Preparation and reactivity of metal-containing monomers
38.* Thermodestruction of polystyrene and polyacrylonitrile modified with triosmium carbonyl cluster monomers

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Modified polystyrene and polyacrylonitrile possessing cluster fragments in polymer chains have been obtained by radical copolymerization of styrene or acrylonitrile with triosmium carbonyl cluster complexes having double bonds capable of polymerization in their ligand surroundings. The thermal stability of the copolymers produced has been studied by DTG analysis. The temperature increase characteristic of both polymer and cluster pyrolysis has been observed for clusters containing polystyrene. The cluster complexes have been also shown to influence to a great extent the destruction of polyacrylonitrile, thus preventing the formation of stable fused structures in polymer chains.

Key words: metal clusters; triosmium carbonyl clusters; styrene copolymers; acrylonitrile copolymers; thermal destruction.

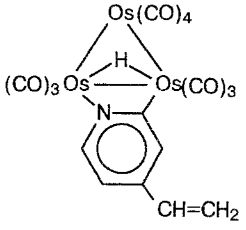
At present metal-containing polymers draw considerable attention from investigators. This is caused by the specific properties of these compounds, which appear clearly in their catalytic reactions.[1,2] The present work is devoted to an investigation of the principles of the thermodestruction of polystyrene and polyacrylonitrile modified by triosmium carbonyl clusters in their polymer chains.

Experimental

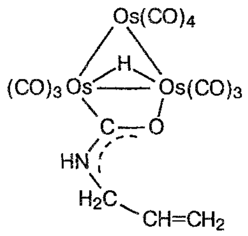
Starting cluster monomers
$(\mu\text{-H})(Os_3(CO)_{10})(\mu\text{-}NC_5H_3CH{=}CH_2)$ (CM **1**),
$(\mu\text{-H})(Os_3(CO)_{10})(\mu\text{-}CONHCH_2CH{=}CH_2)$ (CM **2**),
and $(\mu\text{-H})(Os_3(CO)_{10})(\mu\text{-}COOCH{=}CH_2)$ (CM **3**) were prepared from $Os_3(CO)_{12}$ by the replacement of CO with unsaturated groupings (4-vinyl pyridine (4-VP), allyl amine (AA), and acrylic acid (AAc) according to the modified procedures for the synthesis of arene derivatives of triosmium carbonyl clusters.[3–6]

Radical copolymerization of monomers (CM **1**, CM **2**, and CM **3**) was carried out in a styrene medium, and copolymerization with acrylonitrile was performed in benzene. Azobisisobutyronitrile (AIBN 0.6 mol. %) was used as the initiator. Monomers had been previously dried and distilled *in vacuo*. Polymerization was carried out for 3 h at 70 °C in degassed tubes. Copolymers were precipitated with EtOH, washed, and dried. The content of osmium was found by non-flame atomic adsorption on a Saturn instrument.

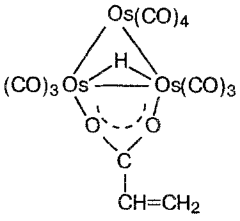
Copolymers were studied by DTG analysis in air under dynamic conditions by a MOM C derivatograph. Comparative analysis of the thermostability of the copolymers was also performed in an argon atmosphere. The temperature rate was 5 grad min^{-1} in all of the cases. Sample weights were approximately equal to each other and ranged from 15 to 20 mg.



CM **1**



CM **2**



CM **3**

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*For part 37, see *Izv. Akad. Nauk, Ser. Khim.*, 1994, 225 [*Russ. Chem. Bull.*, 1994, **43**, 232 (Engl. Transl.)].

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 423—428, March, 1994.

Results and Discussion

It is known[7,8] that decarbonylation of osmium carbonyl clusters begins to occur at ~200 °C and is accompanied by structural changes. Fixing cluster complexes on an inorganic carrier does not increase their thermal stability:[3] at the above-mentioned temperatures clusters undergo deep reconstruction with changes in nuclearity and in chemical structure. On the other hand, a number of metals (Fe, Co, Ni, Mn, and others) as well as their complexes and oxides can effectively influence the destruction processes in various polymers, acting both as inhibitors and as catalysts of thermooxydative destruction.[10—11] A metal introduced, especially in cluster form, is able to modify the macroscopic properties of the polymer. In light of this, we have investigated the thermostability of cluster-containing polymers by DTG analysis.

