APPLIED ORGANOMETALLIC CHEMISTRY
*Appl. Organometal. Chem.* 2001; **15**: 169–177

# Tricarbonylchromium complexes of styrenes in radical copolymerization[†]

Dmitry F. Grishin,* Ludmila L. Semyonycheva, Ilya S. Illichev and Alexander N. Artemov
Research Institute of Chemistry of Lobachevski State University, Gagarin str., 23, building 5, Nizhny Novgorod, 603600 Russia

**The organometallic monomers styrenetricarbonylchromium and *p*-methylstyrenetricarbonylchromium were copolymerized in ethyl acetate solutions with methyl methacrylate and butyl acrylate using azobisisobutyronitrile at 50 °C and a binary system including di-*tert*-butylperoxytriphenylantimony at 30 °C as the free-radical initiators. Comonomers are proposed to form a molecular complex based on the results of ultraviolet and electron spin resonance spectroscopy. A kinetic study shows that chromium-containing monomers at high concentrations in the mixture reduce the rate of copolymerization. The addition of styrenetricarbonylchromium to butyl acrylate significantly slows down the autoacceleration. The reactivity ratios of the comonomer pairs, namely, styrenetricarbonylchromium–methyl methacrylate, styrenetricarbonylchromium–butyl acrylate and *p*-methylstyrenetricarbonylchromium–methyl methacrylate, were determined using the method of Kelen–Tudos for low conversion polymerizations. Copyright © 2001 John Wiley & Sons, Ltd.**

**Keywords: arene complexes; tricarbonylchromium complexes; organometallic monomers; radical copolymerization; chromium-containing polymers**

*Received 17 December 1999; accepted 19 May 2000*

## INTRODUCTION

The synthesis of polymers[1–6] containing organometallic monomers and investigations of their properties[1,4] have accelerated during last two decades. The radical-initiated vinyl addition copolymerization of a variety of organometallic monomers containing carbonyl groups, such as (vinylcyclopentadienyl)tricarbonyl manganese,[1] (vinylcyclopentadienyl)dicarbonylnitrosylchromium,[4] and (2-phenylethyl methacrylate)tricarbonylchromium,[5] have now been well established. The largest part of the available literature deals with the synthesis of organometallic monomers containing transition metals (titanium, molybdenum, tungsten, cobalt, etc.) which are generally complexed with vinylcyclopentadienyl moiety.[1,4,7] These monomers were said to take part both in homopolymerization and copolymerization with common organic monomers.[7,8]

Metal-containing polymers[9] are of interest both from practical and theoretical points of view. As far as practical usage of these materials is concerned, they are very attractive owing to their possible applications as catalysts of chemical processes, X-ray absorbers or materials having optical, biocidal properties, etc. In addition, unsaturated organometallic compounds of transition metals have been investigated actively in recent years as novel chromophores suitable for nonlinear optical applications.[10–12] Theoretically, metal atom introduction into an unsaturated molecule can exert a significant influence on the reactivity of a monomer and on the corresponding macroradical, and hence on the properties of the copolymers produced.

Our interest was concentrated on tricarbonylchromium complexes of arenes in the radical copolymerization with acrylates. The tricarbonyl complexes are preferentially styrene derivatives. Many of these compounds have been synthesized during the last decade. Rausch *et al.* were the first to prepare styrenetricarbonylchromium (STC).[13] Re-

---

* Correspondence to: Dmitry F. Grishin, Research Institute of Chemistry of Lobachevski State University, Gagarin str., 23, building 5, Nizhny Novgorod, 603600 Russia.
E-mail: grishin@ichem.unn.runnet.ru

† Presented at the XIIIth FECHEM Conference on Organometallic Chemistry, 29 August–3 September 1999, Lisbon, Portugal.

Contract/grant sponsor: Russian Foundation for Basic Research; Contract/grant number: 99-03-33346.

cently styrenetricarbonylchromium complexes have been used as a source of optically pure chromium tricarbonyls.[14,15]

Only a few organochromium monomers have been polymerized. These include (benzyl acrylate)-,[16] (2-phenylethyl acrylate)-, (2-phenylethylmethacrylate)-tricarbonylchromium[3,5] and STC.[2] The latter has been readily copolymerized with styrene, methyl acrylate and vinylcymantrene,[2] but it would not homopolymerize.[3] Since the 1970s, the literature is devoid of examples of polymers containing (aryl)-tricarbonylchromium groups. Unfortunately, published works do not explain the reasons for the inability of STC to homopolymerize. Also, the cited literature reports kinetic data on the polymerization and copolymerization of Cp-complexed manganese- and tungsten-containing monomers,[17,18] but information related to the kinetic study of organochromium monomers is very rare.[4,6] Therefore, it is clear that, in the presence of a monomer molecule containing a transition metal atom, macromolecule formation may significantly differ from that in the presence of organic monomers only.

