

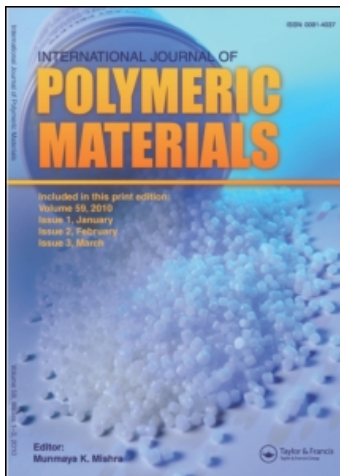
This article was downloaded by:

On: 19 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713647664>

The Current State and Some Frontiers for Development of Polymer Aging and Stabilization

G. E. Zaikov^a

^a Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia

To cite this Article Zaikov, G. E.(1994) 'The Current State and Some Frontiers for Development of Polymer Aging and Stabilization', *International Journal of Polymeric Materials*, 24: 1, 1 – 18

To link to this Article: DOI: 10.1080/00914039408028546

URL: <http://dx.doi.org/10.1080/00914039408028546>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

The Current State and Some Frontiers for Development of Polymer Aging and Stabilization

G. E. ZAIKOV

*Institute of Chemical Physics, Russian Academy of Sciences, 4, Kosygin Street,
Moscow 117334, Russia*

The problems of aging and the search for ways of stabilizing polymers continues from both the standpoint of theory and practice. This is due to major economic problems that may be successfully solved by understanding the scientific fundamentals of the polymer aging processes in different operating and storage conditions, and the effects of environmental conditions, i.e. heat, oxygen, ozone, light, penetrating radiation, corrosive liquid media, biologically active media, mechanical loads, etc.

This review provides data about the development of the theory of degradation processes and the search for ways to stabilize polymeric materials as effected in Russia and States of former USSR, mainly since 1989 till 1992.

KEY WORDS Polymer aging, stabilization, status and frontiers

It became a tradition to sum up the achievements of Soviet Science in the area of Degradation and Stabilization of Polymers by the publication of corresponding papers in the *International Journal of Polymeric Materials*. Apparently, this present review is the last of these publications. This is not due to the collapse of the Soviet Union, which has had little influence on the level of contacts between scientists representing different Republics. The main reason is completely different. It is absolute contempt of the State Authorities toward science.

Nevertheless science in our country is still alive (apparently, due to inertia), and I am trying to show this in my current review, which provides data about the development of the theory of degradation processes and the search for means of stabilization as effected in States of former USSR, mainly since 1989 until the present. Perhaps the effect of “perestroika” on Soviet science will become clear later, and we will suppose to explain its results in the next review, which we intend to present to you in 1995.

REVIEW OF RESEARCH

It is well-known that natural aging of polymers may be caused by many factors (light, ozone, heat, etc.). Recently,¹ Professors Victor B. Ivanov and Victor Ya. Shlyapintokh discovered that light-ozone aging is characterized by certain synergism. This means that the cooperative effect of light and ozone is more than a simple addition of their contributions.

It was observed during a study of the aging of poly(dieneurethanes) that cracks appear faster for the case of exposure to both light and ozone than for the case of exposure only to ozone, although the effect of light on the appearance of cracks is nil.

The synergistic effect of light and ozone is observed in both unstabilized rubbers and rubbers which contain antioxidants and light stabilizers. For example, the protective properties of the antiozonant *p*-phenylenediamine was reduced to near zero under the simultaneous action of light and ozone. This effect is also observed for light-ozone aging of the aforesaid rubbers in presence of Nitrogen containing light stabilizer. In fact, these stabilizers accelerate light-ozone aging, that is, they apparently catalyze ozone aging. On the other hand, blends of these light stabilizers with antiozonants having a physical mechanism of action, promote a synergistic antiozonant effect.

Therefore, we should emphasize two kinds of synergistic effects:

1. The synergistic effect of UV-light and ozone on light-ozone aging of polymers;
2. The synergistic interrelation of antiozonants and light stabilizers on light-ozone aging.

Evidently, both of this phenomena should be taken into account during studies of the aging of polymers and the development of effective systems for protection of polymers.

The previously proposed hypothesis of a "ketoimide" mechanism in the photooxidation of aliphatic polyamides was justified by a series of independent tests.² This mechanism is not analogous to the photooxidation of other polymers and is characterized by a new kind of kinetic regularity of variations in the concentrations of the major intermediate products. These products are ketoimide fragments of the macromolecule ($\sim\text{CONHCOCOCH}_2\sim$) and unsaturated ketones of similar structure. Both products are bifunctional: they are photoinitiators and simultaneously they contribute to transference of the kinetic chain with breakdown of the macromolecule by the alternation of the reactions of two kinds of radicals. This occurs without the effect of light.

In any case of photooxidation in polyamides a stationary concentration of the aforesaid products can be reached. In order to provide the possibility to govern the process, certain quantitative parameters should be revealed. These parameters must characterize the stationary concentrations as well as the kinetics of the process.

One of the clearest examples of the regularities obtained is the kinetics of approaching the stationary stage for the case of the effect of light on polyamide at the maximum wavelength, at which photooxidation may occur. These conditions are characterized by transference of the kinetic chain by products K and K' , of which only K (ketoimide) is a photoinitiator. The kinetic dependence of the concentrations of the products is described by the hyperbolic functions

$$K = K_{st}(\coth((F + Gt)/2))^2$$

$$K' = K'_{st} - (K'_{st} - K'_0)[(\sinh((F + Gt)/2))^{K'_{st}/G'} / (\sinh(F/2))]$$

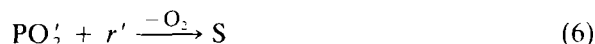
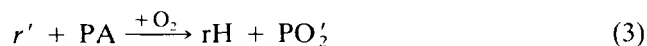
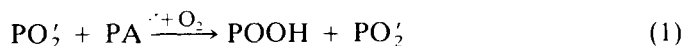
where K_0 , K'_0 , K_{st} , K'_{st} are initial and stationary concentrations of products, respectively. A , F , G , k'_5 are known parameters with known physical origins.

$$F = \text{Ln} \left| \frac{(K_0)^{1/2} - (K_{st})^{1/2}}{(K'_0)^{1/2} - (K'_{st})^{1/2}} \right|$$

$$G = -[(k_7/k_5)I_0((k_7/k_5)I_0 + 4k_2/k_6)]^{1/2} \cdot k_5/2$$

$$A = (2k'_2/k_3)[(k_3k_7I_0/k_6k_2)K_{st}]^{1/2}$$

Indexes of the rate constants correspond to the numbers of reactions indicated below.

