Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Vinyl Polymerization Initiated by Reducing Compounds of Transition Metals. XI. Two-step Selective Graft Copolymerization

N. Moszner[a]; M. Hartmann[a]; J. Opfermann[a]
[a] Department of Chemistry, Friedrich Schiller University, Jena, German Democratic Republic

To cite this Article Moszner, N. , Hartmann, M. and Opfermann, J.(1986) 'Vinyl Polymerization Initiated by Reducing Compounds of Transition Metals. XI. Two-step Selective Graft Copolymerization', Journal of Macromolecular Science, Part A, 23: 10, 1165 — 1177
To link to this Article: DOI: 10.1080/00222338608069486
URL: http://dx.doi.org/10.1080/00222338608069486

J. MACROMOL. SCI.–CHEM., A23(10), pp. 1165-1177 (1986)

Vinyl Polymerization Initiated by Reducing Compounds of Transition Metals. XI. Two-Step Selective Graft Copolymerization

N. MOSZNER, M. HARTMANN, and J. OPFERMANN

Department of Chemistry
Friedrich Schiller University
6900 Jena, German Democratic Republic

ABSTRACT

Grafting of methyl methacrylate onto poly(methyl-4-vinylbenzyl-sulfoxide-co-trichloroethyl methacrylate) is initiated by molybdenum(III) chloride in ethylene chloride. In a second step the obtained graft copolymers are grafted with styrene in the presence of chromium(II) acetate and morpholinocyclohexene in dimethylformamide. By this stepwise selective graft copolymerization technique, polymers can be tailored to give the required properties.

INTRODUCTION

In previous papers [1-6] we showed that reducing compounds of transition metals such as chromium(II) acetate, titanium (III) chloride, vanadium(III) chloride, or molybdenum(III) chloride initiate radical graft copolymerizations onto halogen-containing polymers or polymeric sulfoxides. In the initiation step, free macroradicals ($P^{\cdot}$) are generated by the redox reaction between a metal compound (Me^{z+}) and a polymer backbone (P–X):

$$P\text{–}X + Me^{z+} \longrightarrow {}^{\cdot}P + Me^{(z+1)+} + X^{-}$$

 0022-233X/86/2310-1165$3.50/0

These macroradicals may selectively initiate graft copolymerization of the monomer present. Thus, higher grafting efficiencies can be attained than in the presence of conventional free-radical initiators.

Furthermore, we have found [7, 8] that molybdenum(III) chloride/alkyl halide systems show low initiating activities, whereas molybdenum(III) chloride ($MoCl_3$) efficiently initiates the radical polymerization of methacrylates in the presence of sulfoxides. In contrast, chromium(II) compounds react very slowly with sulfoxides [8, 9] and initiate the radical polymerization of styrene in the presence of halogen compounds [10]. Therefore, by the use of a polymer backbone containing halogen and sulfoxide groups, the consecutive initiation of grafting with a molybdenum(III) and a chromium(II) compound should allow stepwise selective synthesis of graft copolymers. In this way it is possible to tailormake polymers of the desired properties.

The present paper deals with graft copolymerization onto copolymers of unsaturated sulfoxides and 2,2,2-trichloroethyl methacrylate in the presence of $MoCl_3$ and chromium(II) acetate ($Cr(ac)_2$).

EXPERIMENTAL

Materials

$MoCl_3$ and $Cr(ac)_2$ were synthesized as reported previously [4]. Styrene, methyl methacrylate (MMA), ethylene chloride, and dimethylformamide (DMF) were purified by standard methods described earlier [5]. 2,2,2-Trichloroethyl methacrylate (TCEMA) was prepared by esterification of the corresponding alcohol with methacrylyl chloride. Methyl-4-vinylphenylsulfoxide (MVPhSO) and methyl-4-vinylbenzylsulfoxide (MVBzSO) were synthesized according to Ogura et al. [14].