Herein we report the results of the study of interaction between metal-containing and organic monomers by ultraviolet (UV) and electron spin resonance (ESR) spectroscopy, as well as a kinetic investigation of the radical copolymerization of tricarbonylchromium complexes of styrenes and acrylic monomers.

## EXPERIMENTAL

All reactions involving tricarbonylchromium complexes were carried out under an atmosphere of argon using standard techniques.[19] STC, and the related monomer (*p*-methylstyrene)tricarbonylchromium (PMSTC), have been synthesized according to methods[13,20] via the intermediate complex, $(NH_3)_3Cr(CO)_3$. The synthesis of this intermediate has been simplified by using atmospheric pressure conditions. Its physical constants are in agreement with data in the literature.[2,13,20] The overall yields of STC and PMSTC were 62% and 50% respectively. Methyl methacrylate (MMA) and butyl acrylate (BA) were purified by vacuum distillation before use. 2-Methyl-2-nitrosopropane was produced via a method already described.[21] STC and PMSTC were copolymerized with MMA and BA, both in bulk and in ethyl acetate, using azobisisobutyronitrile (AIBN) as the free radical initiator at 50 °C. Di-*tert*-butylperoxytriphenylantimony (DPA) was also used as a radical source at 30 °C. Concentrations of AIBN and DPA of 0.5 wt% and 1.6 wt.% respectively were employed.

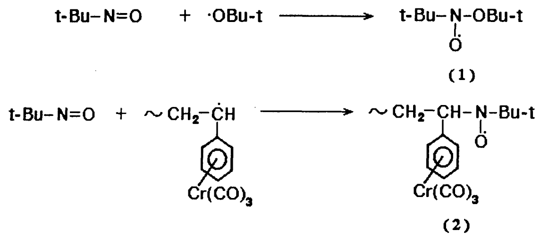
The copolymerizations were conducted using the technique previously described.[3] Weighed batches of STC were dissolved in ethyl acetate, and measured amounts were charged into tubes with appropriate amounts of comonomer and initiator. The tubes were triply degassed and immersed in a constant-temperature bath for a predetermined time. After polymerization, the tubes were cooled and the mixture diluted with a small amount of ethyl acetate. Prepared 5–10 ml solution was precipitated dropwise in 200 ml of heptane bubbled with argon. The isolated polymer was washed three times with fresh portions of heptane. After reprecipitation the polymers were freeze-dried and then weighed.

AIBN was purified by recrystallization from methanol at 50 °C. DPA was prepared according to a published method.[22] Monomer ratios present in the copolymers (i.e. copolymer compositions) were determined by chromium elemental analyses, which were performed spectrophotometrically.[23] The copolymers were characterized by gel permeation chromatography. These measurements were made using a Waters instrument (USA) equipped with a set of five Styragel columns with pore diameters of $10^5$, $3\times10^4$, $10^4$, $10^3$ and 250 and a Waters R-403 differential refractometer. Polystyrene standards with a narrow molecular weight distribution were used for calibration.[24] Gel permeation chromatograms were run in THF at 30 °C. Estimates of $r_1$ and $r_2$ were obtained using the Kelen–Tudos method.[25] ESR spectra were recorded on an AE 4700 radiospectrometer in special tubes. The method used was similar to a published procedure.[26] UV spectra were recorded for the purified compounds and for mixtures in an original cell using a Specord M-40 spectrophotometer. The kinetic study was carried out using a thermometric technique.[27]

## RESULTS AND DISCUSSION

To initiate copolymerization of acrylic monomers and STC (as well as PMSTC) we used the common initiator, AIBN, and the specific organometallic binary initiator STC–DPA.[28]

By spin trapping ESR spectroscopy, STC (PMSTC) was found to react with initiating radicals to form the corresponding propagating radicals. For



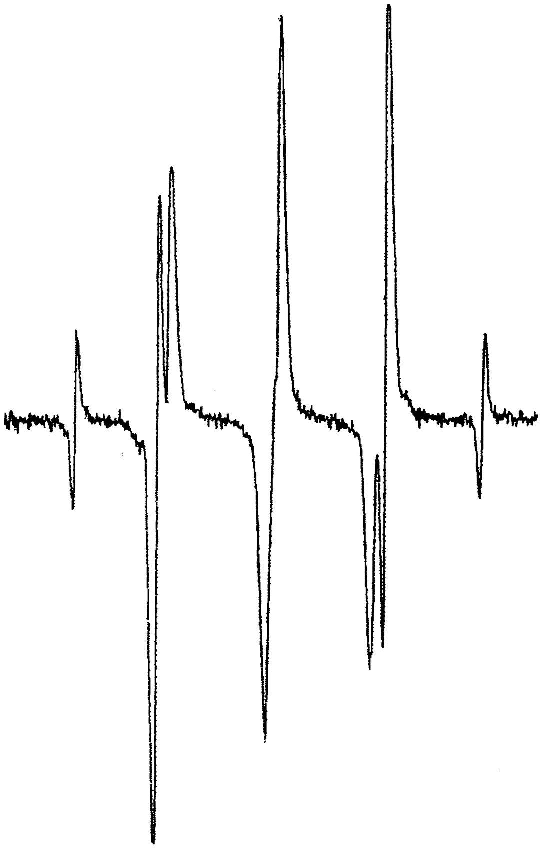
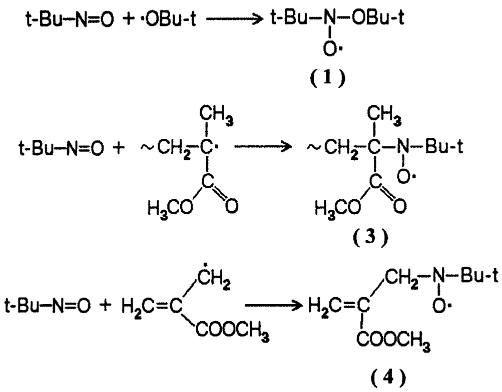


