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# (Arene)tricarbonylchromium(0) complexes in the synthesis of metal-containing polymers based on vinyl monomers

**Summary** — In analogy to azoisobutyronitrile (AIBN), (styrene or p-methylstyrene or toluene)tricarbonylchromium(0) (STC, PMSTC, TTC) complexes were studied as (co)initiators in radical homopolymerization (30°C) of vinyl monomers (Table 1). STC and PMSTC were also used as comonomers and copolymerized with methyl methacrylate (MMA) (Tables 2, 3) and butyl acrylate (BA) (Table 2). Di-*tert*-butylperoxytriphenylantimony (DPA), the most effective low-T initiator of vinyl radical polymerization, was used as initiator (Tables 2, 3) and coinitiator together with STC to copolymerize MMA and BA with STC and PMSTC. The copolymerization data were used to evaluate relative reactivity ratios for the monomers (Table 2). Initial homopolymerization rates were evaluated (Table 1). Chain propagation steps were studied and an original chain propagation model is suggested in compliance with complex-radical polymerization principles.

**Key words**: metal-containing monomer, metal-containing polymer, (styrene)tricarbonylchromium(0), acrylic monomers, radical polymerization, chain propagation model.

The synthesis of polymeric materials containing a chemically bounded metal is a novel branch actively developed in recent years. On the one hand, studies are driven by the practical value of metal-containing polymers that are endowed with special and original properties like enhanced catalytic activity and electric, optic, magnetic properties, *etc.* [1]. On the other hand, metal-containing monomers are suitable models to study chain propagation steps in complex-radical or radical-coordination polymerization [2], because the atom of the metal can coordinatingly interact with both the resulting macroradical and the monomer. This branch of polymer chemistry is important and interesting because of the novel approaches it has introduced into the synthesis of homo- and copolymers exhibiting a uniform composition, and of the theoretical frameworks it has offered to control the polymeric chain propagation step.

The present study is concerned with the application of (arene)tricarbonylchromium(0) complexes in the synthesis of polymers.

Although known not to homopolymerize, (styrene)tricarbonylchromium(0) is known to copolymerize readily with styrene as well as with methyl acrylate and vinylcymantrene [3—6].

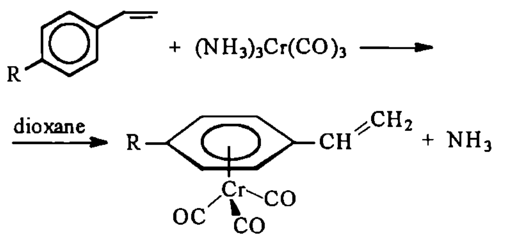
This study is intended to synthesize acrylic homo- and copolymers with the aid of styrene- and (*p*-methylstyrene)tricarbonylchromium(0) (STC and PMSTC) as coinitiators and MCM, and to examine elementary polymerization steps in the presence of the organochromium compounds. These include (toluene)tricarbonylchromium(0) (TTC), STC, and PMSTC. The steps to be studied include initiation, chain propagation, and chain transfer. One major part of the work is to investigate some physical properties of the resulting metal-containing polymers, *e.g.*, molecular weight parameters.

## EXPERIMENTAL

### Materials

All the reactions involving tricarbonylchromium complexes were carried out under an atmosphere of argon by using a standard technique [7]. STC and PMSTC were synthesized (eqns. 1, 2) according to methods [3, 8] *via* an intermediate $(NH_3)_3Cr(CO)_3$; its synthesis was simplified by using modified pressure conditions (rather than various bomb types).

$$Cr(CO)_6 \xrightarrow[2.\ NH_3]{1.\ KOH,\ EtOH,\ \Delta} (NH_3)_3Cr(CO)_3 + CO \qquad (1)$$



(2)

The physical constants measured were consistent with the literature data [3, 5, 8]. The overall yields of STC and PMSTC were 64% and 50%, respectively. Methyl methacrylate (MMA) and butyl acrylate (BA) were purified by standard techniques. 2-Methyl-2-nitrosopropane was produced by the method described in [9]. Azoisobutyronitrile (AIBN) was purified by recrystallization from methanol at 50°C. Di-*tert*-butylperoxytriphenylantimony (DPA) was prepared according to a published method [10].