Procedures

Synthesis of the Polymer Backbones

The copolymerization of TCEMA (1.0 M) with MVBzSO (1.0 M) was carried out in DMF at 60°C with AIBN (50 mmol/L) as initiator. After 26 h the reaction mixture was poured into a large amount of ether. The copolymer obtained [P(MVBzSO-co-TCEMA)] was reprecipitated twice from chloroform solution with n-hexane and dried in vacuo. The monomer conversion was 70.0%. The composition of the copolymer was calculated from the chlorine content determined by elemental analysis. The number-average molecular weight ($\overline{M}_n$) and the chlorine content amounted to 4 400 g/mol and 24.25 wt%, respectively (TCEMA-content of 44.8 mol%). In an analogous manner, TCEMA was copolymerized with

MVPhSO with a yield of 78.9% after 6 h. The $\overline{M}_n$ and the chlorine content of the resulting [P(MVPhSO-co-TCEMA)] were 4 600 g/mol and 24.76 wt%, respectively (TCEMA content of 43.9 mol%). The homopolymerization of TCEMA and the copolymerization of TCEMA with MMA have been described previously [6].

Graft Copolymerization

The copolymerization reactions were carried out in sealed glass tubes containing a given amount of the reducing metal compound dissolved in DMF ($Cr(ac)_2$) or ethylene chloride ($MoCl_3$). Subsequently, monomer and functional polymer were introduced. All operations took place under a steady stream of argon. The tubes were degassed by three freeze-thaw cycles (liquid nitrogen) before they were placed in a constant-temperature bath. After a certain time, polymerizations were terminated by the addition of hydroquinone and excess methanol. The monomer conversions were calculated from the gravimetrically determined yields of the dried polymer. The graft copolymers obtained in the presence of $MoCl_3$ were reprecipitated first from chloroform solution with methanol and then with chloroform/n-hexane. The gel content and the graft efficiency, respectively, of the graft copolymers obtained in the presence of $Cr(ac)_2$ were calculated from the results of extractions of the crude graft products with DMF or benzene.

The cleavage of grafted polystyrene branches from the polymer backbone was carried out by alkaline hydrolysis, as reported previously [6].

Measurements

The number-average molecular weights of starting polymers and of graft copolymers (P([MVBzSO-co-TCEMA]-g-MMA)) were determined osmometrically. Molecular weight determinations of the hydrolyzed/extracted polystyrene branches were carried out by GPC (commercial Knauer gel chromatograph) using gel columns calibrated with polystyrene standards. The eluent was tetrahydrofuran; the temperature was 40°C.

RESULTS AND DISCUSSION

A. Graft Copolymerization of MMA in the Presence of $MoCl_3$—The First Step of Graft Copolymer Synthesis

The graft copolymerization onto P(MVBzSO-co-TCEMA) was carried out in ethylene chloride at 60°C. This solvent dissolves the poly-