It should be pointed out that, according to IR and UV spectroscopy data, cluster fragments (of CM **1—3**) do not undergo any considerable changes during the copolymerization process.

A cluster monomer adds to a double bond site of a growing macro radical and thus limits the growth of the chain. Therefore, it becomes necessary to control CM concentration in a mixture of comonomers: only a low concentration (up to 2 mol. %) gives rise to high molecular fractions with mean molecular weights ($\overline{M}_n$), comparable to $\overline{M}_n$ of styrene and acrylonitrile homopolymers obtained under analogous conditions (Table 1).

Table 1. Characteristics of cluster-containing copolymers possessing styrene and of their metal-free analogs

(co)Polymer	M_2[a] (mol. %)	m_2[b] · 10^5 /mol g^{-1}	$\overline{M}_n$[c]
Polystyrene	—	—	36000
St-4-VP (1.0)[d]	—	—	37000
St-AA (1.0)[d]	—	—	30000
St-AAc (1.0)[d]	—	—	28000
St-CM **1**	0.5	1.2	37000
	1.0	2.8	35000
	2.0	6.0	17000
St-CM **2**	0.3	0.2	29000
	1.0	0.4	21000
St-CM **3**	0.1	0.3	26000
	1.0	2.2	12000

[a] Content of cluster comonomer in a mixture of monomers. [b] Content of cluster links in copolymer. [c] Average molecular weight of polymers. [d] In brackets, the content of comonomer in a mixture with styrene, mol. %.

An examination of the graphic dependence of sample weight loss *vs.* temperature (Fig. 1, TG curve) points out that cluster-containing links have a considerable effect on the process of thermooxydative destruction of copolymers, while their monomer analogs without metal (4-vinyl pyridine, allylamine, acrylic acid), which have the same copolymer content, exhibit almost none of this

