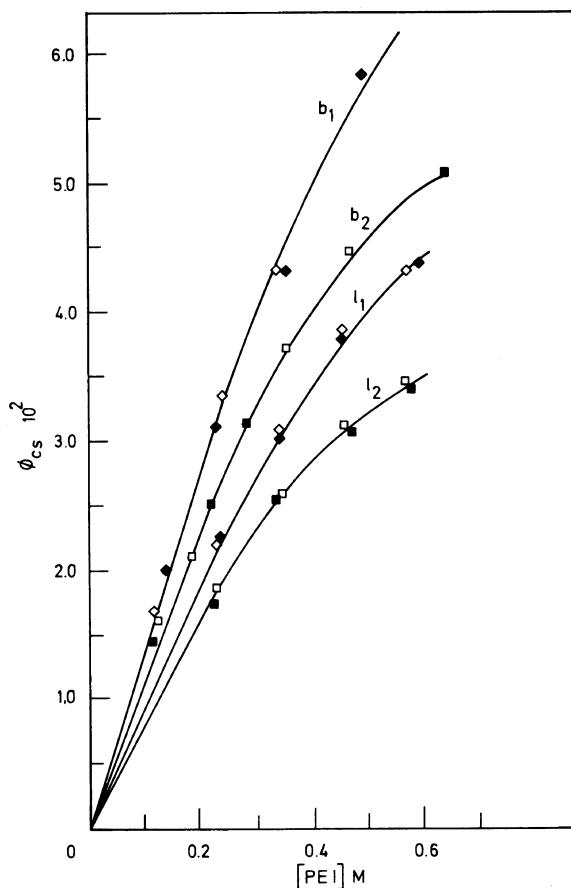
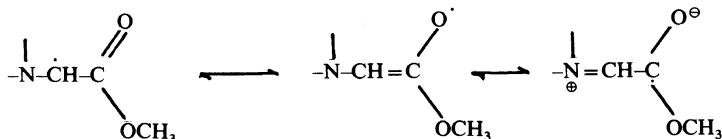


Figure 3. Variation of ϕ_{cs} with PEI concentration: \square , 40°C ; \diamond , 50°C . Open symbol, $[\text{BzPh}] = 2.14 \times 10^{-3} \text{ M}$; black symbol, $[\text{BzPh}] = 4.28 \times 10^{-3} \text{ M}$. l_1 and l_2 , linear PEI; b_1 and b_2 , branched PEI.

expressed in terms of L , being the number average of linkages, *i.e.*, the number of chain scissions (decrease of L) minus the number of newly formed additional linkage B (increase of L)

$$L = S - B = \frac{\bar{X}_{n_0}}{\bar{X}_n} - 1 = \frac{(\eta)_0}{(\eta)} - 1 = k \bar{X}_{n_0} t$$

In order to interprete these experimental results, it is admitted that hydrogen abstraction in the methylene group of the substituent creates captodative resonance stabilized radicals, which on combination cause an increase of molecular weight and consequently of solution viscosity



By plotting $\Delta(\eta)/(\eta)$ against the time of irradiation, one obtains again linear diagrams with a slope equal to $k_{app} \bar{X}_{n_0}$ (Figure 5). The

experimental data's are summarized in Table II.

It is assumed that k_{app} can be expressed by a

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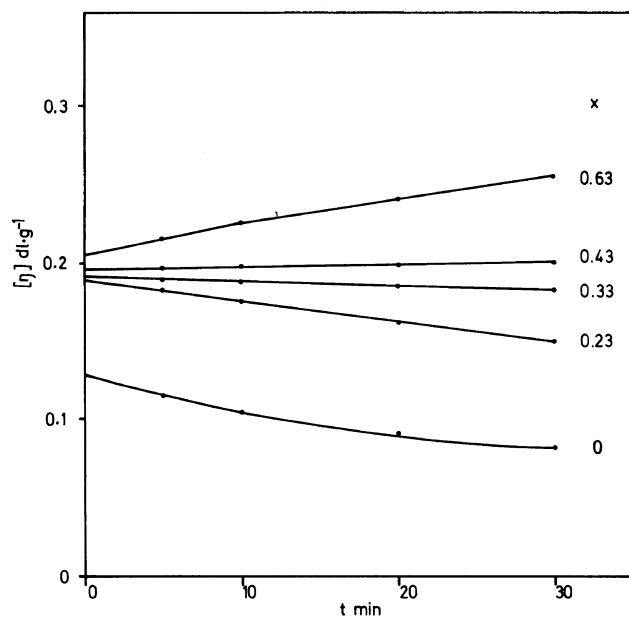


Figure 4. Variation of (η) with time of irradiation for *l*-MOCM-PEI at different degree of substitution X : (Amine) = 0.246; (BzPh) = 4.28×10^{-3} M; $T_{irr} = 40^\circ\text{C}$; MOCM is $\text{CH}_3\text{OCOCH}_2^-$.

