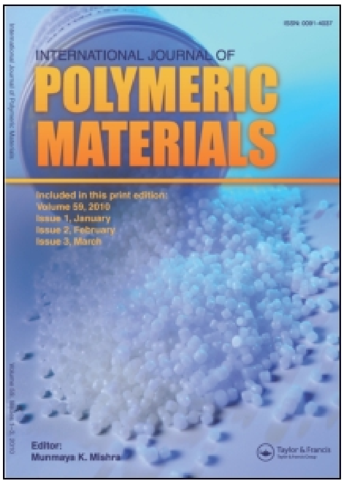

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Peculiarities of the Thermal Degradation of Chlorosulphonated Polyethylenes

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A kinetic study is made of the thermal degradation of chlorosulphonated polyethylenes containing 3–40 wt% of Cl and 1.4–2.2 wt% of sulphur. It is concluded that the instability of these polymers is principally due to activation of the CHCl structures in the β-position to the —CH_2—SO_2Cl groups.

KEYWORDS: Chlorosulphonated polyethylenes, β-chloroallyl groups, SO_2Cl groups, dehydrochlorination, kinetics, mechanism

Chlorosulphonated polyethylene (CSPE) is fairly widely employed in production of artificial leathers, building industry and others. Like all the halogen-containing polymers, CSPE is conspicuous for the low stability. There are two types of framing groups within the macromolecules —Cl and SO_2Cl and consequently under the thermal and other types of physical effects CSPE is decomposed with elimination of two low-molecular products —HCl and SO_2. It is clear that the thermal stability of the macromolecules, as many other service characteristics of CSPE, depends on the degree of the polymer chlorosulphonation the character of distribution of Cl and SO_2Cl in the chain and also on the presence of different labile structures in the macromolecules, such as vicinal chlorines and SO_2Cl groups, β-chlorallyl groups, Cl and SO_2Cl groups at tertiary carbons, etc.

There are some data in the literature that the temperature regime of the reaction influences the character of degradation of CSPE. Elimination of SO_2Cl groups under low temperatures (of the order of 125–160°C) takes place, no molecular chlorine being formed. In 1.5–2 hr of exposure under 150°C the CSPE samples lose almost all the SO_2Cl groups.[1,2] Within the temperature range of 160–200°C there occurs the process of the dehydrochlorination of the macromolecules which in a general case proceeds like that of chlorinated polyethylene (CPE).[3] With the increase in temperature the degradation of the polymer chains will proceed.[4] Evidently, the available literature data formalize the situation. The process of degradation of CSPE, in particular, in the thermal exposure of the polymer products proceeds by the laws essentially differing from the accepted ones.

The main goal of this paper was the kinetic study of the process of degradation of CSPE samples, containing 3–40 wt% and 1.4–2.2 wt% of chlorine and sulphur respectively, and obtained in the identical conditions on the base of PE with MM = 17 000–20 000, in terms of the two products evolved —HCl and SO_2 simultaneously, depending on the structure of the macromolecules.

Among the structural irregularities in the CSPE molecules in the first place one may expect Cl and SO_2Cl groups at tertiary carbons and 1.2-structures, in β-position to C=C bonds, etc., each of which can produce a destabilizing effect. The experiment has shown that the content of chlorines at tertiary carbons in the macromolecules is less than 1 wt%. The NMR ^{13}C spectra patterns obtained at 22.5 MHz with chemical shifts of 64.3 and 66.4 ppm[5] have not allowed a more accurate quantitative evaluation.

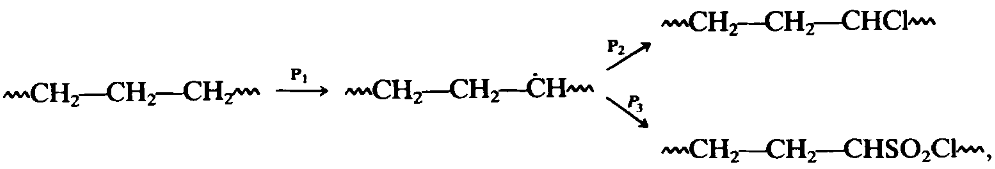
According to the NMR measurements, the absorption bands of —CHCl—CHCl— groups with chemical shifts of 4.7–5.1 ppm[6] are absent untill the chlorine content achieves 37–40 wt%.