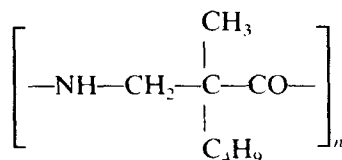


where I_0 is light transmission, PO'_2 is the peroxy macroradical $\sim\text{CH}_2\text{CONHCH}(\text{O}\dot{\text{O}})\text{CH}_2\sim$, r are low-molecular weight radicals of HO_2 or O_2^- , A , K and K' are intermediate products, B is the final product, S means breakdown of the macromolecule.

The aforesaid functional relations have not been discussed in previous studies of the kinetics of the photodegradation of polymers.

The mechanism discovered is valid for different aliphatic polyamides of industrial production and does not depend on the number of CH_2 -links. The mechanism ceases to function in the event of the substitution of H-atoms attached to the α - or β -carbon atoms by alkyl groups. The explanation may be the impossibility of

ketine formation. For example, the photodegradation of poly(3-butyl-3-methyl-azetidin)



displays completely different kinetic regularities.

Cellulose acetate (CA) is now widely used in various industries. However, because of its poor light stability, its performance characteristics deteriorate rapidly with time. Under the action of light oxidative processes, e.g. polymer photolysis, are accelerated. In spite of a wide variety of CA stabilizers, the search for new and more effective photostabilizers appears to be a very real problem.^{3,4}

A new kind of light stabilizers was developed through the mutual research of the Institute of Chemical Physics, the Institute of Elemento-Organic Compounds (both of the Russian Academy of Sciences) and the Institute of Chemistry of the Tadjik Academy of Sciences.⁵ These stabilizers are macroheterocyclic compounds (hexazocyclanes (HC)). Various types of HC derivatives of phthalodinitrile and p-phenylene diamine (conjugated HC—HC-1), as well as derivatives of phthalodinitrile and 9,9-bis(4-dianiline)fluorene (unconjugated HC—HC-2) have been investigated. To ascertain the impact of the structure of the macrocyclic stabilizer on its properties the product of linear condensation of phthalodinitrile and p-phenylene diamine also was studied. All these compounds are powders whose colors vary from yellow to brown, depending on their structure. They are compatible with CA without degrading the properties of the film at concentrations up to 5–7.5%.

The light stabilizer introduced into the composition can simultaneously act by several mechanisms, the principal ones being UV screening, inhibition and photosensitization. The contribution of UV screening to the total effect of the action of the stabilizer was calculated from the formula¹

$$i_p = D_{d+st}(1 - 10^{-D_d}) / (D_d(1 - 10^{-D_{d+st}}))$$

where D_d and D_{d+st} are the optical densities of non-stabilized and stabilized films. The coefficient i_p shows the factor by which the stabilizer decreases light absorption by the polymer. Therefore, if the effect of stabilizer is limited by UV absorption, then the rate of photodegradation must decrease by a factor of i_p in accordance with the amount of light absorbed by polymer.

The main product of CA degradation under the effect of UV irradiation is acetic acid, whose formation rate characterizes the light stability of the composition. Taking into account the coefficient i_p , the total effect of the increase in light stability (A) is determined as the ratio of the rates of the appearance of acetic acid in CA without (W_0) and with (W_{st}) stabilizer

$$A = i_p W_0 / W_{st}$$

The data on the influence of the structure of the light stabilizer on the increase in the light stability of the composition are shown in Table I. This Table demonstrates that for all light stabilizers A is less than 1. This is the justification for the statement that the stabilizers act both as UV screens and photosensitizers.⁶ The highest photostabilizing activity is manifested by the photosensitizer. This could be explained by the fact that this compound has two resonance states, of which one contains free amino groups. Evidently these amino groups act as photostabilizers of CA photodegradation, which agrees with data reported in Reference 1.

By its light stabilizing activity, HC-2 is superior to the photosensitizer III but inferior to HC-1. This is probably associated with the shorter length of the conjugate chain and a decrease in the aromaticity of the system in the case of HC-2.

The most effective stabilizer is HC-1. Its high light stabilizing activity can be caused by either UV screening or inhibition effects. To determine the possible contribution of the inhibition mechanism to the total effect of the action of HC-1, the kinetic parameters of the photooxidation have been measured for non-stabilized CA and for CA stabilized by HC-1. These parameters are the chain oxidation $k_p[\text{PH}]/k_t^{-1/2}$ and the quantum yield of the photoinitiation P_i .

The results obtained are presented in Table II. The HC-1 stabilizer does not affect the parameter of CA chain oxidation. In other words it is not an inhibitor, which interacts with polymer radicals. The quantum yield of photoinitiation P_i sharply decreases in the presence of HC-1. This shows that the transition from pure CA to the stabilized CA leads to a change in the mechanism of photoinitiation. The stabilizer becomes the initiator instead of CA. Essentially the decrease in P_i in the presence of HC-1 is responsible for the total light protection effect. This

TABLE I

Dependence of the total increase in light stability of the composition on the structure of the stabilizer
(Concentration of the stabilizer in CA is 5 wt %)

Stabilizer	$A = \frac{W_0}{W_{st}} \cdot i_p$
HC-1	0.40
HC-2	0.31
III	0.21

TABLE II

Kinetic parameters of the photooxidation of CA at 25°C in dry air

Sample	$k_p[\text{PH}]/k_t^{-1/2}$ (mol/l · s) ^{1/2}	P_i
CA without stabilizer	$(2.2 \pm 0.2) \cdot 10^{-4}$	0.100
CA with 5 wt % stabilizer HC-1	$2.4 \cdot 10^{-4}$	0.004

explains the action of HC-1 when introduced into CA as a UV screen and a photosensitizer.