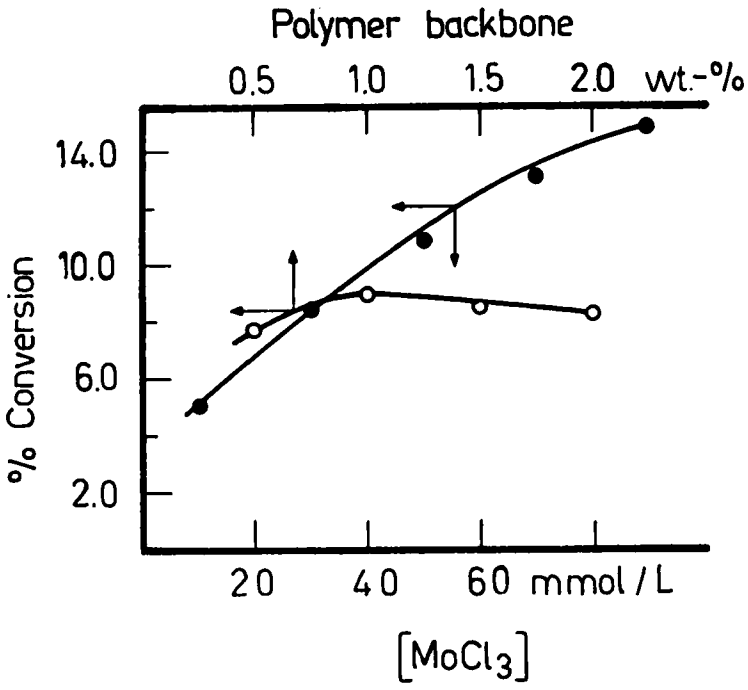

FIG. 1. Graft copolymerization of MMA (2.5 M) onto P(MVBzSO-co-TCEMA) (•: 1.5 wt%) initiated by $MoCl_3$ (○: 3.0 mmol/L). Time: 1.5 h.

mer backbone, the monomer, and $MoCl_3$. Moreover, it shows a lower chain-transfer activity in the free-radical polymerization of MMA than chloroform, which is also a good solvent. The monomer conversion increases with increasing concentration of $MoCl_3$, whereas the polymer yield runs through a maximum with increasing concentration of the polymer backbone (Fig. 1). During the graft copolymerization of MMA onto P(MVBzSO-co-TCEMA), $MoCl_3$ is oxidized to $MoOCl_3$ by the sulfoxide groups of the polymer backbone generating free macroradicals. After the $MoCl_3$ is consumed, dead-end polymerization occurs. However, it must be pointed out that the addition of $MoCl_3$ to a solution with polymer backbone concentration above 1.0 wt% causes partial precipitation of polymer particles. Although these particles dissolve in the course of grafting, polymer concentration above 1.0 wt% does not increase the monomer conversion.

During grafting, the attainable weight increase (quotient of the weight of polymerized monomer to the weight of graft product ob-

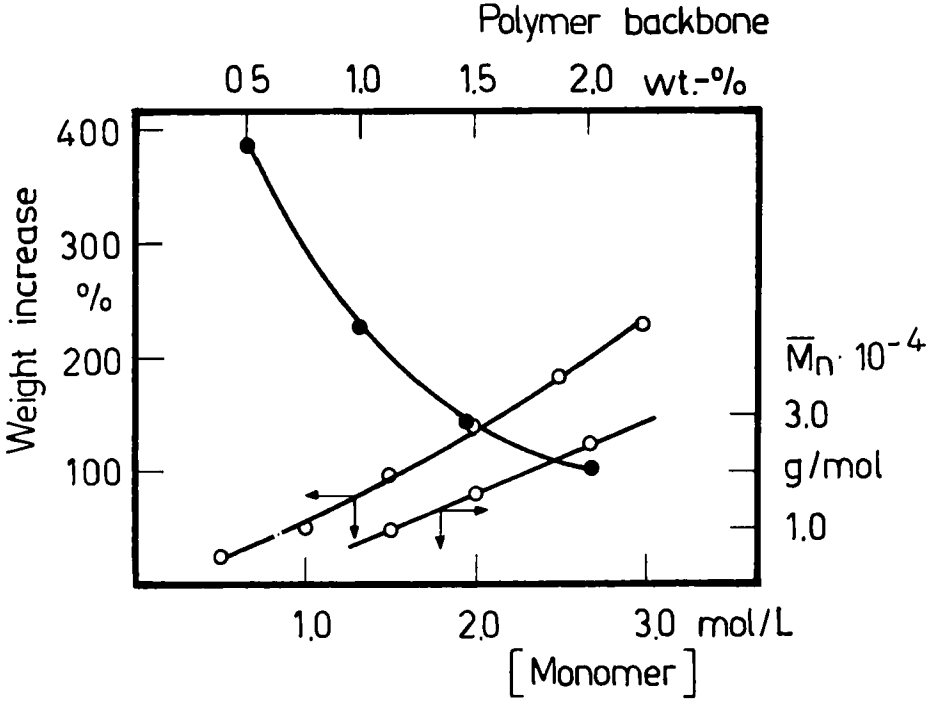

FIG. 2. Weight increase and molecular weight of the grafting of MMA onto P(MVBzSO-co-TCEMA) in the presence of $MoCl_3$. Time: 1.5 h. (•) [MMA] = 2.5 M. [$MoCl_3$] = 3.0 mmol/L. (○) [Polymer backbone] = 1.5 wt%. [$MoCl_3$] = 5.0 mmol/L.