### Homo- and copolymerization methods

Homopolymerization of vinyl monomers was carried out without solvent, by using 0.1 mol % of di-*tert*-butylperoxytriphenylantimony and 0.1 mol % of (styrene or toluene)tricarbonylchromium(0) as a binary initiator.

(Styrene)tricarbonylchromium(0) (0.0257 g) and a solution of DPA (0.0653 g) in methyl methacrylate (11.6 mL) were placed in a special dilatometric tube. The reactants were deaerated by the freeze-pump-thaw procedure. The sealed tubes were heated at 30°C in a water bath. Conversion was determined by monitoring the level of the solution for an appropriate time interval. In a manner similar to that described above, (toluene)tricarbonylchromium(0) was employed as a coinitiator. This method was also used for polymerization of vinyl acetate and styrene.

STC and PMSTC were copolymerized with methyl methacrylate and butyl acrylate in ethyl acetate by using azoisobutyronitrile (AIBN) as the free radical initiator at 50°C and di-*tert*-butylperoxytriphenylantimony (DPA) as a source of redicals at 30°C. In the solutions containing 25 wt. % of the monomers per 75 wt. % of ethyl acetate, the concentrations of AIBN and DPA were 0.5 and 1.6 wt. %, respectively. The copolymerizations were conducted by using the technique described in [11].

Weighed portions of STC or PMSTC were dissolved in ethyl acetate, and measured amounts were charged into the tubes containing appropriate amounts of the comonomer and the initiator. The tubes were triply degassed and immersed into a constant temperature bath for a predetermined period of time. After polymerization, the tubes were cooled and the mixture was diluted with a small amount of ethyl acetate. The solution prepared, 5—10 mL, was added dropwise to 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.

### Methods of determination of polymers

Monomer ratios in the copolymers were determined by the chromium elemental analyses using a spectrophotometric technique [12]. The molecular weight of the homopolymer was estimated by viscometry. The copolymers were characterized by gel permeation chromatography and estimates of molecular weights were obtained by universal calibration [13]. Gel permeation chromatograms were run in THF at 30°C on a Waters Model 301 GPC. A differential refractometer R-403 (Waters) was used as a detector. Estimates of $r_1$ and $r_2$ were obtained by using the Kelen—Tüdos method [14]. ESR spectra were recorded with a radiospectrometer AE 4700 in special tubes. The method used was similar to that published in [15]. UV spectra were recorded for the purified compound mixtures in an original cell by using a Specord M-40 spectrophotometer.

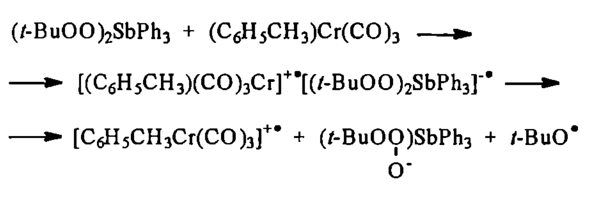
## RESULTS AND DISCUSSION

We have shown previously that organic peroxides of IV—V Group elements (Si, Ge, Sn, Sb) which are thermally stable up to 130°C, generate butoxyl radicals in

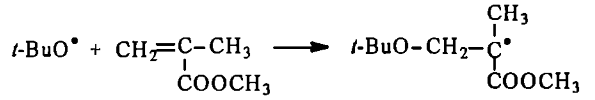
*Fig. 1. The ESR spectrum of the STC-DPA system, 25°C; 2-methyl-1-nitrosopropane (0.08 mol/L) as spin trap; STC:DPA = 1:1 (by moles), [STC] = 0.03 mol/L; hexane as solvent*

the presence of boron alkyls even at room temperature and they can be used as very effective low-temperature initiators of vinyl radical polymerization [16, 17]. In such systems the most active peroxide is di-*tert*-butylperoxytriphenylantimony (DPA). It was of considerable interest to investigate interactions of DPA with (arene)tricarbonylchromium(0) complexes in organic solvents and vinyl monomers.