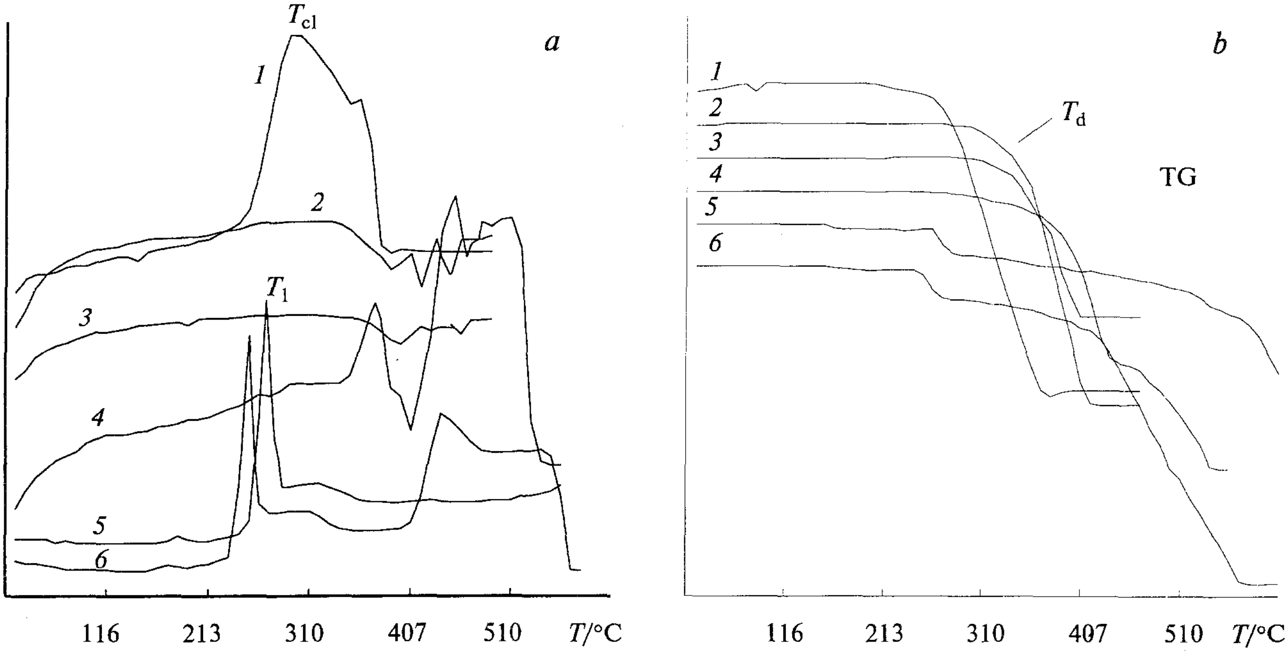


Fig. 1. Specific DTG curves (*a*, DT, *b*, TG) of thermooxydative destruction: CM **1** (*1*); polystyrene (*2*); copolymer of styrene with 4-vinylpyridine (*3*); copolymer of styrene with CM **1** (*4*) (the conditions of polymerization: a styrene medium, 70 °C, [AIBN] 0.6 mol. %, 3 h, the second monomer content ~1 mol. %); polyacrylonitrile (*5*); copolymer of acrylonitrile with CM **3** (*6*). Rate of heating 5 grad min^{-1}. Sample weights from 10 to 17 mg.

influence. At the same time, the thermostability of a triosmium carbonyl cluster included in the polymer chain also increases considerably. It is clear from the derivatograms (see Fig. 1) that, in the case of polystyrene copolymers, reciprocal thermostabilization of polystyrene (PS) and the clusters included in its chain takes place.

The exothermic peak of intricate shape observed on the differential thermal analysis (DT) curve in the 370—450 °C (for styrene copolymers) and in the 420—500 °C (for acrylonitrile copolymers) temperature ranges corresponds to the peak of the DT curve in the 220—350 °C interval that reflects the pyrolysis of the starting triosmium carbonyl cluster. This peak is probably caused by the chemical transformations proceeding under these conditions in the cluster, *i.e.*, decarbonylation, changes in structure, and finally complete oxidation to volatile products. In the case of styrene copolymers, this peak appears at a temperature (T_{cl}, see Fig. 1, *a*) ~150° higher than that of the starting CM **1**. CM **3** has lower thermostability in copolymers of styrene and acrylonitrile. DT curves of these copolymers were observed to have two peaks: the first one, with a smaller area, at temperatures near T_{cl} of starting CM **3**, and the second one with a greater area corresponding to pyrolysis of the more stable form. A similar increase in thermal stability for triosmium carbonyl clusters was also established for cluster-containing copolymers of acrylonitrile (Table 2).

It is important that the thermal stability of triosmium carbonyl clusters increased only when they were chemically bonded to the polymer chain. Decomposition temperatures of CM **1—3** mechanically mixed with polymers corresponded to the temperature range characteristic for pyrolysis of the individual components. It should be noted that pyrolysis of cluster monomers CM **1—3** in an argon atmosphere is also accompanied by exothermic reactions. However, in this case the thermal effect (for the same 220—350 °C temperature range) is lower than that for pyrolysis in the air, which is indicated by a 1.3-fold decrease in the peak area. Oxidation of clusters is accompanied by structural transformations in the cluster framework[12] (decarbonylation, nuclearity change) and, probably, suppression of these processes should lead to an increase in thermal stability. The influence of a polymer chain bearing a chemically bonded cluster complex could manifest itself in the transfer of energy at high temperatures from the rotation-vibration degrees of freedom of the cluster to forward motion degrees of freedom of the polymer chain segments, which would increase the thermal stability of the complex.

A comparison of the derivatograms showed that the metal-free analogs of the cluster monomers, 4-vinyl pyridine, allylamine, acrylic acid, do not significantly change the parameters of the TG and DT curves. On the other hand, clusters containing additions in the form of both mechanical mixtures (probably homogenized during the melting of polystyrene) and copolymer units, dramatically increase the thermal stability of polystyrene. The temperature of the beginning of polymer destruction (T_{d}, see Fig. 1, *b*) of styrene cluster copolymers with CM **1** and CM **2** increases for 50—100 °C, even if they have a low content of cluster units. Some of these temperature values are given in Table 2.