The evidence for the light stabilizing activity of HC-1 is shown in the data (Table III) for the reduction of viscosity loss of CA solutions in acetone after UV irradiation of films stabilized by HC-1 and one of the most effective stabilizers (5, 10, 12-trisulphonamide carbazole (TSC)). The light stabilizing activity of HC-1 is higher than that of TSC and the protective effect of HC-1 begins to manifest itself at relatively low concentrations (0.5%). The maximum effect of light stabilization is reached at HC-1 concentration of 3% of the CA mass. Noteworthy is the high stabilizing effect of HC-1 under prolonged irradiation.

The photostabilizing activity of polyhexazocyclanes (PHC) was investigated in CA and in polycaproamide (PA). The photostabilizing activity of PHC was estimated by the change in the viscosity of 5% CA solutions in dimethylformamide (DMF) and of PA solution in formic acid. The results obtained (Table IV) show, that PHC possesses properties of a stabilizer of photooxidative degradation both for CA and PA, and its photostabilizing activity with respect to CA is higher, than with respect to PA. The comparison of data presented in Tables III and IV prove that the light stabilizing activity of HC-1 is higher than the similar activity of PHC.

TABLE III
Comparative data on the light stability of CA films

Stabilizer	Concentration	Retention of reduced viscosity of 0.5% CA solutions after irradiation time t_i	
		$t_i = 24$ h η_i	$t_i = 48$ h η_i
—	0.0	13	7
TSC	0.5	25	
	2.0	79	
	5.0	70	
HC-1	0.5	79	
	2.0	92	
	3.0	94	66
	5.0	93	

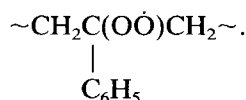
TABLE IV
Comparative data on the light stability of CA and PA films stabilized by PHC ($t_i = 24$ h)

Stabilizer	Retention of viscosity of 0.5% solutions after irradiation	
	CA (in DMF) η_i	PA (in HCOOH) η_i
—	13	64
PHC-1	25	73
PHC-2	76	76
PHC-3	47	80

Further search into novel and effective photostabilizers for CA and PA should be conducted among macrocyclic aromatic compounds with conjugate chains and a structure approaching planar. An important property of all macrocyclic stabilizers is their ability to dye textile materials into yellow-red-brown colours, depending on the nature and the amount of stabilizer.

Professor M. Ya. Mel'nikov and co-workers carry out research, which deals with processes of photoradical degradation. In other words, with degradation which is caused by photochemical reactions of radicals and ion-radicals.

Studies of the mechanism of photodegradation of polystyrene show⁷ that breakdown of the main chain of the polymer is a consequence of the photochemical reaction of peroxy radicals. They are generated from the macroradicals of



The quantum yield of this reaction, accompanied by the appearance of hydroxy radicals, is equal to 10^{-3} at 77 K. Quantum yields of the photochemical reactions of other kinds of radicals (cyclohexadiene radicals or ones obtained from cyclohexadiene radicals) are in the range of $10^{-1} - 2 \cdot 10^{-5}$. Later reactions cause the migration of the free valence and the appearance of low-molecular products, all without breakdown of the main chain.

The photochemical reactions of anion-radicals in polymers of polyvinylacetate, polymethylmetacrylate, polyacetals, aliphatic polyurethanes cause the breakdown of functional groups and the appearance of low-molecular products, of which the effect on the aforesaid polymers, MWD, is negligible.⁸ The mechanism of the dissociation of different kinds of peroxy radicals has been proved in studies of their photochemical reactions.⁹ When grafted to the surface of activated silicon dioxide, these radicals dissociate at the O—O bonds primarily by the reaction of photolysis. The further course of the process is defined by the behaviour of the pair (R $\dot{\text{O}}$ + O). Particularly, the energy of the reverse reaction (250 kJ/mol) is more than the energy of C—O bonds, thus leading to the possibility of the breakdown of the vibrationally-excited radical



The efficiency of this excited radical must be correlated with the strength of C—O bond in peroxy radicals. These results are essential for an explanation of many data about the photoradical degradation of polymers.

In recent years, the effect of continuous-wave laser radiation of argon (514.5 nm) on the degradation of polyvinylalcohol (PVA), polyacrylonitrile (PAN) and polyimide (PI) were reported by Doctor L. Kalontarov in References 10–14. It was shown that the process of degradation was defined by the kinetics of accumulation of the products of thermal breakdown of the macromolecules as a result of the absorption of laser radiation. Two stages of the degradation may be noted on the basis of the typical dependence of the absorption of polymer films during

the period of laser radiation. They are the stage of activation with a period of t_a and the stage of a sharp increase of absorption followed by its damage (the period of t_b). This type of destruction is caused by the reverse positive relation between the heating of the polymer and the absorption of radiation in the area of degradation. The phenomenon of the sharp increase of absorption and temperature under laser degradation is called the light thermochemical instability (TCI). Therefore, the first and the second stages of laser degradation are called the activation stage and the propagation stage of TCI, respectively. The periods of these stages (t_a and t_b) depend on the power of the radiation (P_a).

The non-stationary model of TCI has been reported in Reference 10, where the expression for the period of activation has been given

$$t_a = (2T_0/\alpha\gamma)^{1/2} \exp(\alpha/2) \quad (8)$$

where $T_0 = \mu P_a + T_a$ is the temperature of the sample in the area of radiation by the propagation of TCI, T_a is the ambient temperature, μ is the coefficient, $\alpha = E/RT_0$, $\gamma = (P\varepsilon v)/(\rho c_p S)$, E and v are the activation energy and the exponent multiplier, ρ and c_p are the density and the heat capacity of the polymer film, P is the power of radiation, ε is extinction. The expression (8) is in agreement with experimental data on laser-induced degradation of PVA.

