Preparation and reactivity of metal containing monomers
43.* Synthesis and properties of copolymers of styrene or acrylonitrile with triosmium carbonyl cluster monomers

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The peculiarities of radical copolymerization of styrene or acrylonitrile with triosmium carbonyl clusters whose ligand environments incorporate groups with multiple bonds capable of polymerization (4-vinylpyridine, allylamine, acrylic acid) are described. Using IR and NMR spectroscopy under the model conditions, it was shown that no side processes occur during the reaction of comonomers and azo-*bis*-isobutyronitrile, an initiator of radical polymerization. The cluster complex (the metal core and its ligand environment) is retained during copolymerization. The molecular weight characteristics of the copolymers obtained were studied. The double bonds in the cluster monomers mostly retain the properties inherent in their organic analogs.

Key words: styrene copolymers, acrylonitrile copolymers, triosmium carbonyl clusters.

In recent years, interest in the catalytic properties of anchored metal clusters, specifically in the products of the reactions of individual clusters with inorganic carriers, has been continuously expressed.[1,2] Meanwhile, polymeric carriers also possess a number of useful properties: specified solubility or swelling ability in the reaction medium, controlled mobility of the reaction center or its ligand environment, the ability to operate at various pH, *etc.*

Various methods for chemical grafting of metal clusters have been developed. The most frequently used among these is the method involving polymer-analogous transformations of specially functionalized polymeric carriers and metalloclusters.[3—4] However, the reactions occurring in macroligand—cluster systems are often accompanied by serious complications, such as a change in the nuclearity of the cluster up to its fragmentation to form mononuclear products and metal species of small sizes.

To continue the studies directed at the syntheses and transformations of cluster containing monomers, whose ligand environments contain multiple bonds capable of polymerizing,[5] in the present work we carried out copolymerization of cluster monomers with monomers of the traditional type, *viz.*, styrene and acrylonitrile.

For this study, we chose those cluster complexes, whose analogs, both homogeneous and attached to inorganic carriers, are known as catalysts for various reactions.[6—8]

Experimental

Syntheses of the cluster containing monomers $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}NC_5H_3CH{=}CH_2)$ (**1**), $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}CONHCH_2CH{=}CH_2)$ (**2**), and $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}COOCH{=}CH_2)$ (**3**) have been described in detail previously.[5] Here we present only the spectroscopic characteristics of these compounds that are significant for identification of the polymeric products.

$\mathbf{(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}NC_5H_3CH{=}CH_2)}$ **(1),** IR (cyclohexane), ν(CO)/cm^{-1}: 2101 m, 2061 s, 2051 s, 2020 s, 2008 s, 2000 m, 1988 m, 1973 w; (CH_2Cl_2), ν(C=C)/cm^{-1}: 1597 w. ^{1}H NMR ($CDCl_3$), δ: 8.01 (d, 1 H, heterocycle H); 7.25 (m, 2 H, —CH= + heterocycle H); 5.72 (m, 2 H, =CH_2); −14.85 (s, 1 H, $Os_2(\mu\text{-H})$).

$\mathbf{(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}CONHCH_2CH{=}CH_2)}$ **(2),** IR (hexane), ν(CO)/cm^{-1}: 2106 w, 2067 s, 2056 s, 2022 s, 2013 vs, 2010 sh, 1993 s, 1985 m, 1976 m, 1967 w, 1951 w; (CH_2Cl_2), ν(C=C)/cm^{-1}: 1670 w; (CH_2Cl_2), ν(NC=O)/cm^{-1}: 1504 w; (CH_2Cl_2), ν(NH)/cm^{-1}: 3423 w, 3330 w. ^{1}H NMR ($CDCl_3$), δ: 7.17 (br, 1 H, NH); 6.6 (m, 1 H, —CH=CH_2); 1.59 (m, 3 H, —CH_2—+—CH=CH_2); −14.21 (s, 1 H, $Os_2(\mu\text{-H})$).

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* For part 42, see *Izv. Akad. Nauk, Ser. Khim.*, 1995 [*Russ. Chem. Bull.*, 1995, **44**, 1056 (Engl. Transl.)].

