The Thermo–Oxidative Degradation of Acrylonitrile–Butadiene–Styrene Copolymers during Processing as Studied by Chemiluminescence

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SYNOPSIS

The glow curve obtained upon processing acrylonitrile–butadiene–styrene copolymers (ABS), through various machines, reaches a peak at 180°C. The proper assignment of that peak has required the study of the chemiluminescence (CL) shown by related polymers such as: polybutadiene (PB), styrene–acrylonitrile copolymer (SAN), and polyacrylonitrile (PAN). Three hydroperoxide types associated with the structural units, that is, 1, 2, and cis- and trans-1,4, exhibiting CL peaks at 180, 240, and 340°C, respectively, have been identified in the PB sample. The activation energy (E_a), recorded for the hydroperoxides thermal decomposition, was 15.0 ± 1.0, 17.85 ± 0.9, 20.7 ± 0.8 kcal/mol. PAN shows a CL peak at 180°C. Its occurance is related to the color developed during the thermal treatment. That PAN peak has been attributed to the hydroperoxides generated on the acrylonitrile units neighboring the azomethinic structures. The corresponding E_a is 23.3 ± 1.0 kcal/mol. The same peak (having an identical position and E_a) has been identified with processed ABS and SAN copolymers. As is evident by CL studies, the processing induced oxidation mainly occurs within the SAN phase of the ABS copolymers, though it was also noted within 1,2 units of the PB phase.

INTRODUCTION

The sensitivity to thermal oxidative degradation of acrylonitrile–butadiene–styrene (ABS) copolymers during processing is a matter of both practical and theoretical concern. Special interest has been devoted to the hydroperoxide concentration and generation sites, since hydroperoxides represent initiation centers for the thermal or photooxidative degradation during copolymer use.[1,2]

The chemiluminescence (CL) method (oxyluminescence included) is most appropriate for the analysis of the polymer oxidative degradation during the initial stages when hydroperoxides accumulate and decompose into free radicals. Despite its obvious benefits (effectiveness, simplicity, accuracy) the CL method has not been used for the study of the polymer degradation mechanism that occurs during processing. The understanding of this mechanism may lead to a discovery of the method for improving the polymer stability to thermal oxidation.

The ABS copolymer is a complex blend consisting of a free styrene–acrylonitrile (SAN) copolymer and a SAN–polybutadiene graft copolymer. This article aims at turning the CL method to a better account for the study of the thermal oxidation of both the ABS individual components and of the copolymer as a whole.

EXPERIMENTAL

Polymer Preparation

The ABS, SAN, and polyacrylonitrile (PAN) samples were obtained through emulsion (co)polymerization initiated by potassium persulphate. The samples were coagulated, washed, dried, and then purified through cyclohexane extraction. Table I shows the copolymer compositions.

Three types of PAN samples were prepared under

Table I   The Composition of the ABS, SAN, and MSAN[a] Copolymers (Weight Percentage)

Sample	Polybutadiene	Styrene	α–Methyl–Styrene	Acrilonitrile
ABS Copolymer A	18	60	—	22
ABS Copolymer B	18	20	40	22
SAN Copolymer S–0	—	100	—	0
SAN Copolymer S–1	—	95	—	5
SAN Copolymer S–2	—	88	—	12
SAN Copolymer S–3	—	75.5	—	24.5
SAN Copolymer S–4	—	72.5	—	27.5
SAN Copolymer S–5	—	67.5	—	32.5
SAN Copolymer S–6	—	65	—	35
SAN Copolymer S–7[b]	—	50	—	50
MSAN copolymer S–8	—	21	49	30

[a] α-Methyl styrene–styrene–acrylonitrile.
[b] S–6 and PAN physical mixture up to 50% AN.

different polymerization temperatures. The white colored G type was synthesized at 65°C. The pale yellow colored H type was obtained at 75°C, and the yellow J type at 80°C.

The polybutadiene (PB) samples studied (free of antioxidant agent) were different in terms of structure (as determined by IR spectroscopy[3]) and origin, as shown in Table II. Sample D, on which ABS was synthesized, was used in oxidation experiments in the form of 1.5 mm or 200 μ thick pellicles cast from emulsion. Samples E and F were in the form of 1.5 mm pellicles cut from the polymer bulk.