tained) increases with rising monomer concentration and decreasing polymer backbone concentration (Fig. 2). The weight increase also increases with rising $MoCl_3$ concentration, but for successful grafting in the presence of $Cr(ac)_2$, it is advisable to use a low $MoCl_3$ concentration because the molybdenum(V) species is adsorbed in the crude graft product. Altogether, the weight increase could be varied between 50 and 386% by the experimental conditions used, thus increasing the number-average molecular weight of the polymer backbone from 10 300 to 69 000 g/mol.

The graft copolymerization of MMA onto P(MVPhSO-co-TCEMA) yields higher monomer conversions than that onto P(MVBzSO-co-TCEMA) (Table 1). This result is in agreement with the fact [5, 8] that P(MVPhSO) or diphenyl sulfoxide are more reactive toward $MoCl_3$ than P(MVBzSO) or dibenzyl sulfoxide.

TABLE 1. Graft Copolymerization of MMA (2.5 M) onto P(MVPhSO-co-TCEMA) (1.0 wt%) in the Presence of $MoCl_3$ (time: 1.5 h)

$[MoCl_3]$, mmol/L	Conversion, %	Weight increase, %
0.5	5.2	130.1
1.0	7.4	185.1
3.0	11.4	285.2
5.0	11.8	292.2

B. Graft Copolymerization of Chlorine-Containing Polymers Initiated by $Cr(ac)_2$

The $Cr(ac)_2$/morpholinocyclohexene system is known to initiate the graft copolymerization of mixtures of MMA and styrene onto PVC [1]. In this case the macroradicals are generated by the redox reaction between chromium(II) and C–Cl bonds of the polymer backbone. The weight increase obtained in 48 to 96 h was in the range of 2 to 70%, and the estimated graft efficiency of about 90% confirmed the selective mechanism of the graft copolymerization. Because of the great difference between the reactivity of the C–Cl bonds in PVC and P(MVBzSO-co-TCEMA), it seemed appropriate to investigate the influence of grafting conditions in the presence of $Cr(ac)_2$ and morpholinocyclohexene (MCH) upon the model systems P(TCEMA) and P(MMA-co-TCEMA).

It was found (Fig. 3) that TCEMA-containing polymers act as initiators within a distinctly shorter time than PVC, yielding crosslinked graft copolymers. Furthermore, the results show that a chlorine content lower than 10 wt% ensures an initiation activity in the presence of $Cr(ac)_2$ and MCH. Lee and Minoura [10, 11] have studied the polymerization of styrene in the presence of $Cr(ac)_2$ and low molecular weight chlorine-containing compounds. They observed that the initiating activity of the chlorine compounds depends both on the chlorine content and the reactivity of the C–Cl bonds. In this case the introduction of electron-attracting groups, e.g., carbonyl, causes an increase in the initiating activity. Moreover, the results listed in Table 2 show that the ester group enhances the reactivity of the C–Cl bond in the redox reaction with $Cr(ac)_2$ only for the more reactive methyl chloroacetates and not for the chloroethyl propionates.