A comparative examination of the TG, DT, and DTG curves made it possible to separate the process of destruction of cluster-containing styrene copolymers into roughly two stages. At the first stage, when the rate is the highest, a considerable loss of the sample weight occurs (70—90 %). The DT curves do not indicate any considerable temperature effects, and at the starting interval, the TG curve drops more steeply in the case of the samples with higher thermostability. The second stage corresponds to the exothermic peak of the DT

Table 2. Temperature characteristics (T/°C) of the thermooxydative destruction of cluster-containing monomers, copolymers, and their metal-free analogs

Sample	T_{d}[a]	T_{50}[b]	T_{cl}[c]	T_1[d]	Degree of sample destruction (%)
CM **1**	222	295			100
CM **3**	247	270			98
PS	303	375	—		97
St-4 VP (1.0)[e]	336	386	—		97
St-AA (1.0)[e]	308	382	—		98
St-AAc (1.0)[e]	310	378	—		99
St-CM **1** (0.5)[e]	378	416	450		98
St-CM **1** (1.0)[e]	392	416	450		98
St-CM **2** (0.3)[e]	359	417	437		99
St-CM **2** (1.0)[e]	355	407	444		98
St-CM **2** (1.0)[e] +RCl	338	404			98
St-CM **3** (0.1)[e]	363	402	280 m.p., 426		98
St-CM **3** (1.0)[e]	277	397	278 m.p., 413		99
PAN	273			283	48
AN-CM **1** (1.0)[e]	267	423	405	267	96
AN-CM **2** (1.0)[e]	264	471	457	264	99
AN-CM **3** (1.0)[e]	258	509	275 m.p., 484	258	98
PS+$Os_3(CO)_{12}$[f]	360	411	280, 450 m.p.		99
PAN+CM **1**[f]	243		280	243	95

[a] Temperature at the beginning of sample decomposition.
[b] Temperature at which the sample weight loss is 50 %.
[c] Temperature corresponding to the exothermal peak maximum on the DT curve of pyrolysis of the triosmium carbonyl cluster.
[d] Temperature of the narrow exothermal peak arising on the DT curve during acrylonitrile copolymer destruction.
[e] In brackets, the second comonomer content, mol. %.
[f] Mechanical mixture.

Table 3. Starting and maximum rates of destruction of polystyrene and copolymers of styrene with cluster-containing monomers and with their metal-free analogs

Sample	$m_2{}^a \cdot 10^5$ /mol g^{-1}	$(\mathrm{d}\alpha/\mathrm{d}t)_{0.1}{}^b$ $\cdot 10^2$/min^{-1}	$(\mathrm{d}\alpha/\mathrm{d}t)_{\max}{}^c$ $\cdot 10^2$/min^{-1}	$\alpha_{\max}{}^d$
PS	—	2.5	8.6	0.70
St-4-VP	—	2.3	10.3	0.61
St-AA	—	2.1	8.3	0.77
St-AAc	—	2.0	8.6	0.70
St-CM **1**	1.2	1.7	8.2	0.71
St-CM **1**	2.8	1.1	12.6	0.68
St-CM **2**	0.2	1.9	13.5	0.62
St-CM **2**	0.4	1.9	13.3	0.64
St-CM **3**	0.3	2.1	8.6	0.67
St-CM **3**	2.2	2.1	7.5	0.60
PS + $Os_3(CO)_{12}$	1.4	1.7	11.9	0.68

[a] Content of cluster units in copolymer. [b] Rate of polymer destruction, when the degree of sample decomposition is $\alpha = 0.1$. [c] Maximum destruction rate. [d] Degree of sample decomposition corresponding to the maximum rate of the process.

curve, which appears when pyrolysis of the starting clusters takes place. At this stage, according to the TG curves, some decrease in the rate of sample weight loss is observed, and then the sample completely decomposes (up to 95—100 %). This fact reflects the destructive changes in the cluster monomer units and in the residual mass of the copolymer.

Everything mentioned above suggests that the first stage of styrene copolymer decomposition is generally conditioned by the destructive changes in the polystyrene chains and also by the stabilizing action of the cluster complexes, which is revealed by an increase in the specific temperatures (see Table 2), by a decrease in the initial rates of decomposition, and by an increase in the maximum rates of destruction (Table 3). In light of this, we made an attempt to compare the effective parameters of the destruction of polystyrene and styrene copolymers with those of both cluster-containing and metal-free monomers.