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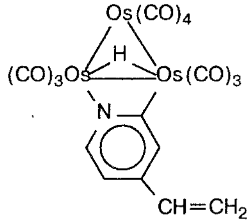
(μ-H)$Os_3(CO)_{10}$(μ-COOCH=CH_2) (3), IR (hexane), ν(CO)/cm^{-1}: 2013 w, 2073 vs, 2062 s, 2027 vs, 2016 vs, 2010 s, 1988 m, 1984 m, 1722 (μ-CO_2); (CH_2Cl_2), ν(C=C)/cm^{-1}: 1645 w. ^{1}H NMR ($CDCl_3$), δ: 5.95—5.16 (m, 3 H, —CH=CH_2); −10.42 (s, 1 H, Os_2(μ-H)).

Radical copolymerization of monomers **1—3** with styrene was carried out in bulk or in a toluene solution, and in the case of acrylonitrile, it was carried out in benzene. Azo-*bis*-isobutyronitrile (AIBN) (0.6 mol. %) was used as the initiator. The starting monomers were preliminarily dried and distilled *in vacuo*. The calculated amounts of the cluster monomer and AIBN were preliminarily evacuated in a glass unit. The monomer and the solvent were refrozen in a reaction tube. The tube was sealed under vacuum. Polymerization was carried out at 70 °C for 3 h. Copolymers of styrene with monomers **1—3** were precipitated with ethanol, washed, dried, and analyzed. Copolymers of acrylonitrile were washed with benzene to remove the unchanged cluster monomer. All of the operations with the cluster containing copolymers (except for special studies) were carried out in air.

The ^{1}H NMR spectra were recorded on a Bruker 4-100 spectrometer, and the IR spectra were obtained on a Specord IR-75 instrument. The molecular weight characteristics of the copolymers were determined by gel permeation chromatography in THF using a Waters 200 instrument. Number-average molecular weights of acrylonitrile copolymers were determined by osmometry in DMF using a high-speed Hewlett-Packard osmometer. The calorimetric studies were carried out on a DAK-1-1 microcalorimeter.

Results and Discussion

We used[5] cluster monomers **1—3** containing a vinyl group in the μ-coordinated ligand for copolymerization with styrene or acrylonitrile.



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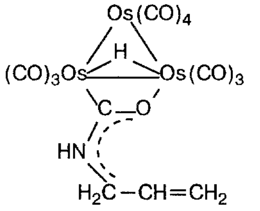

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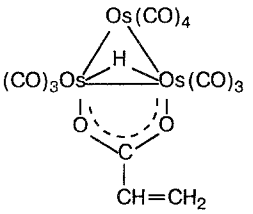

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As regards polymerization, at least several questions associated with the specific character of cluster monomers are of interest. First, whether monomers **1—3**, in which a bulky substituent, *viz*., a cluster metal carbonyl, is present in close proximity to the double bond, are able to add to the growing macroradical? Whether a cluster substituent has a substantial effect on the reactivity of the monomer due to the possible change in the electron density at the double bond? Whether the nature of the double bond (incorporated in 4-vinylpyridine, allylamine, or acrylic acid) manifests itself in the copolymerization of the cluster monomers with styrene or acrylonitrile, as is typical of their normal organic analogs?

Side reactions of osmium carbonyl clusters with the components of the reaction mixture, such as coordination to alkenes[1,10—11] and addition of the unshared donor electron pair of the CN group of the initiator to these clusters,[1] are also possible. Therefore, we carried out preliminary experiments to find out, whether coordination of styrene, acrylonitrile, or AIBN by monomers **1—3** is possible. These reactions would considerably complicate the description of the polymerization processes and the products obtained.

The IR and ^{1}H NMR spectra of the cluster complexes after they were treated with styrene and kept *in vacuo* at 70 °C for 1 h and then the styrene was pumped out did not differ from the spectra of the starting cluster monomers (see Experimental). No variations indicating the occurrence of the reaction were observed in the spectra of the complexes treated with toluene solutions of AIBN: the spectra of solutions of the dried samples were superpositions of the spectra of cluster monomers on the spectrum of AIBN. Based on the IR and ^{1}H NMR spectra we concluded that no side reactions of the cluster complexes with the components of the reaction mixture that could complicate the reaction under study occur.

Homopolymerization of cluster monomers 1—3 occurs with difficulty, probably due to steric causes. In fact, polymerization of **1** in benzene gives an oligomer (in 1—2 % yield) consisting of 5—6 monomeric units.