Polymer Processing

The PAN powders, as obtained from synthesis, as well as a portion of each SAN powder were press molded into tablets at room temperature and 250 kgf/cm² pressure. Another portion of the SAN samples were homogenized by means of a Brabender-type plastograph at 180°C for 10 min.

The ABS powders were mixed with 0.3% Irganox

antioxidant (Ciba–Geigy) and then were processed on machines that provide for various temperature and shear stress conditions (Table III). A BG-45 Samafor extruder with one screw, a double screw LSM 3034 Leistritz-type extruder, a PR–46 Buss kneader, as well as a Berstorff-type roll mill were used.

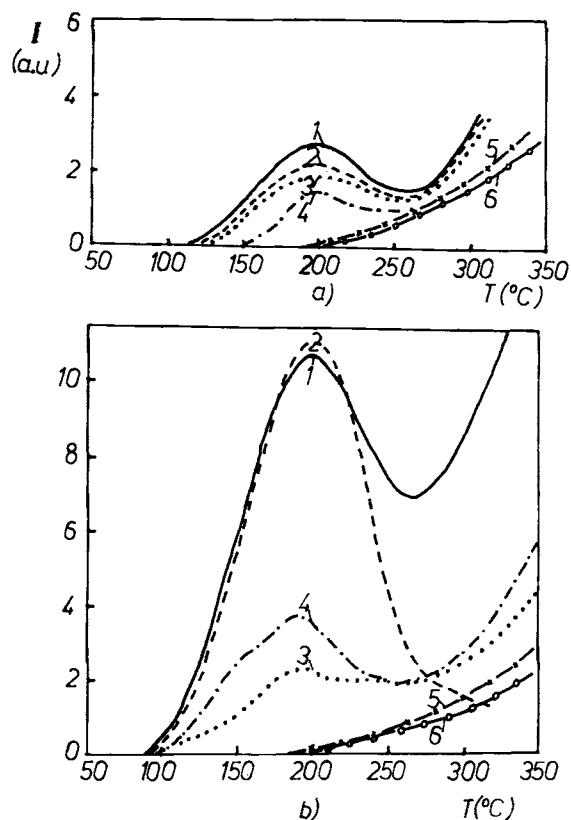## Chemiluminescence Analysis

During the CL analysis, the glow curves were recorded for 20 mg samples by means of Harshaw 3000-A thermoluminescence equipment having a spectral detection range of 350–650 nm, under a flow of purified nitrogen (2.5 L/min) at a heating rate of 2-4°C/s. The CL intensity was expressed in arbitrary units (a.u.). Each a.u. stands for a photocurrent of 7×10^{-11} A, unless different values are given.

The activation energy (E_a) of the hydroperoxide thermal decomposition was determined according to the method of the initial rise proposed by Nikol-

Table II   The Structure of the Polybutadiene Samples as Determined by IR Spectroscopy

Sample	Origin	1,2 Units (%)	1,4 Units (%) Cis-	Trans-
D	Laboratory obtained. Free-radical emulsion polymerisation.	22.8	18.4	58.8
E	Laboratory obtained. Li catalized polymerisation.	67.4	14.3	8.3
F	Buna CB-22 (Bayer). Lantanide catalized polymerisation.	0.4	98	1.6

Figure 1 The chemiluminescence intensity vs. temperature for ABS samples A (diagram a) and B (diagram b) processed on: (1) Samafor extruder, (2) Leistritz extruder, (3) Buss kneader, and (4) roll mill. The samples containing 0.1% carbon black are processed on: (5) roll mill, (6) Samafor extruder.

skii and Burkov.[4] The determination was performed strictly over the CL peak zone, at temperature rises of 10°C and a heating rate of 20°C/s.