It is known[10] that the thermodestruction of polystyrene proceeds mainly by a radical depolymerization mechanism. A formal approach describing the decomposition of polystyrene to gaseous products allows the effective parameters of decomposition in the dynamic mode to be estimated.

$$[\mathrm{PS}] \xrightarrow{k} \text{gaseous products}$$

$$\frac{\mathrm{d[PS]}}{\mathrm{d}t} = -k[\mathrm{PS}],\ k = k_0 e^{-E_{\mathrm{eff}}/RT}$$

Replacing [PS] with the fraction of the decomposed sample α to get dimensionless values gives

$$\ln\left[-\frac{\mathrm{d}\alpha/\mathrm{d}t}{(1-\alpha)}\right] = \ln k_0 - E_{\mathrm{eff}}/RT. \qquad (1)$$

For convenience we propose that $\alpha = 1$ corresponds to the amount of polystyrene decomposed in the first stage.

It can be seen from Fig. 2, *a, b, c* that for the metal-free copolymers and for those with a small content of the cluster monomer, Eq. (1) is depicted in two linear parts. A break in the curve appears at destruction degree 30—40 % and does not correspond to the conversion values of the maximum destruction rate. A break in the Arrhenius curves obtained in the dynamic mode can be caused by several things. The rate of chain radical depolymerization at constant temperature depends on the rate constants of the individual stages of the process.[11] Under the dynamic conditions of a linear increase in temperature, these values are not independent of time, sometimes they can not be described in an analytical way, and they can affect the measured destruction rate in a complex fashion. Another probable cause of the break in the curve observed is the formation of cross-linked structures in polystyrene at rather high degrees of destruction (30—40 %). However, the most probable reason is that destruction may proceed in two sequential or parallel stages: oxidation and depolymerization. In this case, an increase in temperature results in a greater contribution of the process with the greater activation energy value to the reaction rate.

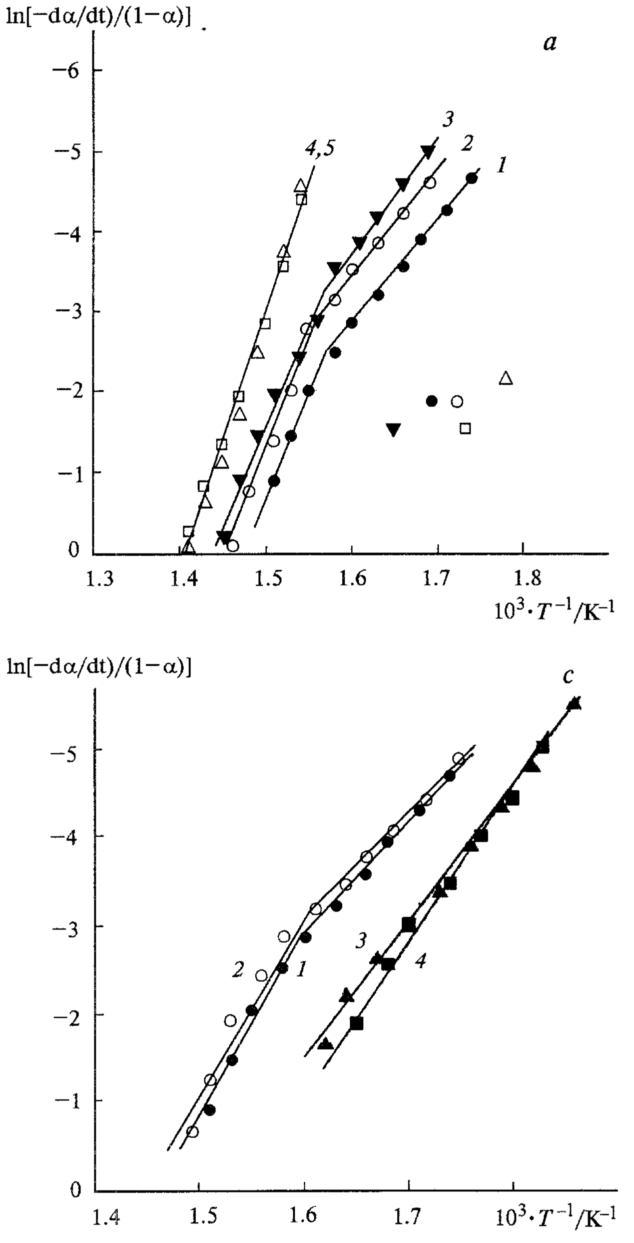
A similar change in the effective activation energy (E_{eff}) from 19 kcal mole^{-1} at the beginning stage to 42 kcal mole^{-1} at the later stages of conversion has been observed for the destruction process of polypropylene under non-isothermal conditions.[12] This phenomenon was explained by sequential occurrence of oxidation and pyrolysis.