The end C=C bonds are, as a rule, considered to be responsible for the overall unsaturation in polyethylene.[7] Its sulphochlorination does not result in the formation of new internal C=C bonds. Moreover, their content decreases from $6 \cdot 10^{-4}$ mol/mol PE (for the initial PE) to $4.5 \cdot 10^{-4}$ mol/mol PE (for the samples of CSPE).

For elucidating the nature of the end unsaturated C=C bonds the kinetics of their interaction with ozone has been studied. The rate constant of this reaction (273 K) has been evaluated as $k = (1.9 \pm 0.9) \cdot 10^{-3}$ l/mol s, which essentially differs from the corresponding rate constants of the reaction of ozone with ~~CH_2—CH=CH_2 and ~~CH_2—CH=CCl_2 groups,[8] but is close to the rate constants of the interaction of O_3 with ~~CH=CHCl and ~~CH=CH—CHCl~~ groups contained, in particular, in the chlorinated polyethylene ($k = 2.2 \cdot 10^{-3}$ l/mol · s),[9] as well as in polychloroprene ($k = 4.2 \cdot 10^{-3}$ l/mol · s) and vinyl chloride ($k = 1.2 \cdot 10^{-3}$ l/mol · s).[8] These data suggest that the macromolecules of CSPE with sufficient degree of probability contain ~~CH=CHCl and ~~CH=CH—CH_2Cl end groups too, which, however, do not condition the CSPE low stability; there is no correlation between the total unsaturation of CSPE and the initial rates of degradation.

The difference of the initial rates of dehydrochlorination which are $1.2 \cdot 10^{-6}$ mol/mol Cl · s (448 K) for CPE with Cl content 40 wt% and $2.6 \cdot 10^{-5}$ mol/mol Cl · s (448 K) for CSPE with Cl content 40 wt% and S content 2.2 wt%, the CSPE sample being based on the CPE sample, permit to suppose that the difference of the CPE and CPSE mechanisms of decomposition is conditioned by the influence of chlorosulfone groups. The SO_2Cl groups are located with a higher degree of probability at the initial carbon atoms, mainly, in the branching points of the macromolecules of ~~CH_2—CH—CH_2SO_2Cl (with a wavy branch bond at the CH). This fact has been corroborated by data on the sulphoclorination of the low-molecular model compounds—branched paraffins and their chlorine derivatives.[10] The substitution of hydrogens in CH_2-fragments proceeds with an essentially lower probability. The experimental data on the kinetics of sulphochlorination of PE permitted to evaluate the ratio of the rate constants of the reaction of substitution of hydrogens for Cl- or SO_2Cl-containing units at least as (8–9)[1], the change in the ratio of $Cl_2:SO_2$ in the reaction zone in favour of SO_2 up to the eightfold surplus[12] only slightly increasing the content of SO_2Cl in the macromolecules of CSPE (up to 2.5 wt%). In the quantitative respect it does not exceed the content of branchings in the macromolecules of initial polyethylene (about 20 for 1000 carbon atoms). The weakening of C—Cl bond in β-position to ~SO_2Cl group and correspondingly, the higher disposition to autocatalytic dehydrochlorination have been determined.[2]

Taking into account that the process of sulphochlorination of polyethylene proceeds by random law,[11] it is possible to evaluate the number of triads which contain —CH_2-, —CHCl- and —$CHSO_2Cl$-units and correspondingly the number of —CHCl-fragments in β-position to SO_2Cl by the Monte-Carlo method:



where P_1 is the probability of radical formation which is determined by the degree of substitution of CSPE; P_2 and P_3 are the probabilities of formation of Cl- and SO_2Cl-containing fragments which are determined by the ratio of the rate constants of chlorination and sulphochlorination of PE and also by the concentrations of Cl_2 and SO_2 in the reaction volume.

It has been established that the content of triads in CSPE (disregarding the defect structures in PE) of the type of ~CHCl—CH_2—CH(SO_2Cl)~ is about 0.5%. The amount of other probable triads with Cl- and SO_2Cl-containing units, such as ~CH_2—CHCl—CH(SO_2Cl)~, CHCl—CH(SO_2Cl)—CHCl~, ~CH(SO_2Cl)—CHCl—CH(SO_2Cl)~ within the macromolecules of CSPE is essentially lower or zero and in a general case may be neglected.