Copolymerization of cluster monomers 1—3 with styrene or acrylonitrile does not result in a substantial change in the structure of the cluster complex incorporated in the polymeric chain. The region characterizing vibrations of the carbonyl groups of the cluster cores in the IR spectra of copolymers of styrene or acrylonitrile with **1—3** almost does not differ from this region in the spectra of the corresponding cluster monomers **1—3**. Only slight changes in the intensities and broadening of some absorption bands of the carbonyl cluster are observed. A comparison of the photoelectron spectra of $Os_3(CO)_{12}$ (CCl_4, λ_{max}/nm) and cluster monomers **1** and **3** (330, 385; 310, 395 and 340, 389, respectively) with the spectra of solutions of their copolymers with styrene (333, 386 and 340, 389, respectively) reflects the peculiarities of their structures. The presence of substituents in the plane of the Os_3 cluster ring has less effect on the photoelectron spectra than that in the case of, for example, Ru_3 clusters in which the presence of three phosphine groups in the ligand environment results in λ_{max}, equal to 320 nm in the unsubstituted cluster, shifting to 500 nm in the substituted cluster.[1] Conjugation with the double bond in monomer **1** apparently leads to redistribution of the electron density at the Os—Os bond and to its shortening. In the polymer, there is no conjugation, and the λ_{max} value is close to that for the unsubstituted compound. In cluster monomer **3**, no conjugation of the double bond with the —O—C—O— bridging ligand exists, and therefore, its spectrum is entirely retained after the polymerization addition.

First, we examined the extent to which the Os_3 cluster core affects polymerization of styrene. We showed that the rate of decomposition of the initiator, the kinetics of heat evolution during the polymerization, or molecular weight characteristics of the resulting polymer did not change in the presence of the cluster when its concentration did not exceed 1 mol. % with respect to styrene.

Using the **1**—styrene system as an example, we identified the effect of the cluster monomer on the yield and composition of the resulting copolymer and on the molecular weight characteristics of the products. The increase in the content of compound **1** in its mixture with styrene from 0.5 to 10 mol. % results in an increase in the proportion of **1** in the copolymer (see Fig. 1, *a*) and in a decrease in the yield of the precipitable copolymer from 65 to 5 %. The yield of oligomeric products correspondingly increases (the proportion of the fraction with $M_n \approx 600$ in the latter specimen is 94 %), and the number-average molecular weight of the copolymer dramatically decreases, from 37000 to 5000. These data apparently indicate that the addition of the cluster monomer to the growing macroradical leads to termination of the polymer chain. A microcalorimetric study of the kinetics of copolymerization showed that the rate of copolymerization carried out in the bulk practically does not change when up to 1.0 mol. % of the cluster monomer is introduced into the reaction mixture (Fig. 2, *a*). The molecular weight characteristics of styrene copolymers with various proportions of the cluster containing monomer, the elemental analysis data, and the data of the analysis for the content of double bonds in these copolymers presented in Table 1 indicate that, in most cases, each polymer chain contains one cluster

Table 1. Comparative analysis of copolymers of styrene with cluster monomers (CM) and with the corresponding organic monomers for the proportion ($\times 10^5$ mol g^{-1}) of double bonds, average number of polymer chains, and the proportion of the cluster monomer

Styrene : CM molar ratio	M_n	$[q]^a$	[C=C]	$[KM]^b$ in the copolymer
Polystyrene	31000	3.2	2.8	
St:4-VP=0.005	44000	2.3	2.7	
St:4-VP=0.01	23000	4.3	2.6	
St:AAm=0.005	30000	3.3	2.5	
St:AAm=0.01	30000	3.3	3.0	
St:AA=0.005	28000	3.6	4.7	
St:AA=0.01	28000	3.6	5.0	
St:$Os_3(CO)_{12}$=0.01	30000	3.3	2.7	
1 0.005	31000	3.2	2.2	1.2
1 0.01	37000	2.7	3.1	2.8
1 0.02	35000	2.9	6.5	6.0
1 0.05	6000	11.6	12.3	19.2
1 0.1	5000	19.1	17.6	32.1
2 0.005	29000	3.4	4.2	0.42
2 0.01	21000	4.8	5.0	0.43
3 0.005	15000	6.7	3.2	1.5
3 0.01	12000	8.3	4.0	3.5

[a] [*q*] is the average number of the polymer molecules in 1 g of sample.

[b] The proportions of the cluster monomers in the copolymers were determined from the data of the elemental analysis for osmium ([CM] = [Os]/3).