It was observed^{12,13} that the period of the second stage of TCI is defined by the rate of the TCI propagation and governed by the expression

$$t_b = \tau_0 \exp(-\beta T_0) \quad (9)$$

where τ_0 and β are constants. Most interesting is the variation of the dependence $t_b(T_0)$ in comparison to $t_a(T_0)$. The expression (8) was obtained on the basis of the assumption of validity of the Arrhenius law for the rate constant of the chemical reaction. The agreement between the experimental data of t_a and those obtained from (8) confirms that this is a correct application of the Arrhenius law for the initial stage of the laser-induced degradation, when changes of the temperature and concentration of products of degradation are small. A qualitative TCI model¹³ demonstrates the nonstationary character of the process of the propagation of instability. This cause a violation of the Arrhenius kinetics and the corresponding non-activation energy dependence of the period of propagation of TCI on temperature T_0 .⁹

The effect of laser radiation on non-linear thermochemical processes in polymers has been discussed in Reference 14 and 15. There have also been observed the effects of self-stabilization of the laser-induced dehydration of PVA, propagation of the waves of degradation, oscillative dynamics in the elimination of volatile products, etc.

The study of the effect of Nd:YAG continuous laser radiation (1064 nm) on the painted PVA films is discussed in Reference 16 and 17. It was shown by the method of mass-spectrometry, that the composition of volatile products is the same for thermal and laser-induced degradation, while the relative contribution of specific components may be different. The conclusion about the thermal mechanism of

laser-induced degradation was drawn, however the dynamics of laser-induced and the usual thermal degradation are different. It was shown in Reference 17, that the stability of painted PVA to laser radiation depends both on the nature of the dye involved and on the way of its interaction with polymer.

The evaluation of the efficiency of antioxidants in polymer systems is a problem, to which solution is of great importance from both theoretical and a practical point of view. The attempts to find a general parameter defining the activity of antioxidants (for, example, redox potential or rate constant of reaction of inhibitor with substratum of peroxy radical— k_7) are still unsuccessful. The main reason for this is the complicated character of the consumption of antioxidants, which includes a number of reactions of the radicals themselves, as well as of the molecular products of the transition of radicals.

One of the possible ways to evaluate the efficiency of antioxidants is the direct study of their consumption. Corresponding research is carried out by E. L. Shanina.^{18,19} Kinetic curves of consumption of antioxidants reflect the diversity of processes which exist in polymers. A comparison of the results corresponding to different initial concentrations of antioxidants enable the evaluation of the contribution of accessory reactions, while the comparison of the kinetic curves in inert media enable evaluation of the contribution of inhibitor oxidation. The later process significantly reduces the efficiency of antioxidants and is, apparently, the main source of secondary reactions.

Let us consider two examples of the study of the kinetics of the consumption of the phenolic antioxidants in polymer systems.

The first is the kinetics of consumption of two industrial stabilizers in isotactic polypropylene. In the conditions of the experiment (130°C, air) it was shown, that the stabilizer of "Irganox 1076" is consumed slower than "Topanol CA." The lower efficiency of the later stabilizer could possibly be explained by its structure, which facilitates the secondary reactions. The experimental data justify this assumption. The kinetics of the consumption of "Topanol CA" corresponding to the initial concentration of the stabilizer of 10^{-2} mol/kg was compared with the kinetics of the consumption of this stabilizer for the case of an initial concentration of $2 \cdot 10^{-3}$ mol/kg. In spite of the 5-times increase in the initial concentration, the kinetic results were almost unchanged. This effect follows the consumption of the stabilizer in secondary processes.

The second example is concerned with the kinetics of the consumption of the stabilizer "Nonox WSP" in PE/PP blend, which is used in the cable industry. Relatively high rates of consumption of the stabilizer enabled monitoring the consumption of stabilizer, even, at 60°C. The higher rate for the consumption of the antioxidant is a feature of the polymer blend. Each of the component polymers is characterized by lower rates, but the blend is characterized by a higher rate of the oxidation in comparison with either of its components.

The data obtained enable an evaluation of the period of antioxidant consumption. The accuracy of this evaluation is not high, but it may be the first step for the further evaluation of applications in stabilizing polymer materials.

There are different reasons for the appearance of higher organic acids in polymers. They can be produced as the polymer is oxidized or may be involved in the

polymer as a component of the antioxidant blend. Unfortunately, the contribution of higher carboxylic acids in the processes of the oxidation of polyolefins have not been sufficiently discussed.

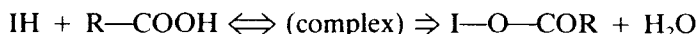
The studies of Professor Shlyapnikov and co-workers^{20,21} deals with the influence of a higher carboxylic acid (stearic acid) on the efficiency of antioxidants of 2,2-methylene-bis(4-methyl-6-tert-butyl-phenol) (MBP) and 3,5-ditert-butyl-4-hydroxyphenylpropionic diethylenglycol acid ester (phenosan-28) in the process of oxidation of molten isotactic polypropylene (PP). The induction period of PP oxidation is markedly reduced as the acid concentration increases. This is for a constant concentration of antioxidant. Thus, we can observe the effect of acid and antioxidants in opposite directions.

The dependence of the induction period (τ) on initial MBP concentration is characterized by a negligible effect of a low concentration of antioxidant on the retardation of oxidation, while certain a critical concentration promotes a sharp increase in the MBP efficiency. The MBP critical concentration depends on the amount of acid and goes up from 0.0012 mol/kg (absence of acid) to 0.0053 mol/kg (concentration of stearic acid is 0.06 mol/kg). It is assumed that the acid cause the appearance of complexes or compounds of bonded antioxidants, which do not contribute to the retardation of oxidation. This leads to an increase in the critical concentration. The behaviour of a single molecule of antioxidant remains the same. Another explanation could be the esterification of phenol by stearic acid.

To justify last assumption Shlyapnikov heated PP samples, which contained both phenol and stearic acid in a nitrogen atmosphere at 200°C. Only slight consumption of phenol in the presence of stearic acid is observed. The rate of consumption goes up as the initial concentration of the acid increases.

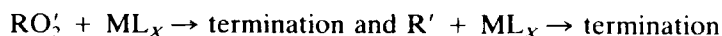
The calculation shows small increase of the effective rate constant due to the consumption of phenol in its reaction with acid. A sharp reduction in the induction period and the critical concentration of antioxidant is not obtained.