**Figure 1** The ESR spectra of the STC–DPA system. $T = 25$ °C. Spin-trap: 2-methyl-2-nitrosopropane (0.08 mol $l^{-1}$). STC:DPA = 1:1 (mol). [STC] = 0.03 mol $l^{-1}$. Solvent: hexane.

example, the ESR spectra of the STC–DPA system exhibits signals of the *tert*-butoxyl radical spin adduct (1) (Fig. 1), a triplet having constant $a_{\mathrm{N}} = 27.3$ G. 2-Methyl-2-nitrosopropane was used as a spin trap. These radicals were produced via decomposition of DPA in its reaction with STC. A triplet of doublets ($a_{\mathrm{N}} = 15.0$ G; $a_{\mathrm{H}} = 1.6$ G) was assigned to spin adduct (2) — the reaction product of the terminal propagating styrenetricarbonylchromium radical and the spin trap. It is interesting to note that the $a_{\mathrm{N}}$ constant of this adduct is somewhat



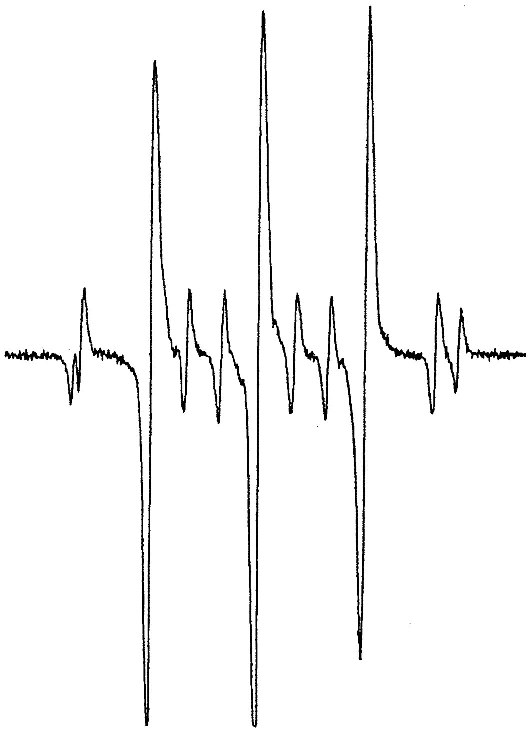
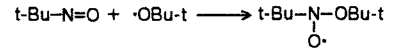


**Figure 2** The ESR spectra of the STC–DPA system in the presence of MMA. $T = 25$ °C. Spin-trap: 2-methyl-2-nitrosopropane (0.08 mol $l^{-1}$). STC:DPA = 1:1 (mol). [STC] = 0.03 mol $l^{-1}$. [MMA] = 4.5 mol $l^{-1}$. Solvent: hexane.

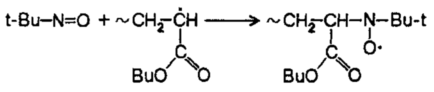
lower than that of the polystyrene radical adduct ($a_{\mathrm{N}} = 15.0$ G; $a_{\mathrm{H}} = 2.2$ G).[26] Delocalization of spin density on the (arene)tricarbonylchromium moiety via a vacant *d*-orbital of the metal atom may be responsible for this phenomenon.

When MMA was introduced, i.e. in studies of the copolymerization of STC with acrylic monomers, spin adduct (1) signals and polymeric MMA radical



$$t\text{-}Bu{-}N{=}O + {\cdot}OBu\text{-}t \longrightarrow t\text{-}Bu{-}\underset{\underset{O\cdot}{|}}{N}{-}OBu\text{-}t$$

**(1)**



$$t\text{-}Bu{-}N{=}O + {\sim}CH_2{-}\underset{\underset{C(=O)OBu}{|}}{\dot{C}H} \longrightarrow {\sim}CH_2{-}\underset{\underset{C(=O)OBu}{|}}{CH}{-}\underset{\underset{O\cdot}{|}}{N}{-}Bu\text{-}t$$