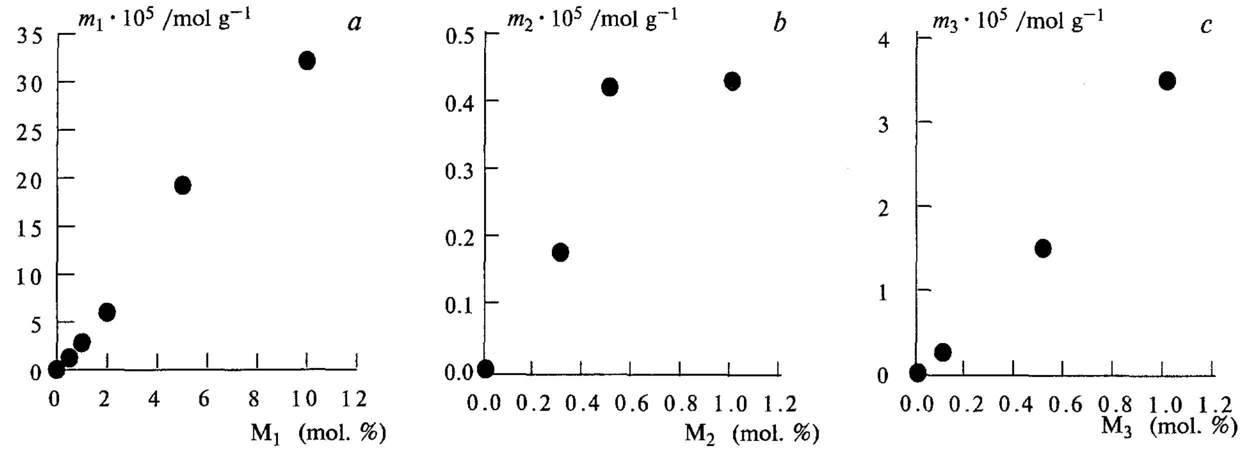


Fig. 1. Dependence of the content of cluster containing units (*m*) in copolymers of styrene with cluster monomer **1** (*a*), **2** (*b*), **3** (*c*) on the proportion of the cluster monomer in the mixture of comonomers (M).