The phenomena observed may be explained by a mechanism, which proposes the reversible formation of complexes between the phenol and the acid as well as a slow reaction between these compounds. That leads to the formation of an ester. The contribution of the latter is essential only for the later stages of the process:



the possible formation of phenol-acid complexes is justified by IR-spectra of solutions of these compounds in carbon tetrachloride. The mixture of MBP with stearic acid exhibits bands at 3840 cm^{-1} (single OH-groups) 3520 cm^{-1} (associated OH-groups), of which absorption is reduced, while absorption of the single OH-group of acid (3540 cm^{-1}) shifts.

The inhibiting properties of the chelates of heavy metals is one of research interest to Dr. V. Vinogradova.²²⁻²⁴ Deactivation of alkyl and peroxy radicals through the application of chelate complexes of different metals is the general goal of this research. Chelate groups of different structure and of different substituent ligands in the reactions of



have been considered. Besides well-known compounds (ditiocarbamates, salicylaldiminates) novel compounds have been investigated. They contain tetrachelate groups and S,N- or S,O-chelate groups.

The effect of chelate additives was studied for (i) autooxidation of model systems of polyoxiethylene solutions, their low-molecular analogs, hydrocarbons and ethers; and (ii) styrene during its polymerization in solution. It is shown that the inhibiting activity of chelates is related to their structures and, consequently, properties of radicals, which propagate the oxidation chain. This means that the activity is different for different substratums of oxidations. Ethers and hydrocarbons are characterized by the inhibitory activity only of those chelates, of which chelate groups contain sulphur or selenium. Moreover, high activity of some of them (chelates of copper and of antimony) is due to reasons which do not depend on the nature of substratums. One feature of the oxidation of polyoxiethylene of different molecular weights is the high inhibitory activity of compounds with tetrachelate groups and sulphur-containing chelates. The later chelates are characterized by more than one-order of magnitude increase in their activity. Data obtained indicate the possibility of repeated termination of polyoxiethylene oxidation chains due to the contribution of chelates of copper and cobalt and/or products of their transition. The structures of the ligands in most of the chelates does not contain functional groups which could cause proton transfer followed by deactivation of peroxy radicals RO_2^{\cdot} (OH- and NH-groups in phenols and amines). Consequently the inhibition follows a redox-mechanism of interaction between peroxy radical and the chelate group.

The comparison of the rate constants of the chain termination due by the interaction between RO_2^{\cdot} and chelates to their potentials of half wavelength of electrochemical oxidation and the reduction of the chelates shows a correlation between antiradical activity of the chelates and their oxidation potential and reduction of the metal complexes. This correlation demonstrates that peroxy radicals, which are responsible for the oxidation of polyoxiethylene, possess dual redox properties. The interaction with aralkyl radical R^{\cdot} (polymerization of styrene) is highest for sulphur-containing chelates of copper (II) and iron (III). Cobalt analogs of these chelates also possess inhibitory activity. Some properties of catalysts were revealed for copper chelates containing atoms of nitrogen and oxygen in the chelate group.

The comparison of the redox properties of chelates with their activity in processes of inhibition of polymerization of styrene show two mechanisms of interaction of chelates with radicals R^{\cdot} , which are:

- (i) redox-mechanism, accompanied by the reduction of copper (II) to copper (I);
- (ii) mechanism of proton transference from a ligand activated in the chelate.

The study of the stabilization of linear polyorganosiloxanes is carried out at the Department of Chemistry of Tbilisi State University by Professor Khananashvili and co-workers. The means of stabilization is insertion of cyclic fragments both along the main chain and on the side chains.

It is known that the insertion of various cyclic fragments into the linear chains of polydimethylsiloxane is followed by the breakdown of the spiral structure of the macromolecule with corresponding changes in the physicochemical properties of the polymers. For example, variation of the organic substuent on the silicon is

sufficient for wide variation of the glass temperature of polymer. There are many ways to structurally modify polysiloxane chains through the insertion of centers of branching, mono- and polycyclic fragments. Therefore, polysiloxanes are very appropriate for the development of novel polymer materials with a wide variety of physicochemical properties.

The main goal of the current research is to study the degradation of polydimethylsiloxane containing 1,3- and 1,5-organocyclotetrasiloxanes, 1,5-organocyclopentasiloxanes, 1,5-organocyclohexasiloxanes, 1,7-organocyclohexasiloxanes.

The main stage of the degradation of these copolymers starts at temperatures which are 80-100°C higher than the corresponding temperatures of linear polydimethylsiloxane.²⁵⁻²⁷

The same result was achieved through the insertion of cyclocarbosiloxanes and fragments of bis-siloxoindanes.^{28,29}

Cyclic fragments located along polymer chains prevent propagation of the chain during polymer decomposition. This could be the explanation for the stabilization of copolymers through the aforesaid insertion of cyclic fragments into the linear chains of dimethylsiloxane.

The synthesis of novel kinds of copolymers, which are intermediate between linear and branched polymers, was reported in References 30 and 31. The synthesis of copolymers, containing organosiloxanes in the side chain were discussed in References 32 and 33.

It was shown, that an increase in the volume of cyclic fragments is followed by a reduction in the thermooxidative stability of the copolymers. In addition, it was proved that the effect of cyclic fragments inserted along the main chain and in the side chains is the same.

Among other polymer blends, blends with elastomers possess some specific properties, which are caused by changes in their structure during treatment. Specifically this is related to the process of vulcanization. Besides the factors which influence the structure of polymer blends, the mechanism of action of crosslinking agents is of great importance. There is an induction period for the formation of the spatial network, the appearance of chemical bonds in or between phases of components, and also differences in crosslinking of phases themselves which are caused by different chemical structures of the elastomers and crosslinking agents. The reactions of the later with each of the elastomers may be the same or different. For this reason Sperling divided the network structures of elastomer blends into special group.