RESULTS AND DISCUSSION

Thermomechanical stresses result in breaking molecular chains and subsequent free radicals generation at the chains' ends. Due to their high mobility and the low O_2 concentration in the melt polymer, the chain-end free radicals abstract H atoms from the labile positions of the macromolecule. As a consequence, less mobile free radicals are formed on the main chain which, due to their longer lifetime, react with the dissolving oxygen and form peroxy radicals that further generate hydroperoxides. A fraction of such hydroperoxides is thermally decomposed, leading to the formation of free radicals that contribute to the chain degradation, but again, the low O_2 concentration results in a short kinetic chain and the hydroperoxides are regenerated without too advanced a degradation. Thus, the hydroperoxide accumulation prevails over the decomposition process, which allows for convenient hydroperoxide identification after processing.

The hydroperoxides within the ABS samples exhibit a CL emission in the temperature range of 180–200°C (for heating rates ranging from 2 to 4°C/s). For the sake of convenience, we shall further deal with the lower limit. The shape and position of the CL signal (Figs. 1a and b) is the same regardless of the ABS sample (A or B in Table I) and of the processing machine used (included in Table III). If 2/3 of ST is replaced by α-methyl-styrene (MST) in sample B, an increased signal intensity is recorded, while its shape and position remain unchanged.

The ABS samples mixed with 0.1% carbon black (curves 5 and 6, Fig. 1) do not show a CL signal. The absence of the signal characteristic to hydro-

Table III   The Processing Conditions of the ABS Samples

Processing Machine	Parameters	Unit	Value	Output Rate (kg/h)	
				Sample A	Sample B
Samafor Extruder	Temperature	°C	230	3	1.5
	Rotational Speed	rpm[a]	30		
Leistritz Extruder	Temperature	°C	210	3	1
	Rotational Speed	rpm	60		
Buss Kneader	Temperature	°C	190	9	3.5
	Rotational Speed	rpm	90		
Roll Mill	Temperature	°C	190	—	—
	Rotational Speed	rpm	18/26		
	Friction Ratio		1.4		

[a] Rotations per minute.
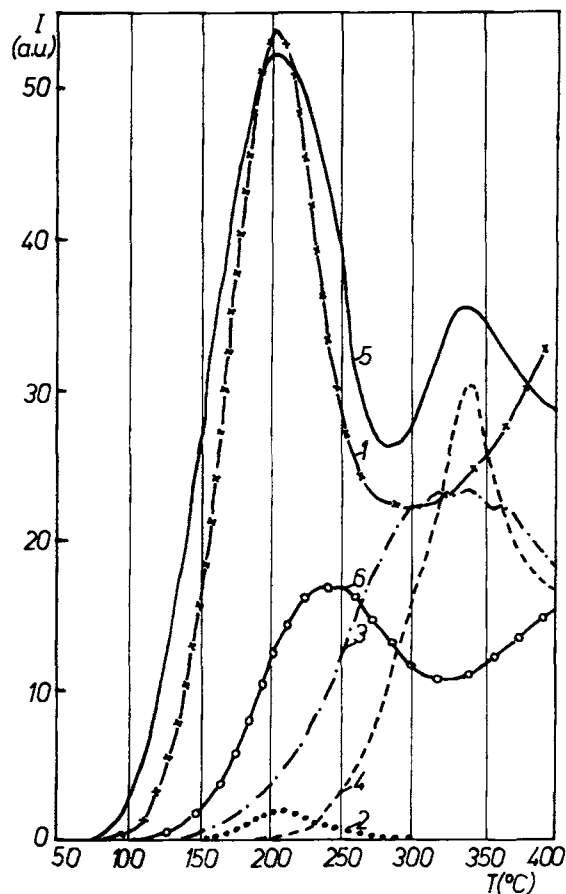
Figure 2 The chemiluminescence emission of polybutadiene samples: (1) a 1.5 mm thick pellicle of sample D stored for 8 months at 20°C, (2) as 1, aged 1 day at 140°C or 4 days at 90°C, (3) as 1, maintained 10 days at 140°C, (4) a 200 μ thick D sample, maintained 4 days at 80°C and 10 atm O_2, (5) sample E aged 1 day at 140°C, and (6) sample F aged 1 day at 140°C.

peroxides is either the result of the carbon black stabilizing effect toward the thermomechanical degradation of ABS copolymers, or that of the luminescence quenching character of the carbon black that has been previously mentioned with respect to fillers.[5] The carbon black added samples, analyzed according to Adeniyi and Kolawole,[1] have proved to be hydroperoxide free.