As shown in Fig. 3, the monomer conversion reaches a maximum

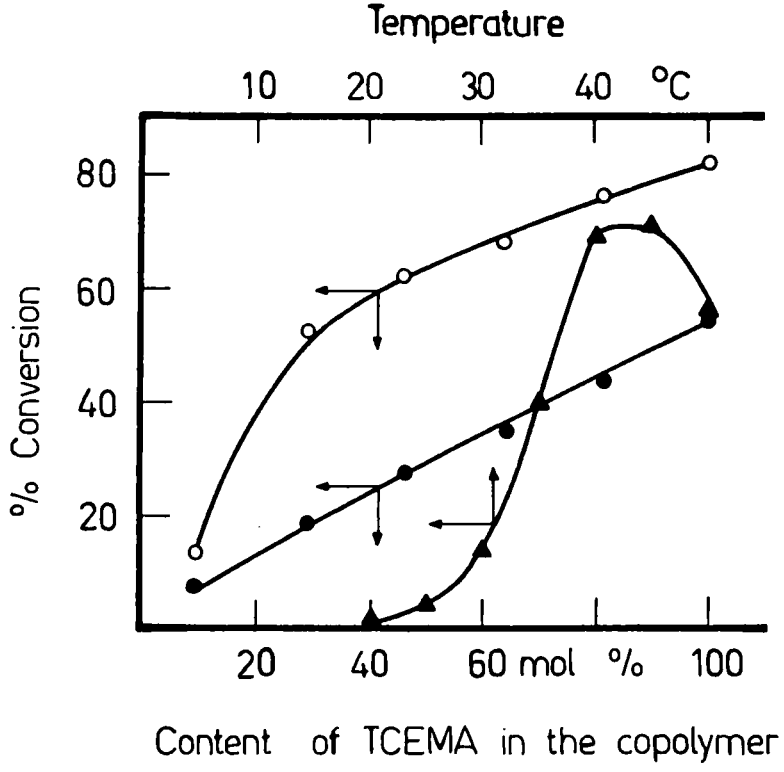

FIG. 3. Graft copolymerization of styrene or mixtures of styrene with MMA (3.0 M) onto P(MMA-co-TCEMA) (2.0 wt%). Time: 2.5 h. (○) Styrene. (●) [Styrene]/[MMA] = 1/1. (▲) Styrene, polymer backbone with 63.69 mol% TCEMA.

value at 45°C. Below 20°C, styrene did not polymerize. This is a consequence of the dead-end course of the graft copolymerization. At about 45°C, the reduction of C–Cl bonds takes place so fast that the initiating $Cr(ac)_2$ is consumed at the beginning of the polymerization, whereas below 20°C the reactivity of $Cr(ac)_2$/MCH toward the C–Cl bond is too low. Furthermore, it can be seen (Table 2 and Fig. 3) that the monomer conversion in the presence of TCEMA-containing polymers is higher than in that of trichloroethyl pripionate. The time-conversion plot of the grafting onto P(MMA-co-TCEMA) shows (Fig. 4) that the rate of polymerization increases with time up to a monomer conversion of ~30%.

This autoacceleration of the styrene polymerization can be explained

TABLE 2. Polymerization of Styrene (2.0 M) in the Presence of $Cr(ac)_2$ (0.02 M), MCH (0.02 M), and Various Chlorine-Containing Compounds (0.1 M)[a]

Chlorine compound	% Conversion at 40°C	% Conversion at 50°C
Methyl chloroacetate	2.3	5.0
Methyl dichloroacetate	4.9	7.7
Methyl trichloroacetate	5.8	4.2[b]
2-Chloroethyl propionate	-	1.0
2,2-Dichloroethyl propionate	-	2.8
2,2,2-Trichloroethyl propionate	-	6.0
Chloroform	5.0	7.7[b]

[a]Time: 1.5 h.
[b]$Cr(ac)_2$ is oxidized within 0.5 h.

on the basis of the well-known gel-effect [12]: At the beginning of polymerization, the viscosity of the monomer solution is only insignificantly increased by the polymer backbone. During the polymerization, the viscosity of the solution is so far increased, as a consequence of the recombination of grafted polystyrene radicals, that a polymer gel is formed. The viscosity increase decreases the rate of chain termination, which results in an increase in the polymerization rate. Since the reaction of P(TCEMA) with $Cr(ac)_2$/MCH in the absence of styrene did not increase the molecular weight of the starting polymer, the recombination of primary radicals (pendent dichloroethyl radicals of the polymer backbone) can be ruled out as a cause for the crosslinking.