The aforesaid assumption can be justified by results, which were obtained in the Laboratory of Professor Shershnev (Moscow Institute of Fine Chemical Technology). Blends of cis-1,4-polyisoprene (PI) with chlorbutylrubber (CBR) have been studied. Two systems of crosslinking were applied. The first of them (thiuram and sulphur) is characterized by a high rate of crosslinking, while the induction period is negligible. The features of the second (sulphenamide with sulphur) are relatively high rates for the second stage of crosslinking and the essential induction period. Because parameters of solubility of PI and CBR are close to each other and equal to 16.44 and 15.42 (J/cm³)^{1/2}, respectively, intensive dispersion of the components is observed. In contrast a rougher dispersion of the blend of polychloroprene (PCP)

TABLE V

The influence of crosslinking systems on the structure of elastomers and their vulcanizers

Composition of blend	Average diameter of particles of dispersed phase μ		
	Raw blend	Vulcanizer	
		Sulphenamide	Thiuram
PI/CBR, 7/3	0.48	1.19	0.82
PCP/CBR, 7/3	0.7	network	1.18

with CBR could be explained by differences in their parameters of solubility (25.32 for PCP). The general feature of blends of these elastomers is more a homogeneous distribution of particles of the dispersed phase of the raw blends compared with vulcanizers. This is well-illustrated by Table V.³⁴

The effect of the change of the phase structure depends on the induction period of crosslinking, i.e. on the period of visco-elastic state. The increase of the diameter of CBR particles in PI matrix is more essential for crosslinking systems which contain sulphenamide and is characterized by an induction period of 15–20 min. An increase in the particles of CBR in PCP matrix is followed by the formation of their continuous structure.

The dependence of the rupture strength on the composition of PI/CBR blend has a maximum at 7/3. This coincides with the minimum of the average value of the Gibbs energy for this composition³⁵ and can be explained by the appearance of elastomer-elastomer emulsion.³⁶ The maximum of the rupture strength depends on the type of crosslinking system. For example it is higher for the sulphenamide group, than for the thiuram group. Co-vulcanization is of decisive importance which is evident, for example, for the sulphenamide system in comparison with the thiuram system, in which there is no co-vulcanization.

The factors contributing to the stabilization of phase structures of elastomers blends could be summarized as follows:

- the nature of elastomer components;
- their ratio in blend;
- the conditions of mixing and vulcanization;
- the mechanism of the action of crosslinking agents;
- formation of chemical bonds;
- the depth of crosslinking in the phase and in the matrix.

The stabilization of the protective properties of polymer coatings in biochemically active media is important for many scientific and practical reasons.

The problem is that the protective properties of coatings depend on many physicochemical factors, of which the most essential are:

- (i) adhesion
- (ii) kinetics for increases in internal stresses, which are of the same order of magnitude as adhesion and cohesion;

- (iii) barrier properties of coatings;
- (iv) inhibiting properties of polymers in respect to electrochemical processes;
- (v) polymer stability with respect to components of the products and wastes of the food industry.

The main research interest of the polymer laboratory of the Institute of Biotechnology and of the head of this laboratory, Professor Rosantsev, is to develop elementoorganic compounds with aromatic conjugation in order to apply them as additives for the stabilization of the structure and protective properties of polymer coatings.³⁷

The influence of these additives on the structure of epoxy coatings, internal stress, other physicochemical properties has been studied for conditions of synthesis and utilization.

By means of NMR-spectroscopy and electronic spectroscopy the mechanism of the effect of insertion of these additives on polymer structure has been shown. The mesomorphic level of the structural order provides a contribution of the functional groups in adhesive and cohesive interactions.

Table VI illustrates data dealing with the influence of organo-silicon additives on the stability of the properties of epoxy coatings in aggressive media.

For the stabilization of properties of coatings in acid media additives were developed on the basis of derivatives of piperidineoxyl (PPO).³⁸

It was shown, that they decelerate bulk and interface processes of oxidation.

The loading of a small amount of PPO in the area of corrosion leads to an improvement in the metal's stability to corrosion due to the adsorption of molecules of inhibitor by the surface of the metals and a corresponding change in the kinetics of the electrochemical reactions (Table VII). The efficiency of the inhibitor is estimated by its stationary potential, current of dissolution and degree of protection.

$$W = (ik - ik'')/ik$$

where ik and ik'' are the currents of corrosion in the absence or in presence of inhibitor, respectively.

Table VII shows, that at 0.5–2% PPO loading in an electrolyte solution leads to a positive shift in the stationary potential, 8-times reduction of the maximum currents of dissolution and an increase in the degree of protection.

TABLE VI

Properties	Without additives	With additive
Internal stress, MPa	4.0	1.5
Adhesion, relative units: initial	1	1
After degradation: in 3% solution of lactic acid	4	2
In 1.5% NaOH solution	2	1
Impact strength, N.m. initial	5	5
After degradation: in 3% solution of lactic acid	1	3.5
In 1.5% NaOH solution	1.5	4
Durability, days in 3% solution of lactic acid	7	350
In 1.5% NaOH solution	34	400

TABLE VII
PPO effect on electrochemical parameters of RT-3

PPO content, %	Stationary potential, mV		Maximum current of dissolution mA/cm ²		Degree of protection %	
	0.5 N	5%	0.5 N	5%	0.5 N	5%
	Na ₂ SO ₄	HCl	Na ₂ SO ₄	HCl	Na ₂ SO ₄	HCl
0	-550	-600	16.7	80.0	0	0
0.5	500	-600	10.0	62.0	39	25
1.0	-450	-570	2.2	43.0	80	50
1.5	-450	-500	3.0	15.0	66	80
2.5	-450	-480	4.4	10.0	66	85
3.0	-550	-530	15.0	80.0	—	0

TABLE VIII
Parameters of the molecular weight of polyacrylamide

No.	Type of effect		Molecular weight, M · 10 ⁶			
	t, °C	Fe ⁺⁺⁺ mg/L	M _η	M _w	M _s	M _η
1	20	—	8.5	7.4	8.3	8.5
2	τ, days	—	0	0	0	0
	45		1.1	8.84	0.91	0.96
3	τ, days	10	28	28	28	28
	20		3.2	8.92	10.8	8.65
4	τ, days	10	16	10	16	16
	45		3.6	5.43	8.52	10.14
	τ, days		12	12	45	45

The same regularities have been observed for the case of loading of 0.5–1% of PPO additives in perphthalic, perchlorvinyl and epoxy coatings. Modified coatings are already applied for the protection of enterprises of the food industry.