The simple CL signal, exhibited by processed ABS samples, may be attributed to a certain ABS component and to a certain position on the macromolecule where the hydroperoxidic group is attached.

It has been proved that the ABS thermal and photooxidative degradation occurs in the PB phase.[1,2] This conclusion has also been extended to the processing.[2] The present article deals with the

thermal oxidation of PB, PAN, and SAN copolymers as well as the thermomechanical oxidation of SAN performed in order to evaluate their sensitivity toward oxidation and to identify the labile oxidizing sites.

Hydroperoxidic Species Formed during the Thermal Oxidation of Polybutadiene

The PB samples listed in Table II have been aged in different ways and their CL signals have been recorded (Fig. 2).

No signal could be recorded with the unaged PB D-sample obtained through emulsion polymerization. After having been stored at room temperature for eight months, the sample shows a strong emission with a peak at 180°C (Fig. 2, curve 1). After a 4 day aging at 90°C or 1 day aging at 140°C the emission has almost vanished (Fig. 2, curve 2). After a prolonged aging (10 days, 140°C), or if the aging is performed in an oxygen tank at 80°C and 10 atm pressure for 4 days, no signal is recorded any longer at 180°C. Instead, another signal, wider and more complex, with shoulders at 280, 305, 330, and 340°C, is recorded with the 1.5 mm thick sample (Fig. 2, curve 3). Two or more shoulders could coexist depending on the thickness of the aged sample. With pellicles as thick as 200 μ, aged as mentioned above in the oxygen tank, only a strong signal occurring at 340°C has been recorded (Fig. 2, curve 4).

The PB sample E, containing mainly 1,2 units, but also a nonnegligible fraction of trans-1,4 units aged for 1 day at 140°C, shows a strong signal at 180°C and another strong signal at 340°C (Fig. 2, curve 5). With longer aging periods a sharp decrease of the 180°C peak is noted.

The PB sample F, consisting almost entirely of cis-1,4 units aged at 140°C for 1 day, shows a signal of mean intensity at 240°C (Fig. 2, curve 6).

According to the structures listed in Table II, the CL signals have been attributed to the hydroperoxide types included in Table IV. The values for the corresponding activation energy, determined by means of the CL technique, are also included.

The hydroperoxide having the maximum emission at 180°C is thought to be associated with the presence of 1,2 units. Since the hydroperoxide type IV, formed initially in this unit, (Scheme 1) cannot give luminescence on decomposition according to the mechanism proposed by Schard and Russel,[6] the emitting species must be formed from IV through some reaction. Two reaction courses (1) and (2) are possible, at the end of which an α–ketone–hydroperoxide, which can be responsible for the recorded

Table IV   The Hydroperoxide Species, the Temperature of Their CL Emission, and the Activation Energy of Their Thermal Decomposition

Species Formula	Temperature of the CL peak (°C)	E_a (kcal/mol)
I. H_2 =CH—C(=O)—CH(O—OH)	180	15.0 ± 1.0
II. (cis) structure with O—OH	240	17.85 ± 0.9
III. (trans) structure with O—OH	340	20.7 ± 0.8

CL,[7] is formed. The reaction course (1) prevails over (2) in view of the chain scission recorded during the PB oxidation. The reactions are analogous to those occurring during the polypropylene (PP) oxidation, where hydroperoxides are initially generated at the tertiary C atom but the CL emission occurs after α-ketone-hydroperoxides are generated.[7] Coincidence or not, the matter is still open to discussion, but the CL peak has the same shape and has been recorded at 180°C in both cases (PB and PP).

Hydroperoxides of types II and III (Table IV) are generated at the allylic C atom of the cis-1,4 and trans-1,4 units, respectively.