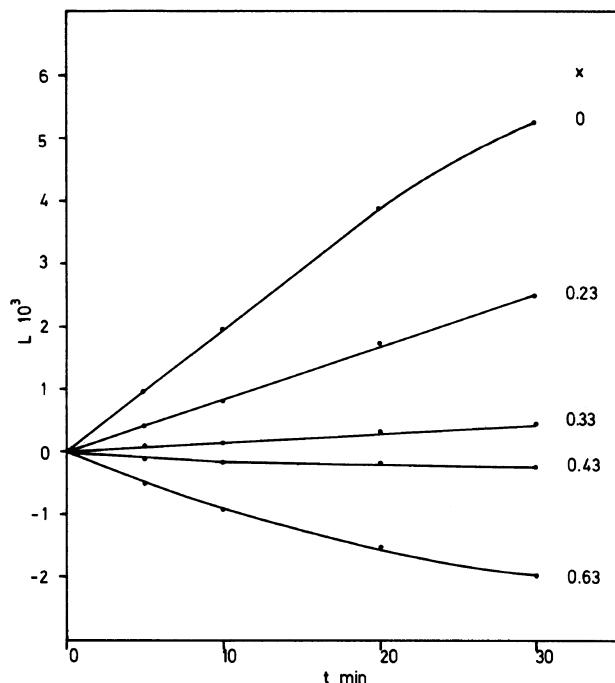


Figure 5. Variation of $\Delta(\eta)/(\eta)$ with time for *l*-MOCM-PEI of different degree of substitution X .

Table II. Degradation of linear *N*-(methoxycarbonylmethyl)_x PEI's ($t_{\text{irr}} = 40^\circ\text{C}$; $\bar{X}_{n_0} = 110$; $(\text{BzPh}) = 4.28 \times 10^{-3}$ M)

X	\bar{M}_{n_0}	C_2 g dl ⁻¹	$k_{\text{app}} \bar{X}_{n_0}$ 10^5 s^{-1}	k_{app} 10^7 s^{-1}
0	4.700	1.036	33.3	30.5
0.23	6.550	1.391	13.3	12.1
0.33	7.340	1.480	3.7	3.3
0.43	8.140	1.700	-2.5	-2.3
0.63	9.720	1.939	-16.7	-15.2

linear equation in function of the degree of substitution x , following the equation

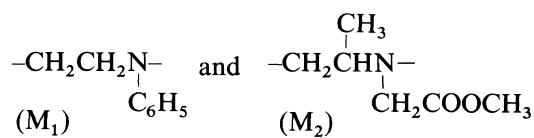
$$k_{\text{app}} = (1-x)k_d + xk_a = k_d - x(k_d - k_a)$$

where the first term corresponds to main chain scissions (k_d) as for *l*-PEI, while the second term refers to the addition (k_a) of the stabilized side chain radicals. On the basis of this equation, the diagrams of the experimental k_{app} 's in function of x give indeed straight lines with an extrapolated value k_d and a negative slope equal to $(k_d - k_a)$. At 40°C $k_d = 2.6 \times 10^{-6} \text{ s}^{-1}$ and $k_a = 4.2 \times 10^{-6} \text{ s}^{-1}$. Compared to the k_d value given above ($3.00 \times 10^{-6} \text{ s}^{-1}$) for *l*-PEI, the agreement is remarkable taking account of the uncoiling of the macromolecules on *N*-substitution, as can be seen from the $(\eta)_0$ values in Figure 4.

The overall reaction of degradation of these copolymers is thus the sum of a chain degradation reaction (with viscosity decrease) for which the unsubstituted -NH-groups are responsible, and a chain branching reaction (with viscosity increase) due to the substituted nitrogen amines.