The calculations show that, taking into account the fact of the substitution of H by SO_2Cl group at the initial carbon in branchings as well as the drop of the sulphochlorination rates of CH_2-fragments with increasing the length of the methylene chain from —CHCl-group,[13] the probability of formation of CHCl-fragments in β-position to the sulphochloride groups is increased.

Thus, in the first approximation one may state that chlorines at tertiary carbons and in β-position to CH_2SO_2Cl groups are the main labile groups in CSPE. In the case of sulphochlorination of the ethyl branchings in polyethylene there may be formed labile groups of the type of ~CCl(CH_2—CH_2—SO_2Cl).

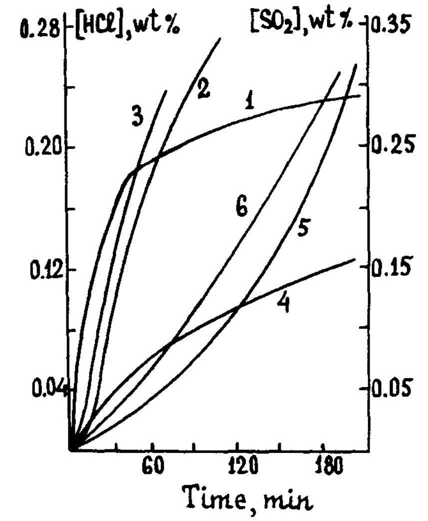


FIGURE 1 Yield of HCl and SO_2 in the degradation of the CSPE films (13.6 Cl, 2.0 S wt%): $l \cdot 10^{-3}$ cm: 1.4–1.3; 1.5–3.0; 3.6–4.5 (448 K, nitrogen).

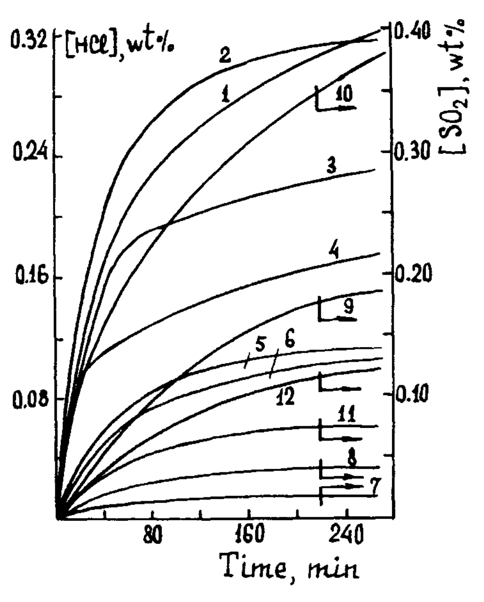


FIGURE 2 Yield of HCl and SO_2 in the thermal degradation of CSPE (448 K, nitrogen): content of Cl and S (respectively), wt%: 1.7–3.1; 1.36; 2.8–6.7; 1.6; 3.9–13.6; 2.0; 4.10–16.5; 2.02; 5.11–37.0; 1.9; 6.12–40.0; 2.2.

The existence of critical sizes of samples is one of the specific features of the degradation behaviour of the halogen-containing polymers, especially those conspicuous for low gas permeability.[14,15]

With the sizes l of samples higher than the critical ones, the process of the HCl elimination will be complicated at the expense of the catalytic effect of HCl accumulated in the sample in the degradation of the polymer products (Figure 1). The kinetic curves of the thermal degradation of CSPE permitted to determine the critical size of the CSPE films relative to elimination of HCl and SO_2, respectively ($l = 2 \cdot 10^{-3}$ cm, 448 K).

The process of the CSPE thermal degradation from the very beginning is accompanied by simultaneous evolution of the two main low-molecular products —HCl and SO_2 (Figure 2), the quantity of SO_2 formed (less than $4\,10^{-4}$ mol/mol SO_2Cl) being essentially small. The elimination of HCl in the degradation of CSPE proceeds far more intensively, though the rate constants at the initial stage of the processes of desulfonation and dehydrochlorination respectively are: (448 K, N_2) $k = (1.1 \pm 0.5) \cdot 10^{-4}\,s^{-1}$ ($E_a = 30 \pm 11$ kJ/mol) and $k = (5.0 \pm 1.6) \cdot 10^{-4}\,s^{-1}$ ($E_a = 26 \pm 8$ kJ/mol). The rate constant of the CSPE desulfonation should be referred to the intensive decomposition of SO_2Cl groups being present in small amounts at tertiary carbon atom.