To put it briefly, the D-type PB on which ABS has been synthesized shows two CL signals, at 180 and 340°C, corresponding to the hydroperoxides of type I and III, respectively. Type I is evidenced after mild oxidation only and shows a great thermal la-

bility due to its low activation energy (15.0 ± 1 kcal/mol). Consequently, the CL signal, recorded at 180°C with processed ABS does not belong to PB. Type IV and, of course, type I hydroperoxides are certainly being generated during processing, but they decompose at the processing temperature.

The Chemiluminescence of the Thermo-Oxidated Polyacrylonitrile

PAN proves to be particularly sensitive to peroxidation. Immediately after its synthesis, the PAN powder shows CL signals characteristic to hydroperoxides. Strong signals have been recorded after having pressed PAN into tablets at 20°C and 250 atm (Fig. 3). A CL curve with a peak at 320°C has been recorded for the white PAN G type (Fig. 3, curve 1).
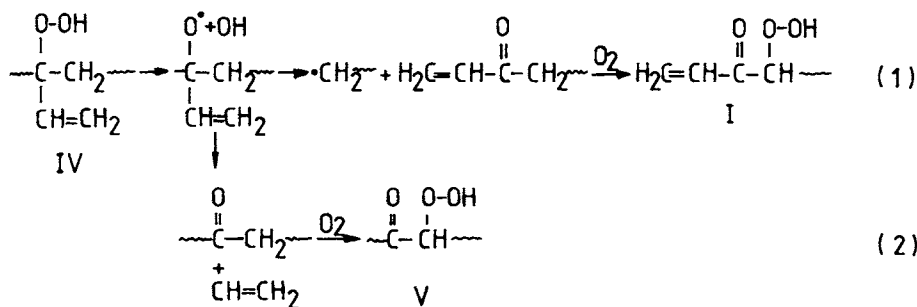
Scheme 1
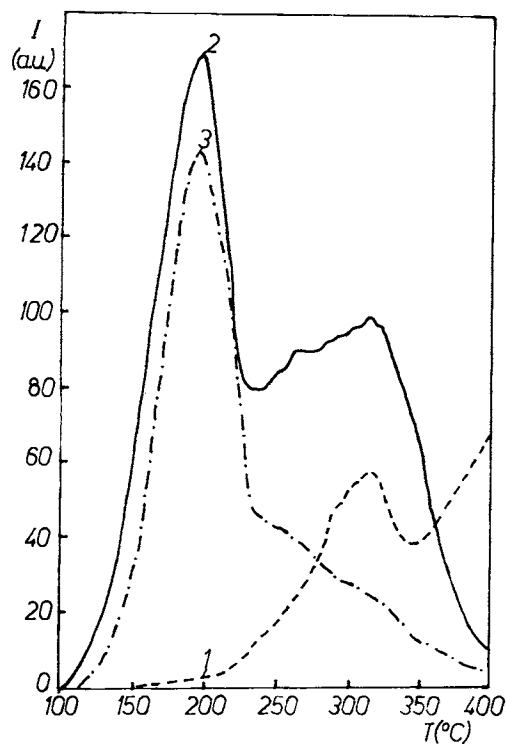
Figure 3 The chemiluminescence emission of press molded PAN samples: (1) sample G, (2) sample H, and (3) sample J.

The CL curve number 2, shown in Fig. 3, has been recorded for the light yellow H sample. The curve has two peaks, a narrow one at 180°C and a wider one at 320°C. The yellow J sample has shown a signal with a strong peak at 180°C and a residue at 320°C (Fig. 3, curve 3).

In order to make sure whether the coloration itself results in the CL emission, several runs have been repeatedly performed on the same sample (more intensely colored each time), but no CL emission has been recorded after the first run. This supports the idea that the coloring structures are not responsible for the CL signals. These signals are assumedly emitted by a species that, though connected to the color, disappears due to the high temperature at which the experiment is performed.

It is well known that the thermal coloration of PAN is a result of the formation of azomethinic structures.[8,9] The CL peak recorded at 180°C with PAN samples suggests the existence of certain azomethinic cycle-associated hydroperoxides. Thus, experimental proofs have been gathered to support the theory, assuming that the PAN cyclization occurs in the presence of oxygen and is initiated by a hydroperoxidic mechanism.[10]

Since the most peroxidizable position in PAN is

the tertiary C atom, the mechanism of hydroperoxide initiated azomethinic cyclization can be drawn as in Scheme 2.