COPOLYMERS OF *N*-PHENYL-ETHYLENIMINE AND *N*-(METHYL-OXY-CARBONYLMETHYL) PROPYLENIMINE

These copolymers present the following structural units:



They were obtained by cationic copolymerization of *N*-phenylaziridine and 1(2-methylaziridinyl)methylacetate; their *N*-phenylethylenimine (PhEI) content varied from 11 to 47 mol%. Their degradation behavior was studied in dimethylsulfoxide solution at 30°C in the presence of 4.28×10^{-3} benzophenone mol 1^{-1} ; for all systems the amine concentration was equal to 0.08 ± 0.001 mol 1^{-1} . Again the changes of solution viscosity were followed viscometrically in function of the time of irradiation. It should be noticed that the intrinsic viscosities of the four copolymers before irradiation were practically equivalent; if one assumes in first approximation that the K and a parameters in the Kuhn-Mark-Houwink equation are equal, their \bar{X}_{n_0} must also be the same; it was estimated to about 100.

From the experimental changes of intrinsic viscosities with the time, only relative rate constants will be obtained; they are nevertheless comparable to each other. For all four copolymers, the solution viscosities increase with time of irradiation. The $\Delta(\eta)/\Delta t$ values, which are the slopes of the diagrams of Figure 6, pass through a maximum around 25% PhEI, and then decrease progressively (34 and 47% PhEI). This behavior differs considerably from the preceding one in which only two main processes exist, namely chain degradation and chain branching. In the present case due account has to be taken of the internal structure of the copolymers, *i.e.*, the distribution of both monomers within the main chain. The interpretation of the data's is based on the following reaction mechanism:

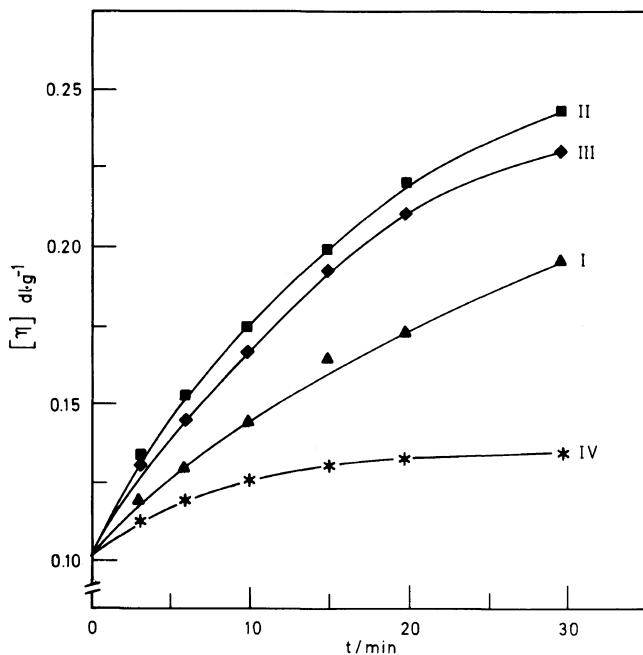
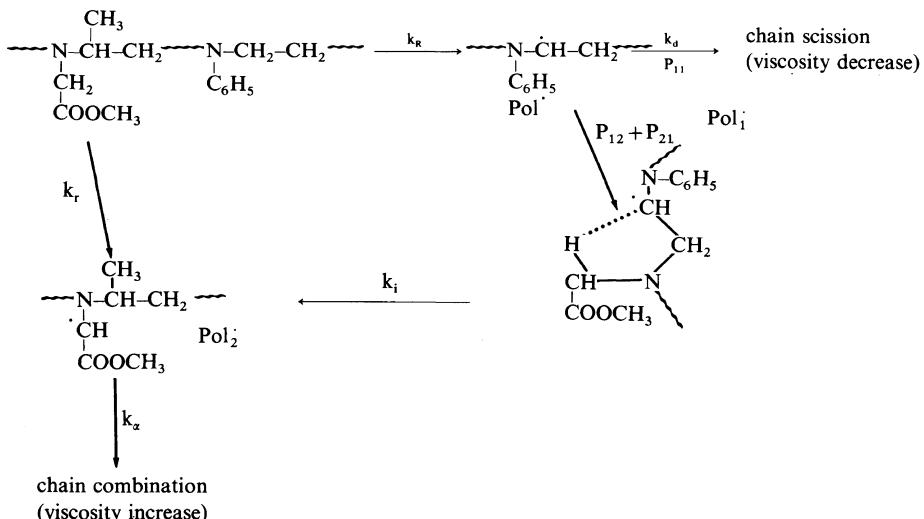


Figure 6. Variation of (η) with time of irradiation for copolymers of *N*-phenylaziridine and 1(2-methylaziridinyl)methyl acetate for different copolymer compositions (see Table III).