**(5)**

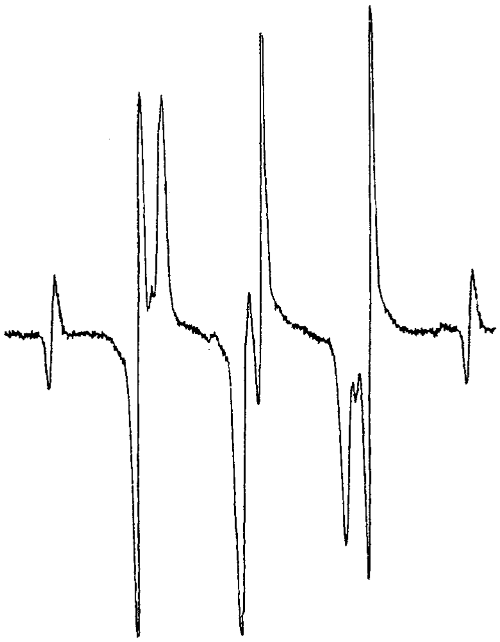


**Figure 3** The ESR spectra of the STC–DPA system in the presence of BA. $T = 25$ °C. Spin-trap: 2-methyl-2-nitrosopropane (0.08 mol $l^{-1}$). STC:DPA = 1:1 (mol). [STC] = 0.03 mol $l^{-1}$. [BA] = 4.5 mol $l^{-1}$. Solvent: hexane.

adduct (3) signals were detected in the ESR spectra (Fig. 2). This spectrum was the combination of a triplet ($a_N = 15.3$ G) and a triplet of triplets ($a_N = 15.1$ G; $a_H = 10.1$ G). The latter signals were assigned to the spin adduct (4), which results from hydrogen atom abstraction of MMA by the propagating macroradical or the initiator radical. Therefore, chain transfer to monomer occurs.

Similar data were obtained in studies of the copolymerization of STC with BA. The ESR spectrum exhibits bands of spin adduct (1) and polybutylacrylate radical adduct (5) ($a_N = 15.0$ G; $a_H = 2.9$ G) (Fig. 3). It should be noted that, in the presence of acrylates, there are no signals due to the poly(STC) radical adduct (2), which had been observed in the spectra obtained when MMA and BA were absent (Fig. 1).

This fact allows us to suggest that a molecular complex is formed between the two monomers (STC···acrylate). Molecular complex formation between the electron-rich (arene)tricarbonylchromium and acceptors has been described in literature.[29] Thus, chain propagation is proposed to occur due to addition of this STC···acrylate complex to the terminal radical. Hence, a poly(acrylate) radical **A**· is expected to terminate the polymeric chain:

$$\sim\mathbf{P}\cdot + (\mathrm{STC} \cdots \mathbf{A}) \rightarrow \sim\mathbf{P} - \mathrm{STC} - \mathbf{A}\cdot$$

where $\sim\mathbf{P}\cdot$ is a propagating macroradical.

A similar mechanism has been put forward by others,[30] based on ESR spectroscopy data for the complex–radical copolymerization of sulfur dioxide and butadiene.

Donor–acceptor monomer complex formation during chain propagation was confirmed by UV–vis spectroscopy. For example, STC solutions in hexane exhibit an absorption band ($\lambda \approx 365$ nm) that can be attributed to ligand–metal charge transfer.[31] This band was found to shift slightly upon introduction of acrylic monomer. In addition, the band shift is enhanced on cooling STC solution in MMA to $-45$ °C. Also, the intensity of the band increased considerably as the temperature was lowered. Reheating of the solution to ambient temperature results in spectra identical to that presented above for MMA.

These data indicate the formation of a labile complex (STC···MMA) with partial charge transfer,[32] where STC actively participates in redistribution of electron density.

The proposed structures of the complexes are presented in Fig. 4.

Therefore, the copolymerization of STC, as well as PMSTC and acrylates, can be considered an

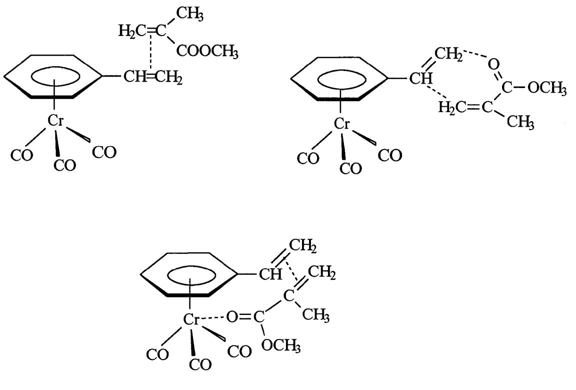


**Figure 4** Proposed structures of the partial charge transfer complexes.

example of coordination-radical polymerization.[33] The influence of a metal atom is one of the features of this type of polymerization. The metal atom influences to a large extent the propagation step of the polymerization. Thus, it was of interest to study the rate law for the copolymerization between the metal-containing monomer and acrylates.