The experimental data on the kinetics of degradation of CSPE including simultaneously the two evolving compounds —HCL and SO_2— strictly testify that the dehydrochlorination of the polymer products can exhaustively characterize the thermal degradation of CSPE. Herewith, there is a general tendency to relative decrease in the evolution of the low-molecular products HCl and SO_2 with the growing degree of sulphochlorination of PE (Figure 3). The portion of HCl evolved in the degradation of the labile groups relative to the initial chlorine content in the macromolecules drops to a certain value (30 wt% of chlorine content in CSPE) and then with further increase in the content of chlorine in

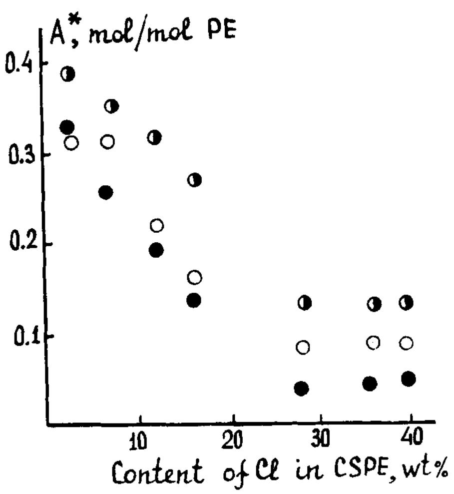


FIGURE 3 Dependence of relative number of the active sites A^* on the content of Cl (wt%) in the thermal degradation of CSPE (423–473 K).

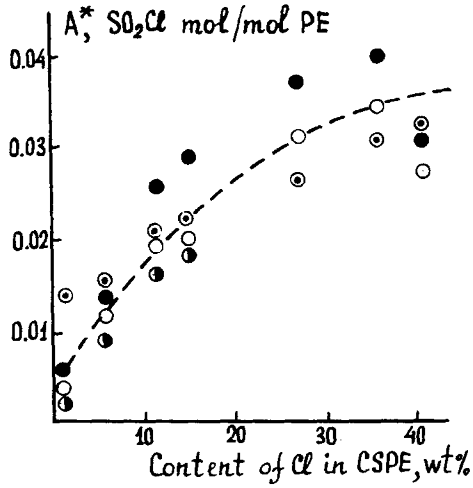


FIGURE 4 Dependence of the number of active sites A^* and SO_2Cl groups (⊙) on the chlorine content (wt%) in the thermal degradation of CSPE (423–473 K).

CSPE remains constant (Figure 3). It is important that the content of the active sites (labile groups) A^* (mol/mol PE) in CSPE changes with the content of SO_2Cl groups in the polymer products (Figure 4), i.e. it is the presence of SO_2Cl groups which causes the specificity of the HCl elimination process from the chloro-containing groups (the short-range neighboring group effect). Thus, the activation of the chlorine atoms in CHCl groups in β-position to —CH_2SO_2Cl groups is one of the main reasons for the marked decrease in the stability of the CSPE macromolecules as that in the tert-chloride groups. The process of dehydrochorination of CSPE (when A^* is constant) proceeds with the other kinetic parameters (when the times of degradation are great). If we attribute the rates of dehydrochlorination to all the other chloro-containing groups excluding A^*, we shall have a set of the kinetic constants in the range of $(7.3–2.3) \cdot 10^{-6}\,s^{-1}$ (448 K), the rate constant of the HCl elimination from CSPE decreasing with increase in the chlorine content in the polymer products.

One may assert fairly confidently that this is the consequence of the overall decomposition of the fragments of ~CH_2CHCl ($k = 0.8 \cdot 10^{-8}\,s^{-1}$) and also chloroallyl ~CH=CH—CHCl~ groups (the latter being formed in the elimination of HCl from normal ~CHCl—CH_2—CHCl~ units).

The intensive process of the macromolecular cross-linking caused the difficulty in obtaining more accurate data on the correlation of the dehydrochlorination rate of CSPE with the contents of the chloro-containing groups. Even under 423 K the structurization of the macromolecules occurs no later than three minutes after beginning the exposure.

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