Aromatic tertiary amines (*N*-phenyl EI) are well known to give with excited benzophenone a photoexcited charge transfer complex within which hydrogen exchange proceeds very rapidly. It is assumed that the primary radical Pol_1^\cdot , resulting from this process, isomerizes

into the radical Pol_2^\cdot with rate constant k_i if the neighboring unit is monomer M_2 . This Pol_2^\cdot free radical is identical with that formed by direct hydrogen abstraction from the methylene group of the side chain, but the mechanism is much faster. The intramolec-

Table III. Degradation of copolymers of 1-phenylethylenimine and 1(2-methylaziridinyl)methyl acetate

Copolymer composition mole fraction <i>N</i> -phenyl EI	$\frac{dL}{dt}$	Dyad probabilities ^a		
		P_{12}	P_{21}	P_{11}
0.11	4.1	0.904	0.19	0.096
0.23	5.7	0.795	0.36	0.2
0.34	4.9	0.695	0.49	0.305
0.47	2.7	0.57	0.63	0.42

^a $r_1 = 0.86$ and $r_2 = 0.53$.

ular isomerization requires however the presence of crossed dyads of which the probabilities can be calculated on the basis of the r_1 and r_2 parameters following the classical expressions

$$P_{12} = \frac{f_2}{r_1 f_1 + f_2} \quad \text{and} \quad P_{21} = \frac{f_1}{r_2 f_2 + f_1}$$

On the other hand chain scission proceeds only through the $k_d P_{11}$ path. Assuming this reaction mechanism, the k_{app} values, which are obtained from a plot of ΔL against Δt

$$\frac{\Delta L}{\Delta t} = k_{app} \bar{X}_{n_0} = k'_{app}$$

are assumed to be expressed by

$$k_{app} = k_a f_2 + f_1 [k_a (P_{12} + P_{21}) \alpha - k_d P_{11}]$$

where f_1 and f_2 are the molar fractions of monomer 1 and 2 in the copolymer, P_{12} , P_{21} , and P_{11} the corresponding dyad probabilities and α the ratio of k_i/k_a . The parameters r_1 and r_2 were determined experimentally and found equal to 0.86 and 0.53 respectively (see Experimental).

The kinetic data are reported in Table III. From a set of 4 equations, one for each individual copolymer, the following relative rate constants are obtained $k_a = 5.2 \times 10^{-4}$, $k_d = 31 \times 10^{-4}$, $\alpha = 2.24$, and $k = 11.70 \times 10^{-4}$.

They have to be divided by the degree of polymerization \bar{X}_{n_0} (≈ 100) to obtain the corresponding absolute rate constants. The aro-

matic substitution on the nitrogen atoms of the main chain affects thus considerably the overall reaction mechanism of chain degradation and branching in substituted polyethylenimines.

EXPERIMENTAL

Linear polyethylenimine (l-PEI) was obtained by polymerization of 2-phenyl-3-oxazoline in the presence of 0.5 to 1 mol% of phenyl-3-oxazolinium perchlorate in dimethylformamide solution at 150°C during 45 h.³⁻⁶ After reaction and dilution with chloroform the polymer was precipitated in hexane (twice). The poly(*N*-benzoyl) ethylenimine was hydrolyzed at 100°C in hydrochloric acid 6*N* during 48 h. *l*-PEI hydrochloride was precipitated in methanol. Free *l*-PEI was obtained from the aqueous solution of the hydrochloride on addition of sodium hydroxide 2*N*.

Linear N-(methoxycarbonylmethyl) PEI copolymers were obtained by reaction of *l*-PEI (M_n 4700) with methyl chloroacetate in dry methanol at 35°C in presence of triethylamine during two to seven days. The degree of substitution X was calculated from the nitrogen content on the basis of a calibration curve of X in function of the percent nitrogen. After reaction methanolic solution of sodium hydroxide was added, sodium chloride precipitated and was filtered off. The filtrate purified by dialysis against pure methanol (membrane Sigma D 2273). The copolymers were isolated by freeze-drying.