The ESR method using spin trapping showed (arene)tricarbonylchromium(0) compounds to react with DPA to yield *tert*-butoxyl radicals capable of initiating radical polymerization (Fig. 1). The spin trap used was 2-methyl-2-nitrosopropane. In the presence of the spin trap, adducts of *t*-BuO-N(O)-Bu-*t* ($a_N$ = 27.3 G) were detected. We suggest the following scheme of interactions of the compounds discussed. Here, (toluene)tricarbonylchromium(0) is an example of the (arene)tricarbonylchromium complexes:



$$(t\text{-BuOO})_2\text{SbPh}_3 + (\text{C}_6\text{H}_5\text{CH}_3)\text{Cr(CO)}_3 \longrightarrow \\ \longrightarrow [(\text{C}_6\text{H}_5\text{CH}_3)(\text{CO})_3\text{Cr}]^{+\bullet}[(t\text{-BuOO})_2\text{SbPh}_3]^{-\bullet} \longrightarrow \\ \longrightarrow [\text{C}_6\text{H}_5\text{CH}_3\text{Cr(CO)}_3]^{+\bullet} + (t\text{-BuO}\underset{\text{O}^-}{\text{O}})\text{SbPh}_3 + t\text{-BuO}^\bullet \tag{3}$$



$$t\text{-BuO}^\bullet + \text{CH}_2{=}\underset{\text{COOCH}_3}{\text{C}}{-}\text{CH}_3 \longrightarrow t\text{-BuO}{-}\text{CH}_2{-}\overset{\text{CH}_3}{\underset{\text{COOCH}_3}{\text{C}^\bullet}} \tag{4}$$

Dilatometry data indicated that polymerization of MMA, vinyl acetate and styrene proceeded at a high initial rate up to a conversion of 20—30% under the action of TTC, STC in the presence of DPA at 30°C (Fig. 2). The data listed in Table 1 present the initial rates of vinyl monomer polymerization carried out with the binary initiator. In addition, the results concerning polymer molecular weights are related to the products resulting at low conversions. For styrene and vinyl acetate the process ceases to proceed whatsoever. For MMA, it goes up to a very high conversion. The former monomers exhibit low polymerization rates as compared with that of MMA. This fact demonstrates the very high selectivity of the initiating compositions based on organochromium compounds. The special effect of STC coinitiator is associated with its concentration in the polymer, higher than that of TTC. This result may be explained only in terms of incorporation of this metal-containing monomer into the propagating chain as a monomer. This point of view was supported by the ESR data which demonstrated the formation of the polymeric radical spin adduct of (styrene)tricarbonylchromium(0) together with the adduct of oxygen-centered radical, when STC reacted with DPA. Thus, STC would act both as a coinitiator and a monomer of polymerization.

**Table 1. Homopolymerization of vinyl monomers in the presence of (arene)tricarbonylchromium(0) (0.1 mol %) — DPA (0.1 mol %) (30°C) the initiator**

| Entry | Monomer | [ATC[a]] | Yield[b], % | Initial rate $V \cdot 10^5$ mol/L · s | Molecular weight |
|---|---|---|---|---|---|
| 1 | MMA | STC | 16.8 | 9.1 | 105 000 |
| 2 | | TTC | 18.5 | 22.9 | 97 000 |
| 3 | Styrene | STC | 6.3 | 0.9 | 56 500 |
| 4 | | TTC | 8.6 | 4.5 | 38 000 |
| 5 | Vinyl acetate | STC | 1.7[c] | 0.9 | — |
| 6 | | TTC | 3.8 | 3.5 | 44 000 |

[a] (Arene)tricarbonylchromium(0). [b] Polymerization was stopped to measure the molecular weight of the product obtained. [c] Limited