The appearance of papers in the area of governance of stability of water soluble polymers,^{39,40} apparently, is due to the wide application of these materials by oil industry for removal of heterogeneity in oil layers.

For this purpose polymers of acrylamide are widely used. The application of polyacrylamides (PAA) to increase oil productivity has some advantages. But there are also essential disadvantages to their application, of which the main is the degradation of polyacrylamide as a result of the combined effect of high temperature, pressure, tensile stress, solutes of metals, oxygen, hydrosulphur, etc.

The study of a large number of commercial samples of polyacrylamide showed drastic changes in viscosity of polyacrylamide solutions, which becomes worse, even during the use of traditional stabilizers of ions of iron and hydrosulphur. This effect is particularly acute at high temperatures.

The reduction of viscosity of PAA solutions, particularly at high temperatures in the presence of ions of iron is caused by degradation of PAA molecules themselves followed by the reduction of molecular weight and by intermolecular processes which are more complicated. These are crosslinking, conformational changes

followed by a reduction in the volume of the polymer molecule at constant or increasing molecular weight (Table VIII). This result is consistent with data about sedimentation, light diffraction and viscosimetry. Indexes in the table correspond to the aforesaid techniques (η = viscosimetry, w = light diffraction, s = sedimentation).

Several new types of stabilizers for polyacrylamides have been studied in combination with metal deactivators. The combined application of these compounds enabled essential improvement in the viscous parameters of PAA solutions.

The effect of additives on the stability of copolymers of acrylamide with cation-monomers has been studied in order to allow application of these polymers for oil extraction and purification of oil-containing ground water. The point is that the advantages of these copolymers is reduced during the processes used for treatment and storage. Among additives, the highest stabilization activity was observed for mercaptobenzimidazole and thiourea. Copolymers, which contain 0.3 weight% of these additives, do not lose their solubility, and their viscosity is higher than the viscosity of un-stabilized copolymers.

The regularities of transport of organic and inorganic acids were reported in Reference 41. Transport features of polymers define chemical stability and fields of application for polymeric materials. The permeability of films of biodegradable polymer of poly- β -hydroxybutyrate (PHOB) to hydrochloric, formic, acetic, propionic and butyric acids has been studied at ambient temperature. The results of the study are presented in Table IX and justify the assumption that this polymer is a moderately hydrophobic polymer. This is in agreement with data obtained for measurements of water uptake. Transport parameters of the acids investigated are essential for the prediction of the rate of drug release from reservoir type systems.

In different applications, one of the processes of polymer degradation was learned during a study of copolymers of maleic anhydride and vinyl acetate. This is an example of successful cooperation between Western and Soviet scientists. The thermal degradation of MAN/VAc copolymer has been studied by thermal volatilisation analysis (TVA) at the University of Glasgow in the laboratory of Doctor Ian McNeill. The formation of conjugated double bonds and hydroxyl groups as well as the development of insolubility due to intermolecular dehydration are the most essential rearrangements occurring under isothermal investigation at 205°C.^{42,43} The behavior of the initial copolymer in the presence of water and the way in which the sorption of water is altered by controlled degradation was a secondary objective of this study.

The general conclusion regarding the thermodynamics of water uptake could be as follows. The first stage of the interaction of the copolymer with water vapor is characterized by a reversible sorption up to the equilibrium value. An increase in

TABLE IX

Permeability of 1 N acids through films of PHOB. Thickness of film = 15–20 μ . (Average values, $P \cdot 10^6$, mol·cm²/l·sec)

HCl	HCOOH	CH ₃ COOH	C ₂ H ₃ COOH	C ₃ H ₇ COOH
3.0	1.14	0.94	0.25	0.004

the activity of the water vapor causes irreversible binding of the sorbed water, rupture of chemical bonds in the copolymer with a change in its structure (hydrolysis), and finally dissolution. The critical concentration for hydrolysis is only reached in sorption at activities close to 1 (liquid phase). The general pattern of water uptake by partially degraded copolymer is the same as for the original material and the differences are in the depth of the structural changes following the point of equilibrium sorption. The residues obtained after degradation for 10 and 20 minutes are insoluble in water although some hydrolysis was observed. Degradation for 30 min. causes swelling in which the stage of irreversible sorption is restricted.

The change of the hydrophilic character of the copolymer due to different degrees of degradation was applied to system where a variation of the hydrophobic/hydrophilic balance was required, such as in the controlled release of drug.⁴⁴

Simultaneous control of the chemical structure of the polymer and of its transport properties provides good opportunities to develop polymer systems for which the required velocity of drug release can be reliably obtained.

Because space in the Journal is limited I cannot review all the research which has been done in the area of Polymer Degradation and Stabilization in the States of the former USSR. At the same time the achievements of Professor Minsker,⁴⁵ Professor Askadskii⁴⁶ and Professor Prokopchuk⁴⁹ should be mentioned here. The reader can obtain other interesting information from the papers presented in the current issue.