Branched PEI (b-PEI) was a commercial sample of Polyscience Ltd. and was prepared by cationic polymerization of ethylenimine with hydrochloric acid as catalyst at 85°C. It was isolated from its 30% aqueous solution by evaporation of the water under reduced pressure; the polymer was purified by dissolving in ethanol and reevaporation of the solvent (twice). Its structure has been described

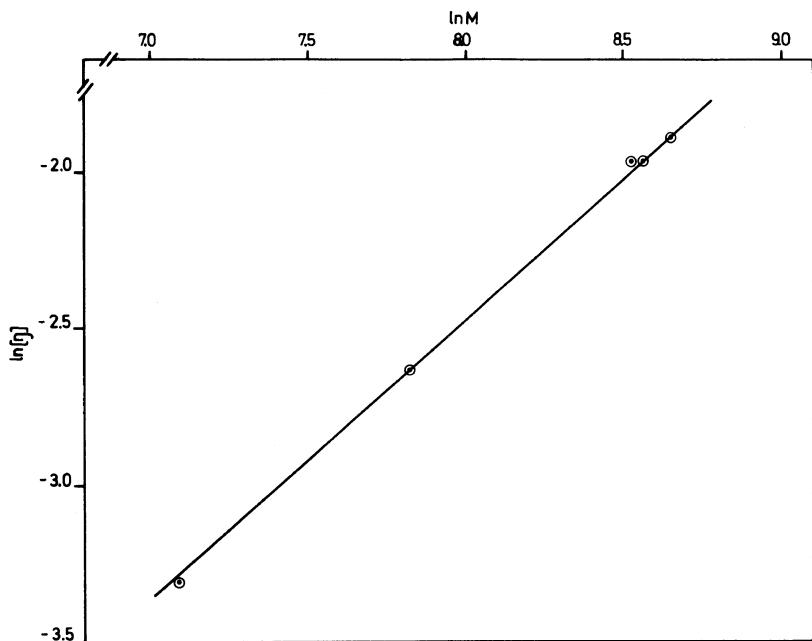
Figure 7. Determination of K and a parameters for *I*-PEI.

Table IV. Copolymerization of 1-Phenylethylenimine (M_1) and 1(2-methylaziridinyl)methyl acetate (M_2) (Temperature, -29°C ; 0.5 mol% dimethylsulfate)

Monomer mixture mole fraction f_1	Time min	Conversion	Copolymer composition F_1
0.147	80	8.5	0.234
0.299	70	11.0	0.377
0.351	65	12.9	0.414
0.526	60	12.0	0.564
0.652	40	7.6	0.673
0.742	45	11.0	Undeterm. ^a

^a Copolymer insoluble in CDCl_3 .

previously.⁷⁻¹⁰

Copolymers of *N*-phenylethylenimine^{11,12} and 1-(2-methylaziridinyl)methyl acetate^{13,14} were prepared in bulk at -29°C in the presence of dimethylsulfate as cationic initiator.

The copolymerizations were stopped by addition of a mixture chloroform-triethylamine (9:11); the copolymers were precipitated in hexane at 2–3°C, and dried in vacuum. Their

composition was determined by $^1\text{H-NMR}$ on the basis of the aromatic *ortho* and *para* hydrogens (δ 6.75) and of the methyl ester protons. The results are summarized in Table IV. From these data the copolymerization parameters were calculated using the method of Fineman and Ross.¹⁵ They were found to be equal to $r_1 = 0.86$ and $r_2 = 0.53$ for phenylethylenimine and 1-(2-methylaziridinyl)methyl acetate respectively.

Kinetics

The rate of degradation was measured in dimethylsulfoxide solution by following the decrease of dilute solution viscosity with time of irradiation in the presence of benzophenone. On the basis of the equation of Salomon and Ciuta¹⁶ intrinsic viscosities were calculated from the specific viscosities and further transformed in molecular weights following the Kuhn-Mark-Houwink equation ($\eta = KM^a$). The K and a values of this equation were determined experimentally on the basis of number average molecular weights obtained

by vapor pressure osmometry on five samples. For *l*-PEI $K = 6.7 \times 10^{-5}$ and $a = 0.89$. For *b*-PEI $K = 3.97 \times 10^{-4}$ and $a = 0.72$ (Figure 7).

In the case of the methyloxycarbonylmethyl substituted *l*-PEI-*N*-CH₂COOCH₃ the molecular weights were calculated assuming $K = 6.7 \times 10^{-5}$ (as for unsubstituted *l*-PEI) and $a = 1$ taking account of the more rigid chain resulting from the introduction of bulky substituents.

In the case of the copolymers of *N*-phenylethylenimine and 1-(2-methylaziridinyl)methyl acetate only viscosity data were used.

Acknowledgment. The authors are indebted to the Ministry of Scientific Programmation, Belgium, for its financial support.

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