The effective values of the activation energy given in Table 4 were obtained using Eq. (1) under conditions of rising temperature, *i.e.*, they are approximate. It is probably expedient to compare E_{eff}, energies of different copolymers in the same temperature range. Thus, E_{eff} of polystyrene destruction under isothermal conditions at temperatures above 350 °C was found to be[11—13] 55—58 kcal mol^{-1}, which is in rather good agreement with our estimation (56 kcal mol^{-1}).

Under the conditions of dynamic gravimetry, E_{eff} values can also be found[14] by the slope of the dependence:

$$\ln\frac{W_0 - W_t}{W - W_t} = \frac{E_{\mathrm{eff}}\theta}{RT_s^2}, \qquad (2)$$

where W_0, W_t, and W are the starting, current, and residual sample weights, respectively (at the end of the linear part of the TG curve); θ is the difference between T and T_s, when the process goes at the maximal rate. It can be seen from Table 4 that the values of E_{eff} obtained by this method occupy an intermediate position between those estimated by the slope of the two linear segments, and they also attest to the increase in the activation



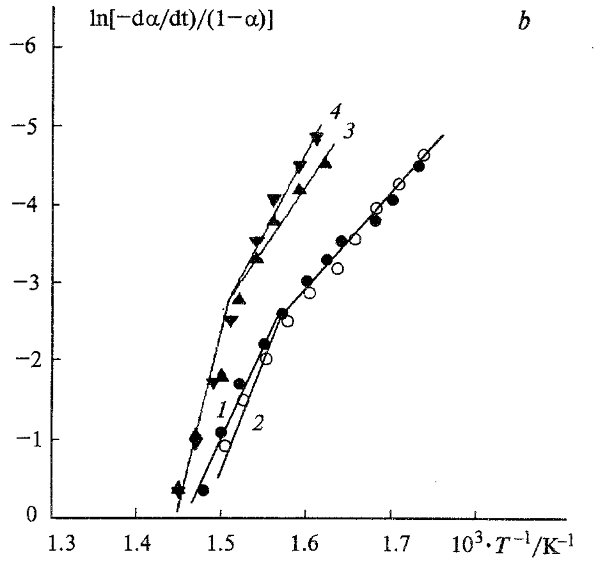


Fig. 2. Dependences of the logarithm of the specific rate of destruction on inverse temperature; *a*: polystyrene (*1*); copolymer of styrene with 4-vinylpyridine (*2*); copolymers of styrene with CM **1** (*3—5*) (0.5 (*3*), 1 (*4*), 2 (*5*) mol. %); *b*: polystyrene (*1*); copolymer of styrene with allylamine (*2*); copolymers of styrene with CM **2** (*3—4*) (0.5 (*3*), 2 (*4*) mol. %); *c*: polystyrene (*1*); copolymer of styrene with acrylic acid (*2*); copolymers of styrene with CM **3** (*3—4*) (1 (*3*) and 2 (*4*) mol. %).

barriers of the destruction of cluster-containing styrene copolymers.

Undoubtedly, all the effects described above need further detailed investigations of the mechanism of the inhibiting action of the cluster additions in the process of polystyrene destruction. The present results only allow some assumptions explaining the increase in the thermal stability of polystyrene in the presence of osmium carbonyl clusters to be advanced.