The rates of polymerization, degree of conversion and copolymer composition are determined by the monomer ratio in the initial mixture.

A thermometric method was used to study the overall rate of MMA copolymer formation when initiated by AIBN at 65 °C. The monomer mixtures employed contained STC concentrations up to 10 mol%. It was found that using 10% of STC hardly influences the kinetics of the polymerization (Fig. 5a). The process continues up to a conversion of 91–94% in 5–8 h at 65 °C. The maximum conversion diminishes significantly with an increase in organometallic monomer concentration. For example, at 30 mol% the conversion does not exceed 50%. Simultaneously, the polymerization rate slows significantly. Further increase in the STC concentration leads to heterogeneity, since the STC solubility in MMA (as well as in other esters) is about 0.4 mol of arenetricarbonyl in 1 mol of MMA.

Therefore, to enable copolymerizations to be conducted over a wide set of monomer ratios, solutions were employed. Ethyl acetate was used as the solvent, since it dissolves both monomers very well. The AIBN-initiated polymerization was carried out at 50 °C for a number of STC:MMA ratios up to conversions that did not exceed 30% (Table 1). Data listed in Tables 1 and 2 demonstrate

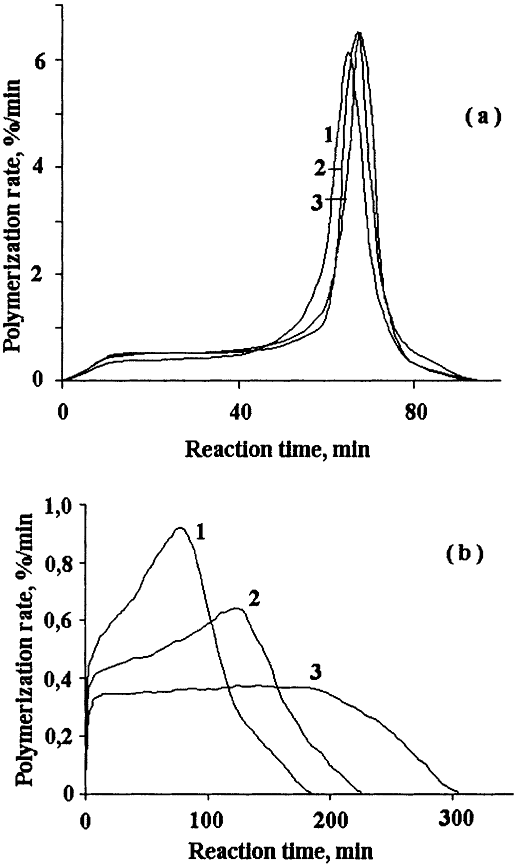


**Figure 5** The kinetics of copolymerization: (a) the STC–MMA mixture. $T = 65$ °C. Initiator: AIBN (0.5 wt%). (**1**) STC: 0%; (**2**) STC: 5%, (**3**) STC: 10%. (b) The STC–BA mixture. $T = 50$ °C. Initiator: AIBN (0.5 wt%). (**1**) STC: 0%; (**2**) STC: 1%; (**3**) STC: 3%.

**Table 1** Copolymerization of styrenetricarbonylchromium ($M_1$) and MMA ($M_2$) at 50 °C in ethyl acetate[a]

| Polymer | Initial $M_1$ (mol%) | Polymerization time (h) | Yield (%) | $M_1$ in copolymer (mol%) |
|---|---|---|---|---|
| 1 | 5.8 | 3.8 | 11.3 | 6.9 |
| 2 | 10.0 | 5.0 | 13.1 | 13.4 |
| 3 | 12.2 | 4.3 | 7.6 | 14.9 |
| 4 | 19.2 | 6.5 | 10.9 | 17.2 |
| 5 | 27.0 | 12.6 | 14.3 | 25.1 |
| 6 | 30.0 | 12.0 | 9.3 | 26.4 |
| 7 | 35.8 | 15.5 | 21.1 | 30.3 |
| 8 | 40.0 | 13.0 | 7.7 | 33.7 |
| 9 | 46.2 | 21.0 | 23.6 | 34.4 |
| 10 | 50.0 | 15.0 | 7.2 | 42.3 |
| 11 | 56.5 | 23.5 | 16.9 | 48.2 |

[a] 75 vol.% of ethyl acetate was used in solution. Initiator: AIBN (0.5 wt.%).

**Table 2** Copolymerization of styrenetricarbonylchromium ($M_1$) and MMA ($M_2$) at 30 °C in ethyl acetate[a]

| Polymer no. | Initial $M_1$ (mol%) | Polymerization time (h) | Yield (%) | $M_1$ in copolymer (mol%) |
|---|---|---|---|---|
| 1 | 5.0 | 8.4 | 4.3 | 7.4 |
| 2 | 10.0 | 18.8 | 4.3 | 13.3 |
| 3 | 20.0 | 24.6 | 2.9 | 24.2 |
| 4 | 30.0 | 33.8 | 2.3 | 34.3 |
| 5 | 40.0 | 34.0 | 2.1 | 40.8 |

[a] 80 vol.% of ethyl acetate was used in solution. Radical source: DPA (1.6 wt.%).