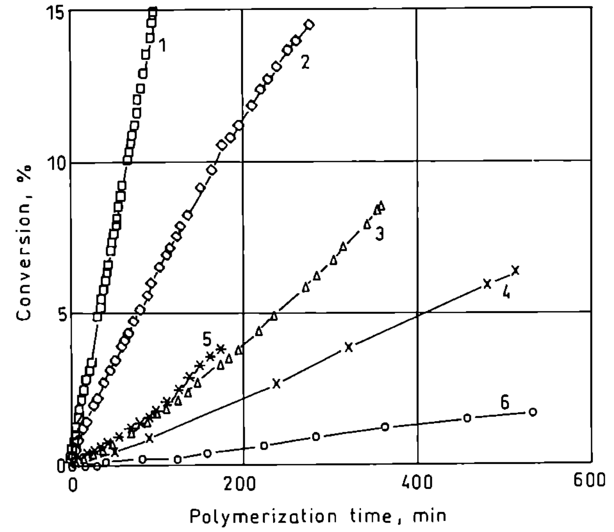


*Fig. 2. Initial kinetics curves of vinyl monomer polymerizations in the presence of the (arene)tricarbonylchromium(0) —di-tert-butylperoxytriphenylantimony binary initiator, 30°C; ATC:DPA = 1:1 (by moles); [ATC] = 0.1 mol %; (arene)tricarbonylchromium(0) — DPA, vinyl monomer: 1 — TTC—DPA, methyl methacrylate, 2 — STC—DPA, methyl methacrylate, 3 — TTC—DPA, styrene, 4 — STC—DPA, styrene, 5 — TTC—DPA, vinyl acetate, 6 — STC—DPA, vinyl acetate*

Interestingly, when MMA is introduced into the STC-DPA system, the ESR spectrum exhibits bands assignable to the spin adduct of *tert*-butoxyl radical *t*-BuO-N(O)-Bu-*t* ($a_N$ = 27.3 G), one of polymeric methyl methacrylate radical adduct *t*-Bu-N(O)-C($CH_3$)($COOCH_3$)-$CH_2$~ ($a_N$ = 15.3 G), and also signals of the *t*-Bu-N(O)-$CH_2$-C($COOCH_3$)=$CH_2$ ($a_N$ = 15.1 G, $a_H$ = 10.1 G) adduct. The latter results are due to abstraction of the MMA hydrogen atom with the propagating macroradical or the initiator radical. This fact shows the chain to be transferred to the monomer.

It is essential to note that there are no bands due to poly(styrene)tricarbonylchromium(0) radical spin adduct, which had been observed in the system when MMA was absent. This fact suggests that, between copolymerized monomers, a charge-transfer complex is formed. As a result of this observation, chain propagation is proposed to occur owing to the addition of the complex to the terminal radical. Hence, the poly(methyl methacrylate) radical is expected to terminate always the polymeric chain:

$$\sim P^{\bullet} + (STC \ldots MMA) \rightarrow \sim P\text{-}STC\text{-}MMA^{\bullet} \quad (5)$$

where ~P• is a propagating macroradical.

A similar mechanism based on ESR spectroscopy data has been suggested for the complex-radical copolymerization of sulfur dioxide and butadiene [18]. UV spectroscopy confirmed the formation of the monomer complex to occur during the chain propagation step. The electronic spectra of an STC solution in hexane have exhibited an absorption band (λ ~365 nm) attributable to ligand-metal charge transfer [19]. Introduction of methyl methacrylate into the solution resulted in a decreased intensity of the band. Moreover, the band intensity diminished as the concentration of methyl methacrylate was raised (Fig. 3). These data unambiguously indicate to the formation of a labile complex (STC ... MMA) with partial charge transfer. The constant of complexation of STC with methyl methacrylate was calculated as 0.060. A similar effect was observed when a saturated ester, ethyl acetate, was used instead of methyl methacrylate (Fig. 4). In this case, the decrease in band intensity was not so remarkable as that in the presence of methyl methacrylate. The complexation constant was 0.033. The complex formation was assumed to be close to that reported elsewhere [20], where (arene)tricarbonylchromium(0) complexes reacted with such electron acceptors as 1,3,5-trinitrobenzene and tetracyanoethylene.