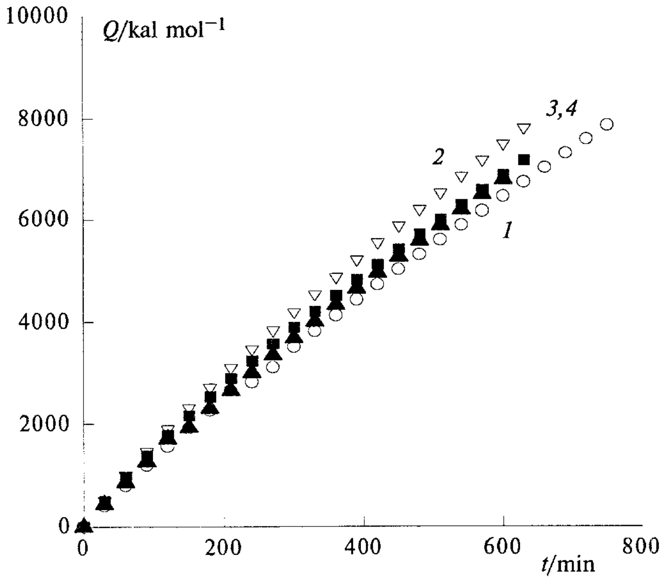


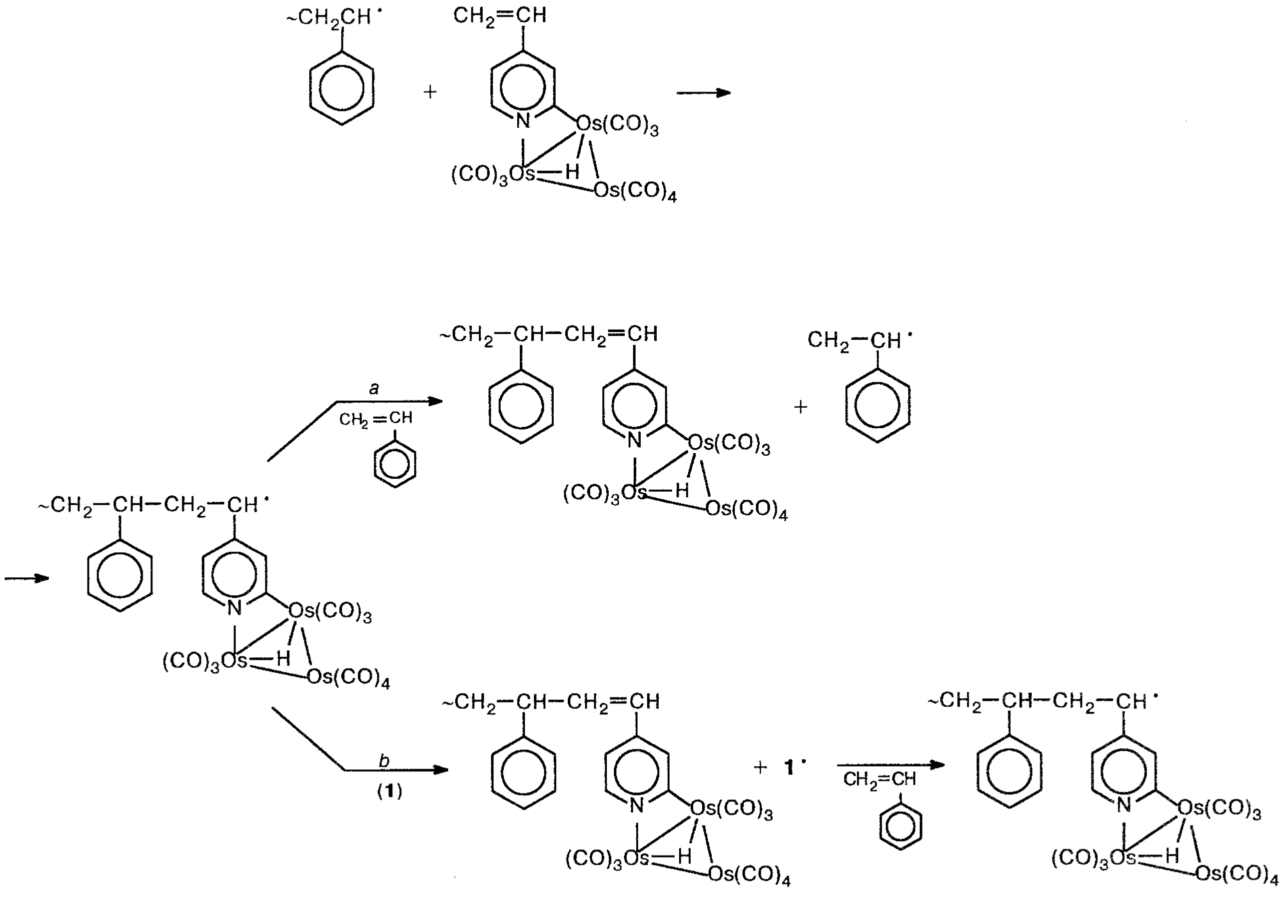
Fig. 2. Kinetics of specific heat evolution during the radical polymerization of styrene (*1*) and copolymerization of styrene with 4-vinylpyridine (1.0 mol. %) (*2*) and cluster monomer **1** at a content of the cluster monomer of 0.5 mol. % (*3*) and 1.0 mol. % (*4*).

unit and one terminal double bond. A comparison of all of these data suggests that cluster monomer **1** adding to the growing polymeric chain restricts its growth with no decrease in the concentration of active radicals, owing to the rapid chain transfer (Scheme 1).

According to this scheme, styrene (path *a*) or the cluster containing monomer (path *b*) can act as the chain transfer agents. The steric hindrance that interferes with homopolymerization of the cluster containing monomer equally affects the chain transfer to this monomer, and, therefore, its probability is extremely low. It is likely that the chain transfer occurs *via* a styrene molecule.