**Table 3** Copolymerization of *p*-methylstyrenetricarbonylchromium ($M_1$) and MMA ($M_2$) at 50 °C in ethyl acetate[a]

| Polymer no. | Initial $M_1$ (mol%) | Polymerization time (h) | Yield (%) | $M_1$ in copolymer (mol%) |
|---|---|---|---|---|
| 1 | 5.0 | 5.0 | 9.5 | 3.5 |
| 2 | 10.0 | 9.4 | 12.8 | 6.9 |
| 3 | 20.0 | 9.1 | 8.6 | 9.4 |
| 4 | 40.0 | 18.6 | 11.8 | 24.7 |
| 5 | 50.0 | 19.6 | 11.7 | 34.4 |
| 6 | 60.0 | 23.0 | 10.8 | 42.7 |

[a] 80 vol.% of ethyl acetate was used in solution. Initiator: AIBN (0.5 wt.%).

that the increase in the STC concentration reduces the rate of polymerization. For example, to reach a conversion of 7% in copolymerizations containing 12.2 mol%, 40.0 mol% and 50.0 mol% of STC takes 4.3 h, 13.0 h and 15.0 h respectively (Table 1).

The copolymerization of MMA with STC in ethyl acetate at 30 °C using the binary initiator STC–DPA at various monomer ratios gave a yield not exceeding 4.3 mol.%. An increased STC concentration also slowed down the conversion. The copolymer was enriched in STC for the majority of the monomer ratios studied (Table 2).

A kinetic study was performed both for the copolymerization of the STC derivative, such as PMSTC with MMA, and of STC with BA. As in the presence of small amounts of STC, the overall rate of PMSTC–MMA polymerization slightly depended on the MCM content (up to 5 mol%). An influence of the MCM content on the kinetic curve shape was also observed when STC was copolymerized with BA. The introduction of MCM into the system leads to a decrease in the gel effect (Fig. 5b). It is of interest to note that the rate of the BA–STC (97:3 mol.%) copolymerization remained practically the same throughout the process.

**Table 4** Copolymerization of *p*-methylstyrenetricarbonylchromium ($M_1$) and MMA ($M_2$) at 30 °C in ethyl acetate[a]

| Polymer no. | Initial $M_1$ (mol%) | Polymerization time (h) | Yield (%) | $M_1$ in copolymer (mol%) |
|---|---|---|---|---|
| 1 | 5 | 16.0 | 4.0 | 8.0 |
| 2 | 10 | 17.0 | 3.6 | 9.2 |
| 3 | 20 | 27.5 | 5.3 | 22.6 |
| 4 | 40 | 35.5 | 1.5 | 28.9 |
| 5 | 60 | 40.6 | 1.6 | 45.6 |

[a] 50 vol.% of ethyl acetate was used in solution. Radical source: DPA (1.6 wt.%).

**Table 5** Copolymerization of styrenetricarbonylchromium ($M_1$) and BA ($M_2$) at 50 °C in ethyl acetate[a]

| Polymer no. | Initial $M_1$ (mol%) | Polymerization time (h) | Yield (%) | $M_1$ in copolymer (mol%) |
|---|---|---|---|---|
| 1 | 5 | 3.3 | 13.7 | 4.9 |
| 2 | 5 | 8.6 | 38.3 | 4.7 |
| 3 | 10 | 3.8 | 14.9 | 8.0 |
| 4 | 10 | 11.0 | 45.0 | 10.2 |
| 5 | 20 | 4.3 | 18.4 | 21.7 |
| 6 | 20 | 15.0 | 46.5 | 20.7 |
| 7 | 25 | 3.5 | 10.9 | 25.5 |
| 8 | 40 | 4.2 | 11.8 | 42.0 |
| 9 | 40 | 16.5 | 51.7 | 36.0 |

[a] 50 vol.% of ethyl acetate was used in solution. Initiator: AIBN (0.5 wt.%).

**Table 6** Copolymerization of styrenetricarbonylchromium ($M_1$) and BA ($M_2$) at 30 °C in ethyl acetate[a]

| Polymer no. | Initial $M_1$ (mol%) | Polymerization time (h) | Yield (%) | $M_1$ in copolymer (mol%) |
|---|---|---|---|---|
| 1 | 5 | 13.5 | 7.0 | 4.9 |
| 2 | 10 | 20.0 | 7.3 | 10.9 |
| 3 | 20 | 25.3 | 4.7 | 23.2 |
| 4 | 40 | 28.5 | 3.0 | 24.7 |
| 5 | 60 | 28.3 | 2.7 | 46.9 |

[a] 50 vol.% of ethyl acetate was used in solution. Radical source: DPA (1.6 wt.%).