The (nonluminescent) homolytic decomposition of the hydroperoxide VI generates OH and tertiary alcoxy free radicals that break in the α-position, forming a carbonyl group. The OH free radicals add to the nitrile group, which results in a cyclization process (species VII). This species tautomerizes generating species VIII responsible for the coloration recorded with as little as three condensed cycles.[8] At the same time, the formation of species VIII creates one more easily oxidizable position, that is, the secondary C atom next to the C=C bond. The hydroperoxide generation at this position (species IX) represents a possible explanation for the CL emission at 180°C recorded for the colored PAN samples. The high intensity of this emission (Fig. 3) could be explained by the involvement of the ketone designated by X (generated in an excited state) in the already existing extended molecular conjugation system resulting in luminescence stimulation.

The PAN easy peroxidation, followed by the generation of a species having a CL maximum emission at 180°C as well as the fact that the PB hydroperoxides, showing a CL maximum at the same temperature, are thermally unstable and cannot be identified after aging at temperatures exceeding 140°C, lead to the assumption that the hydroperoxides identified in the processed ABS sample belong to the AN units of the SAN copolymer.

The Chemiluminescence of Processed SAN

The CL signals of SAN and MSAN samples listed in Table I have been recorded. The SAN samples pressed into tablets exhibit a CL signal at the same temperature as PAN (180°C). The signal intensity increases with the increasing AN content of the SAN copolymer (Fig. 4).

In order to have the SAN samples treated as during processing, a Brabender-type plastograph has been used to homogenize them at 180°C for 10 min. Increased CL signals have been also recorded with the increased AN content in the SAN copolymer (Fig. 5). The CL intensity is a linear function of the AN content for samples homogenized on the plastograph but changes slope around 30% AN (0.457 mol fraction) for samples oxidized during press molding (Fig. 6). This particular AN content corresponds to an almost equimolecular copolymer structure generated during the synthesis within the azeotrope mixture. A brief assessment of the copo-
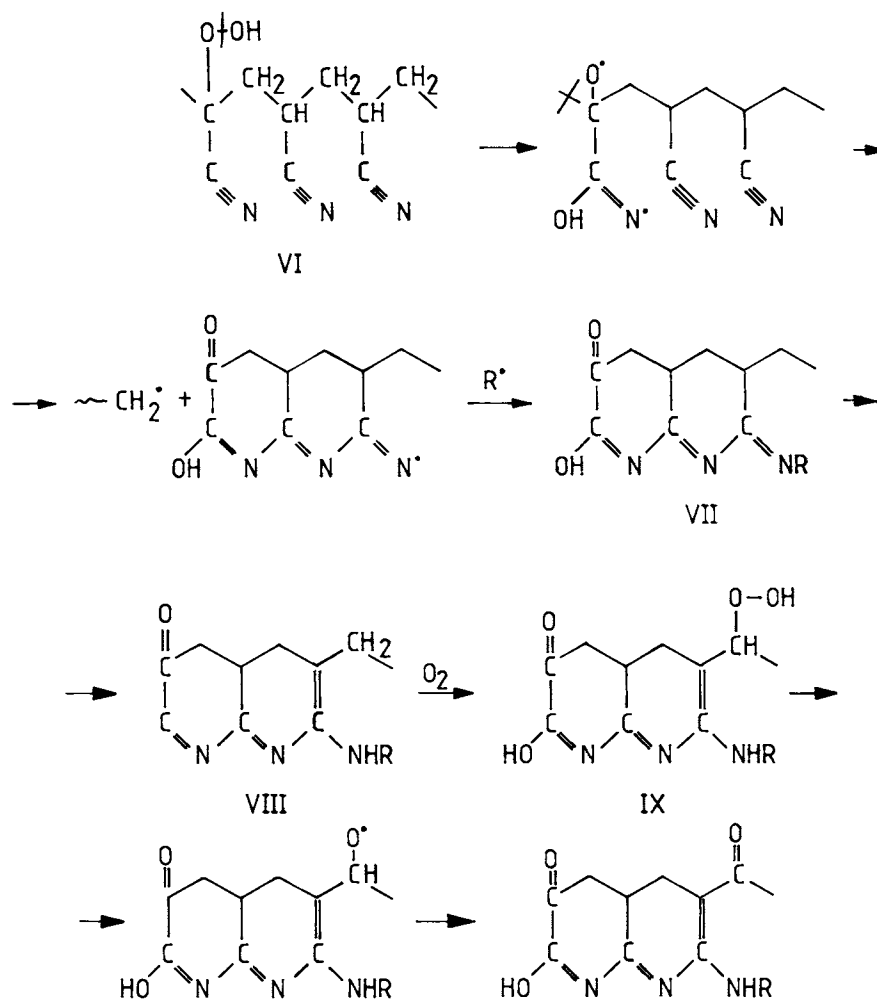
Scheme 2