It is known[11] that the constants of the inherent chain transfer in the homopolymerization of styrene or 4-vinylpyridine (4-VP) are four orders of magnitude lower than the rate constants of growth for the corresponding monomers. Based on the values of the constants of copolymerization of styrene with 4-VP (r_1 = 0.5 to 0.7; r_2 = 0.7 to 0.7), one might expect that the rate constant for the reaction of the styrene radical with 4-VP would be twice as great as the growth rate constant (K_g) for styrene. Since K_g for styrene at 60 °C is close to $1.5 \cdot 10^2$, the constant for the reaction of the styrene

Scheme 1



radical with 4-VP should be ~300. This is apparently the upper limit for the rate constant of the reaction of styrene with **1**, because this value may be lower due to the presence of the bulky substituent in the molecule of **1**. Based on the molecular weight characteristics of the high-molecular weight fraction precipitated, one can evaluate the lower limit for the constant of the reaction between the styrene radical and the double bond of **1** using the Mayo equation:[12]

$$1/P_n = 1/P_0 + C_s S/M,$$

where P_n is the average degree of polymerization; P_0 is the degree of polymerization in the absence of the chain termination agent; $C_S = K_s/K_g$ is the relative rate constant of the reaction of the polymeric radical with the molecule of the chain termination agent; K_s is the absolute rate constant of the reaction of the polymeric radical with the molecule of the chain termination agent; S is the concentration of the chain termination agent; M is the concentration of the monomers.

This evaluation (Fig. 3) affords the value $C_s = 0.2$. Since K_g for styrene at 70 °C is close to $2 \cdot 10^2$, the K_s value lies between 40 and 300.

If we use the lower value of K_s to estimate the possible effect of the cluster monomer on the kinetics of polymerization,[13] we shall obtain the following result. Provided that the accuracy of the experimental data is not lower than 3 %, cluster monomer **1** present at a concentration of 1 mol. % will have no effect on the rate of polymerization of styrene only when the probability of chain regeneration is higher than 97 %, *i.e.*, almost all of the radicals formed from **1** transfer the kinetic chain, most likely to styrene molecules, rather than terminate it. This conclusion is confirmed by the fact that the number of double bonds in 1 g of the polymer corresponds to the content of the cluster and to the number of polymeric chains (see Table 1).

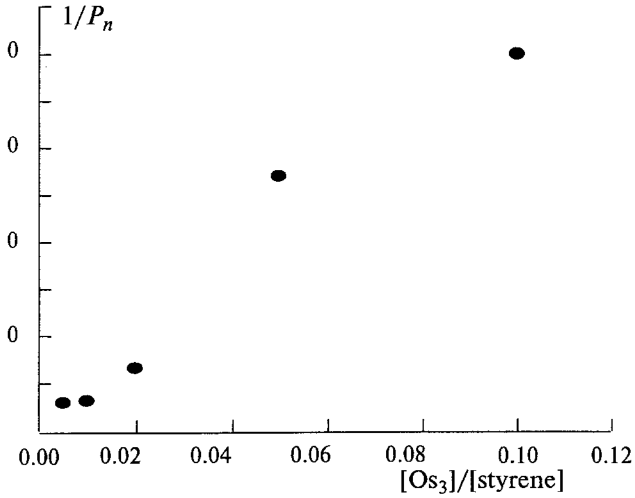


Fig. 3. Dependence of the reciprocal of the average degree of polymerization, P_n, on the (**1**)/styrene molar ratio in the reaction mixture.

Thus, the polymers obtained are macromolecules of polystyrene with terminal cluster groups.

It should be noted that the bulky cluster ligands in monomers **1**—**3** do not disrupt the effect of the nearest environments of the double bonds. In fact, one can correlate the reactivity ($1/r_1$) of 4-VP, allylic monomers, and acrylates toward styrene radicals (1.6; 0.01 to 0.03; and 4.0, respectively) and the reactivity of **1**—**3**. According to their copolymerization constants, allylic monomers poorly copolymerize with styrene; however, their presence in the system leads to the degenerate inherent chain transfer, which is due to the lability of the allylic hydrogen atom. In conformity with these specific features, the content of cluster monomer **2** in copolymers with styrene is almost an order of magnitude lower than that of **1** (see Fig. 1, *a*, *b*), and only 10—20 % of polystyrene chains contain cluster monomer **2** (see Table 1).

In the study of the copolymers of styrene with monomer **3**, the inconsistency between the average number of the polymeric chains and the content of the cluster monomer in the copolymers, and also the decrease in M_n compared with that of styrene copolymers with **1** and **2**, remain unknown. Neither the kinetics of heat evolution (see Fig. 2, curve *4*) observed in the copolymerization of styrene with **3** nor the constants of copolymerization with the corresponding noncluster monomers (for acrylates, r_1 = 0.6 to 0.75; r_2 = 0.2 to 0.4) differ from those for the copolymerization of styrene with **1**.