Some dependencies of copolymer compositions on the compositions of initial monomer mixtures for copolymerizations of PMSTC with MMA and STC, both with MMA and BA in an ethyl acetate solution at low conversions using AIBN and the binary system as initiators, were obtained. These data are summarized in Tables 1, 3 and 5 and in Tables 2, 4 and 6 for the copolymerizations carried out in the presence of AIBN and binary initiator respectively.

Relative ratios are of interest as they characterize the reactivity of growing radicals. These parameters may differ significantly for a regular radical process and complex–radical polymerization. Relative ratio constants (Table 7) were calculated with the Kelen–Tudos method and derived from the data shown in Tables 1–6. The relative ratios of STC and PMSTC were equal to zero and agreed with the literature.[2,13,20] The constants of copolymerization obtained listed in Table 7 allowed us to draw some conclusions. MMA and BA had similar constants at the same process temperature and in the presence of the same initiator. This fact is consistent with the known regularity of a small decrease of the

**Table 7** Reactivity ratios for the copolymerization of styrenetricarbonylchromium ($M_1$) and *p*-methylstyrenetricarbonylchromium ($M_1$) with organic monomers ($M_2$)[a]

| Monomer pair | Initiator | Temperature ( °C) | $M_1$ | $M_2$ | $r_2$[b] |
|---|---|---|---|---|---|
| 1 | AIBN | 50 | STC | MMA | 0.71 |
| 2 | DPA | 30 | STC | MMA | 0.60 |
| 3 | AIBN | 50 | STC | BA | 0.75 |
| 4 | DPA | 30 | STC | BA | 0.65 |
| 5 | AIBN | 50 | PMSTC | MMA | 1.44 |
| 6 | DPA | 30 | PMSTC | MMA | 1.10 |

[a] In ethyl acetate solution.
[b] $r_1 = 0$.

**Table 8** Molecular weight and intrinsic viscosity determinations for a series of copolymers of styrenetricarbonylchromium and *p*-methylstyrenetricarbonylchromium ($M_1$) with organic monomers ($M_2$)[a]

| No. | $M_1$ | $M_2$ | $M_1$ in monomer feed | Initiator | Yield (%) | $M_n \times 10^{-3}$ | $M_w \times 10^{-3}$ | $M_w/M_n$ | $[\eta]$ dl g$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | — | MMA | — | AIBN | 10 | 142 | 257 | 1.8 | 0.581 |
| 2 | STC | MMA | 5 | AIBN | 57 | 114 | 197 | 1.7 | 0.481 |
| 3 | STC | MMA | 10 | AIBN | 47 | 82 | 139 | 1.7 | 0.377 |
| 4 | STC | MMA | 20 | AIBN | 46 | 73 | 142 | 1.9 | 0.382 |
| 5 | STC | BA | 5 | AIBN | 38 | 181 | 369 | 2.0 | 0.700 |
| 6 | STC | BA | 10 | AIBN | 45 | 151 | 320 | 2.1 | 0.630 |
| 7 | STC | BA | 20 | AIBN | 47 | 105 | 215 | 2.0 | 0.470 |
| 8 | STC | MMA | 5 | DPA | 29 | 48 | 85 | 1.8 | 0.189 |
| 9 | PMSTC | MMA | 40 | AIBN | 12 | 40 | 65 | 1.6 | 0.225 |

[a] In ethyl acetate solution.

constants with decrease in temperature (here, from 50 to 30 °C). Changing from STC to PMSTC resulted in a significant increase in relative ratio of MMA: from 0.71 to 1.44 when initiated with AIBN (Table 7, entries 1 and 5) and from 0.60 to 1.10 in the presence of DPA (Table 7, entries 2 and 6). The constants of copolymerization were fitted to the $m_1$ *vs* $M_1$ plots for monomer pairs, such as MMA–STC, MMA–PMSTC and BA–STC.

The molecular weight distribution of the metal-containing polymers was studied by gel permeation chromatography. The calculated values of molecular weight and the polydispersity coefficients obtained for some samples of MMA–STC, MMA–PMSTC and BA–STC copolymers are presented in Table 8. It should be noted that all the synthesized metal-containing polymers exhibited monomodal chromatograms. In all cases the molecular weight values for the copolymers synthesized with AIBN as initiator decrease as the STC content in the copolymer increases (Table 8, samples 2–7). When PMSTC is used in copolymerization the molecular weight of the polymer falls significantly (Table 8, sample 9). The introduction of DPA as an initiator exerts a similar influence both in the molecular weight and intrinsic viscosity (Table 8, sample 8). This fact is explained by the active participation of DPA[28] and PMSTC in the chain transfer reaction.

As a conclusion, it is worth noting that incorporation of a transition metal atom into an unsaturated molecule exerts a significant influence on reactivity of both monomer and corresponding macroradical, as well as on polymeric chain propagation factors and kinetic features of the polymerization. Taking into account the features of elementary steps of the process, the synthesis of polymers including chromium-containing monomers and acrylates can be considered as an example of complex–radical polymerization.