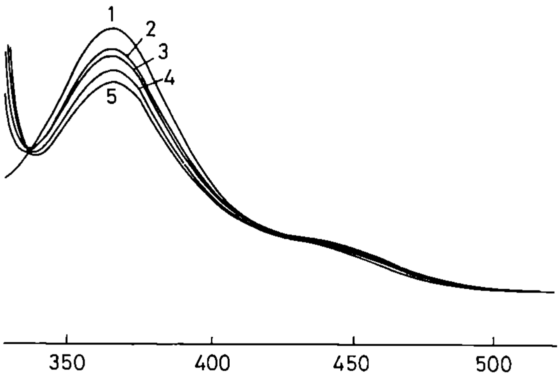


*Fig. 3. The UV spectrum of (styrene)tricarbonylchromium(0) solution in hexane—methyl methacrylate as solvent; hexane—methyl methacrylate ratio (vol. %): 1 — 100:0, 2 — 70:30, 3 — 50:50, 4 — 30:70, 5 — 10:90; [STC] = 5.35 · $10^{-4}$ mol/L*

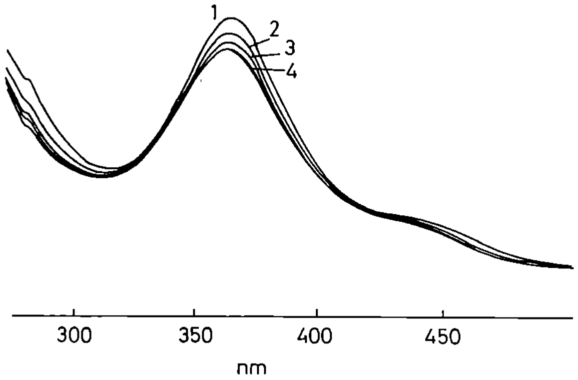
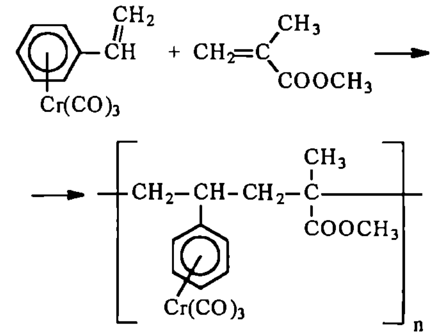


*Fig. 4. The UV spectrum of (styrene)tricarbonylchromium(0) solution in hexane—ethyl acetate as solvent; hexane—ethyl acetate ratio (vol. %): 1 — 100:0, 2 — 70:30, 3 — 50:50, 4 — 30:70; [STC] = 5.65 · $10^{-4}$ mol/L*

In addition to the homopolymerization of acrylic monomers, we studied copolymerization of MMA and BA with STC and PMSTC, both in the bulk and in ethyl acetate as solvent, at 50°C in the presence of AIBN and at 30°C with the STC-DPA system as initiator:



(6)

The Kelen—Tüdos method was used to calculate the relative reactivity ratios of the monomers by using dependencies of copolymer compositions on monomer ratio along the initial sections (Table 2). The reactivity ratios of STC and PMSTC are equal to zero in all the examples listed. These data are consistent with the available information on the impossibility of synthesizing polySTC under classical conditions of radical polymerization [3—5, 11].

**Table 2. Reactivity ratios for the copolymerization of (styrene)tricarbonylchromium(0) ($M_1$) and (*p*-methylstyrene)tricarbonylchromium(0) ($M_1$) with organic monomers ($M_2$)$^{a)}$**

| Entry | [ATC]$^{b)}$ | Comonomer ($M_2$) | Initiator$^{c)}$ | Temperature, °C | $r_2^{d)}$ |
|---|---|---|---|---|---|
| 1 | STC | MMA | AIBN | 50 | 0.71 |
| 2 | STC | MMA | DPA | 30 | 0.60 |
| 3 | STC | Butyl acrylate | AIBN | 50 | 0.75 |
| 4 | STC | Butyl acrylate | DPA | 30 | 0.65 |
| 5 | PMSTC | MMA | AIBN | 50 | 1.44 |
| 6 | PMSTC | MMA | DPA | 30 | 1.10 |

$^{a)}$ In 75 wt. % ethyl acetate solution. $^{b)}$ (Arene)tricarbonylchromium(0). $^{c)}$ [AIBN] = 0.5 wt. %, [DPA] = 1.6 wt. %. $^{d)}$ $r_1$ = 0.