lymerization process reveals an occurrance proba-
bility of 3% for the AN—AN sequences.

As a result of the oxidation process taking place
during the tablet pressure molding of SAN with more
than 30% AN, adjacent hydroperoxide or microdo-
mains of increased hydroperoxide concentration
could be formed, which may favor their interaction
during the decomposition and result in increased
luminescence intensity.[11]

Figure 6 shows that the CL intensity recorded
lies by the line drawn for the SAN samples having
more than 30% AN, for reasons that are still un-
known.

The polystyrene sample (S–0, Table I), homog-
enized by means of a plastograph under the same
conditions as SAN, does not exhibit a CL signal
(Fig. 5). It has been proved, however, that during
the SAN processing, acetophenonic groups are gen-
erated,[12] which indicates the presence of hydroper-

oxides associated with the tertiary C atom of the
styrene units. These hydroperoxides are not lumi-
nescent because of their structure.

If about 2/3 of the ST in the SAN sample is re-
placed by MST, the CL signal characteristic of SAN
hydroperoxides is recorded as well but with a much
higher intensity (Fig. 5, curve 7). This shows the
MST sensitizing effect exerted upon the oxidation
of MSAN and ABS type B copolymers. An expla-
nation of this effect is provided further on. The $^{\cdot}CH_3$
free radicals, generated through the scission of the

thermally labile $CH_3 \overset{\mid}{\underset{\mid}{-C-}}$ linkage, contribute to

the increased frequency of the abstraction acts of
the H atoms belonging to the tertiary C atoms of
the AN units. Consequently, an increase in the
amount of free radicals that can bind O_2 has taken
place.
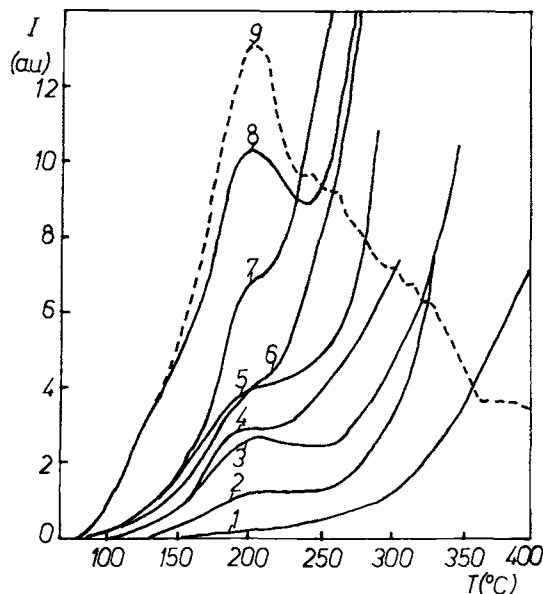
Figure 4 The chemiluminescence signal of the press molded SAN samples S-0 to S-7, having different acrylonitrile content: (1) 0% (pure polystyrene), (2) 5%, (3) 12%, (4) 24.5%, (5) 27.5%, (6) 32.5%, (7) 35%, (8) 50%, and (9) PAN signal 10 times attenuated.