*Acknowledgements* The authors thank the Russian Foundation of Basic Research (grant no. 99-03-33346) for financial support.

## REFERENCES

1. Pittman CU Jr, Marlin GV, Rounsefell RD. *Macromolecules* 1973; **6**: 1.
2. Pittman CU Jr, Grube PL, Ayers OE, McManus SP, Rausch MD, Moser GA. *J. Polym. Sci. Part A-1*; 1972; **10**: 379.
3. Pittman CU Jr, Marlin GV. *J. Polym. Sci. Part A-1* 1973; **11**: 2753.
4. Pittman CU Jr, Rounsefell TD, Lewis EA, Sheats JE, Edwards BH, Rausch MD, Mintz EA. *Macromolecules* 1978; **11**: 560.
5. Pittman CU Jr, Ayers OE, McManus SP. *Macromolecules* 1974; **7**: 737.
6. Kozyreva NM, Kirilin AI, Chernyshev AV, Korshak VV. Manuscript in VINITI from 11.08.88, No. 50-B88. Moscow, 1988.
7. Macomber DW, Hart WP, Rausch MD, Priester RD, Pittman CU Jr. *J. Am. Chem. Soc.* 1982; **104**: 884.
8. Pittman CU Jr, Rausch MD. *Pure Appl. Chem.* 1986; **58**: 617.
9. Pomogailo AD, Savostyanov VS. *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* 1985; **25C**: 375.
10. Long NJ. *Angew. Chem. Int. Ed. Engl.* 1995; **34**: 6.
11. Kanis DR, Ratner MA, Marks TJ. *Chem. Rev.* 1994; **94**: 195.
12. Frazier CC, Harvey MA, Cockerham MP, Hand HM, Chauchard EA, Lee CH. *J. Phys. Chem.* 1986; **90**: 5703.

13. Rausch MD, Moser GA, Zaiko EJ, Lipman AL Jr. *J. Organomet. Chem.* 1970; **23**(1): 185.
14. Davies SG, Furtado OML, Hepworth D, Loveridge T *Synlett* 1995; 69.
15. Gibson SE, Jefferson GR, Prechtl F. *J. Chem. Soc. Chem. Commun.* 1995; 1535.
16. Pittman CU Jr, Voges RL, Elder J. *Macromolecules* 1971; **4**: 302.
17. Pittman CU Jr, Lin CC, Rounsefell TD. *Macromolecules* 1978; **11**: 1022.
18. Pittman CU Jr, Priester RD, Jayaraman TU. *J. Polym. Sci. Part A-1* 1981; **19**: 3351.
19. Mahaffy CAL, Pauson PL. *Inorg. Synth.* 1979; **19**: 154.
20. Kozyreva NM, Chernyshev AV, Korotkov AK. Manuscript in VINITI from 13.10.93, No. 2582-B93. Moscow, 1993.
21. Terabe S, Konaka R. *J. Chem. Soc. Perkin Trans. 2* 1972; **14**: 2163.
22. Dodonov VA, Dregich AI, Aksenova IN, Semyonycheva LL USSR Inventor’s Certificate no. 1567584. *Byul. Izobr*. 1990; **20**: 89.
23. Borisova LN, Guseva TV. *Khimia Elementoorg. Soed. (Chemistry of Organoelement Compounds)*, Gorky Gos. University: Gorky, 1978; 79.
24. Moris S. *J. Liq. Chromatogr.* 1990; **13**: 1719.
25. Kelen T, Tüdos F, Turczanyi B. *Kinetic. Catal. Lett.* 1971: **2**: 439.
26. Dodonov VA, Grishin DF, Cherkasov VK, Razuvaev GA. *Vysokomol. Soedin. Ser. A* 1982; **24**(3): 451.
27. Arulin VI, Yefimov LI. *Trudy po khimii i khim. Tekhnol. Gor. Gos. Univ.* 1970; 74.
28. Grishin DF. *Russ. Chem. Rev.* 1993; **62**(10): 951.
29. Solladié-Cavallo A. *Polyhedron* 1985; **4**(6): 915.
30. Stoyachenko IL, Shklyarova EI, Kaplan AM, Golubev VB, Zubov VP, Kabanov VA. *Vysokomol. Soedin. Ser. A.* 1976; **18**(6): 1420.
31. Sennikov PG, Kuznetsov VA, Egorochkin AN, Sirotkin NI, Nazarova RG, Razuvaev GA. *J. Organometal. Chem.* 1980; **190**(2): 167.
32. Kobayashi H, Kobayashi M, Kaizu Y. *Bull. Chem. Soc. Jpn.* 1975; **48**: 1222.
33. Kabanov VA, Zubov VP, Semchikov YD. *Compleksno–radicalnaya polymerizatsia (Complex–radical polymerization)*. Khimia: Moscow, 1987.