Molecular weight distribution of metal-containing polymers was examined by gel permeation chromatography. Each of the polymers obtained exhibited a monomodal chromatogram. Sample molecular weight values and polydispersity ratios for the STC and PMSTC copolymers are listed in Table 3. With PMSTC or DPA used, the intrinsic viscosity was lower (Table 3, entries 6—8). In the presence of DPA, polydispersity is seen to increase significantly (Table 3, entries 7, 8). DPA [15] and PMSTC are believed to be responsible for this phenomenon, *i.e.*, these compounds can participate in chain transfer reactions. The lower molecular weights of the copolymers support this hypothesis, *e.g.*, compare the MMA-PMSTC pair with the MMA-STC pair, each obtained in the presence of AIBN (entries 2, 5), or the pair of MMA-STC copolymers synthesized in the presence of DPA with that obtained in the presence of AIBN (entries 2, 7).

**Table 3.** Molecular weights and polydispersities of the copolymers

| Entry | Monomer feed | MCM mol % | Initiator | Yield % | $M_n \cdot 10^{-3}$ | [η] dl/g | Polydispersity $M_w/M_n$ |
|---|---|---|---|---|---|---|---|
| 1 | MMA | 0 | AIBN | 10 | 142 | 0.581 | 1.8 |
| 2 | STC—MMA | 5 | AIBN | 3 | 148 | 0.569 | 1.7 |
| 3 | STC—MMA | 10 | AIBN | 8 | 91 | 0.431 | 1.8 |
| 4 | STC—MMA | 20 | AIBN | 46 | 74 | 0.380 | 1.9 |
| 5 | PMSTC—MMA | 10 | AIBN | 14 | 84 | 0.379 | 1.6 |
| 6 | PMSTC—MMA | 40 | AIBN | 12 | 38 | 0.225 | 1.6 |
| 7 | STC—MMA | 5 | DPA | 6 | 22 | 0.189 | 2.4 |
| 8 | PMSTC—MMA | 5 | DPA | 14 | 22 | 0.205 | 3.0 |

In the system with DPA, arenetricarbonyl complexes of chromium are thus seen to initiate the acrylic radical polymerization. STC (or PMSTC) is found to be incorporated into the polymer chain under such conditions. Taking into account the features of the elementary stages of the process, the synthesis of polymers including chromium-containing monomers and acrylates can be considered an example of complex-radical polymerization.

## APPENDIX

**Table A1.** Copolymerization of styrenetricarbonylchromium ($M_1$) and MMA ($M_2$) at 50°C in ethyl acetate[a)]

| Polymer No. | Initial $M_1$ mol % | Polymerization time, hr | Yield, % | $M_1$ in copolymer, mol % |
|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 |
| 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 | 16.9 | 16.9 | 48.2 |

[a)] 75 vol. % of ethyl acetate was used in solution; AIBN (0.5 wt. %) as initiator.

**Table A2.** Copolymerization of styrenetricarbonylchromium ($M_1$) and MMA ($M_2$) at 30°C in ethyl acetate[a)]

| Polymer No. | Initial $M_1$ mol % | Polymerization time, hr | 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; DPA (1.6 wt %) as radical source.

**Table A3.** 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, hr | 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; AIBN (0.5 wt. %) as initiator.

**Table A4.** 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, hr | 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; DPA (1.6 wt. %) as radical source.

**Table A5.** Copolymerization of styrenetricarbonylchromium ($M_1$) and BA ($M_2$) at 50°C in ethyl acetate[a)]

| Polymer No. | Initial $M_1$ mol % | Polymerization time, hr | Yield, % | $M_1$ in copolymer, mol % |
|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 |
| 1 | 5 | 3.3 | 13.7 | 4.9 |
| 2 | 5 | 8.6 | 38.3 | 4.7 |

| 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|
| 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; AIBN (0.5 wt. %) as initiator.

T a b l e A6. **Copolymerization of styrenetricarbonylchromium ($M_1$) and BA ($M_2$) at 30°C in ethyl acetate**[a]

| Polymer No. | Initial $M_1$ mol % | Polymerization time, hr | 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; DPA (1.6 wt. %) as radical source.

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