Copolymerization of cluster monomers 1—3 with acrylonitrile in toluene solutions is complicated by some features peculiar to homopolymerization of acrylonitrile: the resulting polymer precipitates even at low degrees of

Table 2. Comparative analysis of copolymers of acrylonitrile with cluster monomers **1**—**3** concerning number-average molecular weights, the proportion of the cluster units ($\times 10^5$ mol g^{-1}), and the average percentage of polyacrylonitrile chains incorporating cluster units

Polymer	M_n	[KM]* in the copolymer	%
PAN	18000		
AN:**1**=0.005	15000	0.61	9
AN:**1**=0.01	15000	1.12	17
AN:**2**=0.005	17000	0.41	7
AN:**2**=0.01	15000	0.61	10
AN:**3**=0.005	12000	0.62	7
AN:**3**=0.01	8000	0.64	5

* The proportions of the cluster monomers in the copolymers were determined from the data of the elemental analysis for osmium.

conversion, and polymerization occurs under heterogeneous conditions. The effects that accompany this process (simultaneous occurrence of polymerization in solution and in the solid phase, polymerization on a replica, scavenged radicals, *etc.*) substantially complicate the process and hamper interpretation of the results.

In general, in spite of the heterogeneous nature of the reaction, the proportion of cluster units in the copolymers obtained by copolymerization of acrylonitrile with cluster monomers **1—3** (Table 2) qualitatively correlates with the reactivities of 4-VP, allylic monomers, and acrylates toward the acrylonitrile radical, which are 9 (r_1 = 0.11), 0.2 to 0.3 (r_1 = 3 to 5), and 0.9 (r_1 = 1.1), respectively.[10] The heterogeneous character of the copolymerization is probably responsible for the fact that the products obtained are mixtures of the homopolymer and a small amount of polyacrylonitrile chains incorporating the cluster units. In the case of the copolymerization of acrylonitrile with monomer **3**, the yield of the copolymer decreases from 70 to 48 %, and the number-average molecular weight decreases, as the concentration of **3** in the mixture of comonomers increases from 0.5 to 1.0 mol.%. The decrease in the molecular weight observed in copolymerization of both styrene and acrylonitrile with **3** compared to the reactions with the two other cluster monomers is difficult to explain. To explain this fact, additional studies are required.

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References

1. *Metal Clusters in Catalysis,* Eds. B. C. Gates, L. Guczi, and H. Knozinger, Elsevier, Amsterdam—Oxford—New York—Tokyo, 1986, 648.
2. L. N. Arzamaskova and Yu. I. Ermakov, *Zh. Vsesoyuz. Khim. obshch. im. D. I. Mendeleeva,* 1987, **32**, 75 [*Mendeleev Chem. J.*, 1987, **32** (Engl. Transl.)].
3. B. C. Gates and J. Lieto, *Chem. Technol.*, 1980, **10**, 248.
4. A. D. Pomogailo, *Platinum Metals Rev.*, 1994, **38**, 60.
5. V. A. Maksakov, V. P. Kirin, S. N. Konchenko, and N. M. Bravaya, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1293 [*Russ. Chem. Bull.*, 1993, **42**, 1236 (Engl. Transl.].
6. B. C. Gates and H. H. Lamb, *J. Mol. Catal.*, 1989, **52**, 1.
7. S. C. Brown and J. Evans, *J. Mol. Catal.*, 1981, **11**, 143.
8. R. Barth, B. C. Gates, Y. Zhao, H. Knözinger, and J. Hulse, *J. Catal.*, 1983, **82**, 147.
9. P.-L. Zhou and B. C. Gates, *J. Chem. Soc. Chem. Commun.*, 1989, 347.
10. *Sopolimerizatsiya* [*Copolymerization*], Ed. D. Ham, Khimiya, Moscow, 1971, 282 (Russ. Transl.).
11. E. T. Denisov, *Konstanty skorosti gomoliticheskikh zhidkofaznykh reaktsii* [*Rate Constants of Homolytic Liquid-Phase Reactions*], Nauka, Moscow, 1971, 292, 340 (in Russian).
12. C. J. Walling, *J. Polym. Sci.*, 1955, **16**, 315.
13. Kh. S. Bagdsar'yan, *Teoriya radikl'noi polimerizatsii* [*The Theory of Radical Polymerization*], Nauka, Moscow, 1966, 155 (in Russian).

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