The stabilization of polystyrene by cluster-containing units can be explained by at least two factors. Probably, the cluster-containing units actively interact with the initiators of the thermooxydative destruction of polystyrene (oxygen or radicals), especially at high temperatures, when the cluster species are capable of advanced conversions (decarbonylation, oxidation, change in nuclearity). In addition, similar properties are also exhibited by the gaseous products of the pyrolysis of carbonyl clusters, *e.g.*, CO, which can participate in chain breaking reactions at high temperatures.[10]

Blocking the terminal unit in the cluster-fragment form can be another factor increasing the activation barriers of destruction. This is confirmed by the follow-

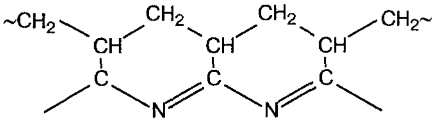
Table 4. Effective activation energies (E_{eff}/kcal mol^{-1}) of the thermodestruction of polystyrene and its copolymers with 4-vinylpyridine, allyl amine, acrylic acid, and cluster-containing monomer analogs

Copolymer	$E_{\mathrm{eff}}(1)$	$E_{\mathrm{eff}}(2)$	E_{eff}^{14}
PS	27	56	34
St-4-VP (1.0)	26	57	42
St-AA (1.0)	25	66	34
St-AAc (1.0)	25	67	34
St-CM **1** (0.5)	32	48	38
St-CM **1** (1.0)	—	69	57
St-CM **1** (2.0)	—	64	43
St-CM **2** (0.3)	32	83	44
St-CM **2** (0.5)	45	72	58
St-CM **2** (1.0)	34	65	60
St-CM **3** (0.1)	33	—	34
St-CM **3** (1.0)	30	—	31

Note. In brackets is given the content of comonomer in a mixture with styrene, mol. %.

ing experiment. We managed to remove the triosmium carbonyl fragment from the copolymer of styrene with CM **2** by a reaction with the nitroxyl radical (IR and UV spectroscopy, microanalysis), and the allylamine group was left as the end unit. The T_d temperature of this sample proved to be 30 °C higher than that of the statistic copolymer of styrene with allylamine, but 20 °C lower than that of the corresponding cluster-containing copolymer (see Table 2). The activation barriers of destruction of this copolymer appeared to be equal to that of the metal-free copolymer of styrene with allylamine. At the first stage of the process, E_{eff} corresponds to the effective activation energy of polystyrene destruction, which may attest to the inhibition of the oxidation of the copolymer by the cluster complex in a certain temperature range.

Cluster-containing units influence the thermal destruction of acrylonitrile copolymers in a somewhat different way, and the following specific features are observed. T_d of cluster-containing copolymers scarcely changes, but, unlike acrylonitrile the homopolymer ($\alpha \sim 50$ %), they completely decompose ($\alpha \sim 100$ %) under these conditions. At ~250 °C, the derivatograms (see Fig. 1, *a*, curves *5*, *6*) exhibit a narrow exothermal peak (T_1). At this stage, the conjugate nitrile structures are formed.[10,11]



The exothermal peak of cluster-containing copolymers arises at a lower temperature (see Fig. 1, *a*, curve *6*, Table 2) than that of homopolymers. After this, all of the TG curves of the copolymers manifest some stabilization in copolymer weight and then complete decomposition at the stage corresponding to pyrolysis of the cluster fragment. In the case of the mechanical polyacrylonitrile—CM **1** mixture, the temperature interval in which the above-mentioned process is observed is ~150° lower than for the copolymer, and lies in the temperature range of cluster pyrolysis.

The mechanism of the thermal destruction of polyacrylonitrile is rather complicated, the process includes a number of stages[10,11] and exhibits a radical character. The products of the destruction of the acrylonitrile homopolymer are non-volatile naphthidine compounds. Bearing this in mind, it is possible to propose that the above-described influence of cluster-containing units on the pyrolysis of polyacrylonitrile is due to the products of their thermolysis, which inhibit the radical processes leading to stable naphthidine structures. However, quite different factors might be of paramount importance. It should not be excluded that destruction in the unchanged sections of the polyacrylonitrile macromolecule can be caused by the highly exothermic character of the pyrolysis of triosmium carbonyl clusters. The products of the destruction of these clusters are also able to actively initiate destruction.

Detailed investigations of the pyrolysis products of cluster-containing copolymers could give a deeper understanding of the mechanism of the participation of triosmium carbonyl clusters in these processes.

The authors are grateful to A. M. Bochkin and A. S. Rozenberg for useful debates and valuable advise in the course of the discussion of this work.

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Received July 7, 1993