References

1. V. Ya. Shlyapentokh. Chemical Transformation and Stabilization of Polymers. Khimiya, Moscow (1979).
2. A. V. Dubovitskii and L. M. Postnikov, *J. Chem. Biochem. Kinetics*, 1992, in press.
3. I. Ya. Kalontarov, A. A. Stotskii, K. M. Makhkamov, N. P. Tkacheva and V. I. Sobolev, *Izvestiya VUZov. Ser. Khim.*, **19**, 1863 (1976).
4. L. E. Maksimova, V. I. Shishkina, I. Ya. Kalontarov, F. F. Niyazi and A. Abdirazakova, *Reports of Tadjik Academy of Sciences*, **13**, 713 (1980).
5. S. A. Siling, A. L. Margolin, I. Ya. Kalontarov, S. V. Vinogradova, F. F. Niyazi, Yu. V. Chaiko and Sh. S. Dzhumayev, *Acta Polymerica*, **42**, 133 (1991).
6. Yu. V. Makedonov, A. L. Margolin, N. Ya. Rapoport and L. S. Shibryaeva, *Polymer Science USSR*, **28A**, 1380 (1986).
7. M. Ya. Melnikov, E. N. Seropegina, N. I. Osokina and V. I. Pergushov, *Khimiya Vysokikh Energii*, 1992, in press.
8. M. Ya. Melnikov and E. N. Seropegina, *Radiat. Phys. Chem.*, **33**, 151 (1989).
9. E. M. Korol'kova, V. A. Radtsig and M. Ya. Melnikov, *Khimicheskaya Physica*, **10**, 41 (1991).
10. L. I. Kalontarov, R. Marupov and N. S. Abdullaev, *Khimicheskaya Physica*, **6**, 1380 (1987).
11. L. I. Kalontarov, R. Marupov and T. Shukurov, *Vysokomolekulyarnye Soedineniya*, **31B**, 33 (1989).
12. L. I. Kalontarov, R. Marupov, T. Shukurov and O. A. In, *Khimicheskaya Physica*, **9**, 294 (1990).
13. L. I. Kalontarova and R. Marupov, *Chem. Phys. Lett.*, **181**, 27 (1991).
14. L. I. Kalontarov and R. Marupov, *J. Mater. Sci.*, **26**, 5770 (1991).
15. L. I. Kalontarov, R. Marupov and A. T. Bekmukhamedov, *Makromol. Chem.*, **193**, 735 (1992).
16. L. I. Kalontarov and A. T. Bekmukhamedov, *Polymer Science USSR*, **33A**, 1986 (1991).
17. L. I. Kalontarov, R. Marupov and A. T. Bekmukhamedov, *Intern. J. Polymeric Mater.*, 1992, in press.
18. E. L. Shanina, V. A. Belyakov and G. E. Zaikov, *Polymer Degrad. Stab.*, **27**, 309 (1990).
19. E. L. Shanina and G. E. Zaikov, *Plasticheskiye massy*, 1992, in press.
20. A. P. Mar'in and Yu. A. Shlyapnikov, *Vysokomolekulyarnye Soedineniya*, **31B**, 386 (1989).
21. A. P. Mar'in and Yu. A. Shlyapnikov, *Polymer Degrad. Stab.*, **36**, 1 (1992).

22. A. B. Mazaletskii, V. G. Vinogradova and G. V. Panova, *Neftekhimiya*, **29**, 414 (1989).
23. A. B. Mazaletskii, V. G. Vinogradova and G. V. Panova, *Kinetika i Katalis*, **31**, Issue 5, 1065 (1990).
24. V. G. Vinogradova, A. N. Zverev, *Zhurnal Obshchei Khimii*, 1992, in press.
25. K. A. Andrianov, A. I. Nogaideli, N. N. Makarova and O. V. Mukbaniani. *Izvestiya USSR Academy of Sciences*, **6**, 1383 (1977).
26. S. M. Meladze, O. V. Mukbaniani and L. M. Khananashvili, *Polymer Science USSR*, **26A**, 250 (1984).
27. O. V. Mukbaniani, N. A. Koyava and L. M. Khananashvili, *Polymer Science USSR*, **27A**, 2261 (1985).
28. V. A. Achelashvili, O. V. Mukbaniani, V. Yu. Levin, S. M. Meladze, I. A. Inaridze and L. M. Khananashvili, *Izvestiya Georgian Academy of Sciences*, **16**, 1 (1990).
29. V. A. Achelashvili, O. V. Mukbaniani, L. M. Khananashvili, V. Yu. Levin, N. G. Komalenkova and E. A. Chernyshev, *Polymer Science USSR*, **32A**, 480 (1990).
30. V. A. Achelashvili, O. V. Mukbaniani, N. A. Koyava, L. M. Khananashvili and G. I. Sturua, *Notes Georgian Academy of Sciences*, **122**, 537 (1986).
31. O. V. Mukbaniani, V. A. Achelashvili, L. M. Khananashvili, S. M. Meladze, N. A. Koyava and G. I. Sturua. *Notes Georgian Academy of Sciences*, **122**, 105 (1986).
32. I. G. Esartiya, O. V. Mukbaniani and N. A. Koyava, *Proceedings of the 7-th All-Union Conference on Chemistry, Technology and Application of Silicon-containing Compounds*, Tbilisi-Moscow, Part I, 217 (1990).
33. I. G. Esartiya, O. V. Mukbaniani and L. M. Khananashvili, *Notes Georgian Academy of Sciences*, **144**, 277 (1991).
34. V. A. Shershnev, et al. *Vysokomolekulyarniye Soedineniya*, **28B**, 859 (1986).
35. A. A. Taguer, et al. *Polymer Sciences USSR*, **31A**, 2327 (1989).
36. V. N. Kuleznev, *Polymer Blends*, Khimiya, Moscow, 1980, p. 282.
37. L. A. Sukhareva, et al. Patent USSR, No. 1341989, 1987.
38. E. G. Rosantsev, *Nitroxyl radicals: synthesis, chemistry, applications*, Khimiya, Moscow, 267 (1987).
39. I. A. Golubeva, L. I. Tolstykh, E. P. Gallyamova and S. S. Zeldina. *Intern. J. Polymeric Mater.*, **16**, 131 (1992).
40. O. N. Tkachenko, I. A. Golubeva, E. V. Boune and V. F. Gromov, *Plasticheskiye massy*, 1992, in press.
41. L. P. Razumovskii, A. L. Iordanskii and G. E. Zaikov, *Proceedings 5-th International Symposium on Solubility Phenomena*, Moscow, 236 (1992).
42. I. C. McNeill, et al. *J. Polymer Sci. Polym. Chem. Ed.*, **15**, 2381 (1977).
43. I. C. McNeill, A. Ya. Polishchuk and G. E. Zaikov, *Polymer Degrad. Stab.*, **37**, 223 (1992).
44. A. Ya. Polishchuk, *Intern. J. Polymeric Mater.*, 1993, in press.
45. S. R. Ivanova, Al. Al. Berlin and K. S. Minsker, *Polymer Science USSR*, **33A**, 342 (1990).
46. A. A. Askadskii, et al. *Polymer Science USSR*, **32A**, 1517 (1989).
47. N. R. Prokopchuk, A. G. Alexeev, T. V. Starostina and L. O. Kisel', *Reports of Belorussian Academy of Sciences*, **34**, 1026 (1990).