Table V shows the activation energy for the PAN, SAN, and MSAN hydroperoxide decomposition as compared to that recorded for the hydroperoxides
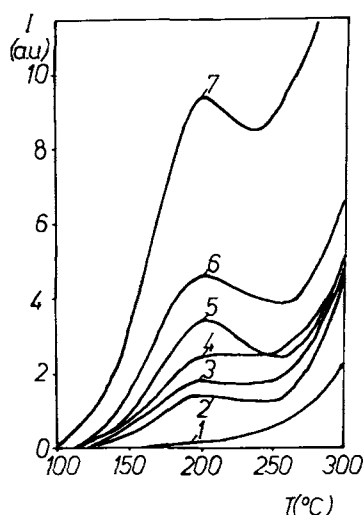
Figure 5 The chemiluminescence signal of plastograph homogenized SAN samples S-0 to S-7 having different acrylonitrile content: (1) 0%, (2) 5%, (3) 12%, (4) 27.5%, (5) 35%, (6) 50%. Curve (7), the MSAN S-8 sample of 30% AN.
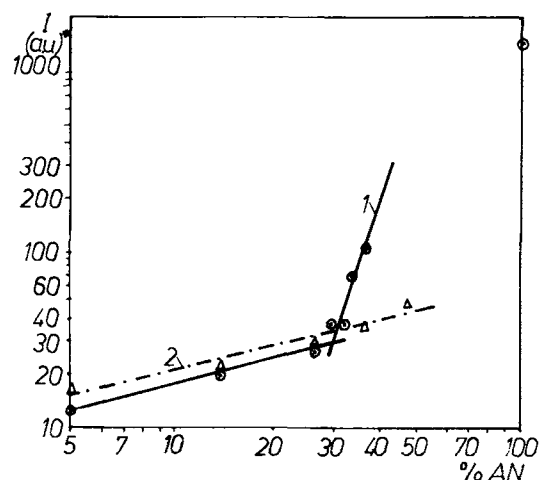
Figure 6 The chemiluminescence intensity of the SAN samples as a function of the acrylonitrile content: (1) press molded, (2) homogenized on Brabender plastograph at 180°C for 10 min. ×1 arbitrary unit = 3.5×10^{-12} A.

in type A ABS, determined from the 180°C signal. It can be seen that the activation energy recorded for the SAN and ABS hydroperoxides is almost equal to the corresponding values recorded for PAN hydroperoxides and exceeds the value recorded for PB hydroperoxides (Table IV). This is the proof of the major oxidation process occurring in the SAN phase of the ABS copolymers.

Such a result, apparently contrary to the results gathered so far,[1,2] may be explained as follows. Processing induced shearing phenomena occur in the continuous SAN phase and not in the dispersed PB phase (0.1-0.3 μ), which is thus protected. Although the phenolic stabilizer is initially mixed with the whole mass of ABS powder, it subsequently concentrates in PB due to its affinity,[13] thus leaving the SAN phase unprotected. Obviously, the morphology of the ABS copolymer plays an important part in

Table V The Activation Energy of the Decomposition of Hydroperoxides in PAN, SAN, MSAN, and Type A ABS

Polymer	CL Peak Temperature (°C)	E_a (kcal/mol)
PAN	180	23.2 ± 1.0
SAN (30% AN)	180	21.0 ± 0.8
MSAN (30% AN)	180	17.80 ± 0.9
ABS-type A	180	22.8 ± 1.3

the oxidation of the constituent phases during processing. Further investigation will be devoted to that issue.

CONCLUSIONS

Three hydroperoxide types have been identified in polybutadiene. They are associated to the allylic C atom of the 1,2 and cis- and trans-1,4 units. The polybutadiene hydroperoxides (formed through a degradation process starting in the 1,2 units), which emit a CL signal at 180°C, break off easily due to their low activation energy and cannot withstand the processing stage.

The processed ABS copolymers show a chemiluminescence signal having a peak at 180°C. The signal is apparently caused by the hydroperoxides generated in the acrylonitrile units that neighbor the azomethinic structures: the activation energy for their thermal decomposition is close to the value recorded for the PAN and SAN hydroperoxides.

The hydroperoxide generation at the ABS copolymer processing mainly occurs within the SAN continuous phase as a result of the shearing process involved.

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