Finally, the gel-effect also influences the molecular weight of the grafted polystyrene branches obtained by alkaline hydrolysis of the graft products. For example, the $\overline{M}_n$ of grafted polystyrene is 27 000 g/mol (cf. Fig. 4: [Cr(II)] = 30 mmol/L) or 43 000 g/mol ([Cr(II)] = 10 mmol/L). In contrast, the $\overline{M}_n$ of the polystyrenes obtained under comparable conditions with $Cr(ac)_2$/MCH and trichloroethyl propionate are lower (between 7 000 and 12 500 g/mol for [Cr(III)] = 30 and 10 mmol/L).

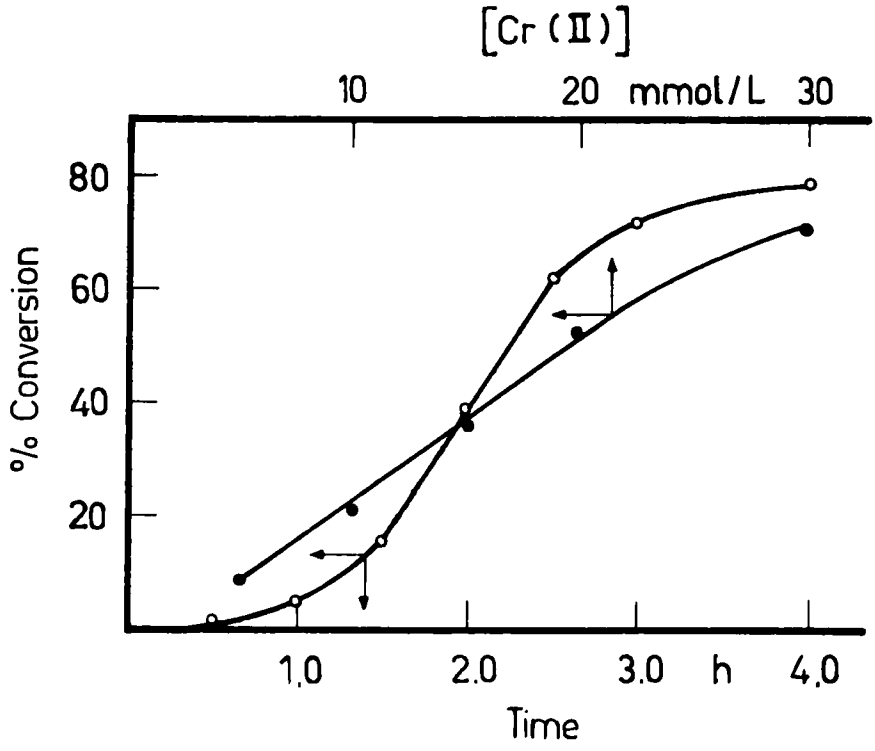

FIG. 4. Grafting of styrene (3.0 M) onto P(MMA-co-TCEMA) initiated by $Cr(ac)_2$/MCH. (○) $[Cr(ac)_2] = [MCH] = 2 \times 10^{-2}$ M, polymer backbone with 46.51 mol% TCEMA. (●) $[Cr(ac)_2]/[MCH] = 1/1$, starting polymer with 29.41 mol% TCEMA. Time: 2.5 h.

C. Second Step of Graft Copolymer Synthesis

Before use, the crude graft products of the first step of the graft copolymer synthesis were purified by reprecipitation. The chlorine content of the purified polymers ranges from 5.32 to 9.86 wt%. Table 3 and Fig. 5 show the effect of time and the influence of the concentrations of $Cr(ac)_2$ and of the polymer backbone on the graft copolymerization of styrene onto P(MVBzSO-co-TCEMA) grafted with MMA. Evidently, the monomer conversion and, thereby, the composition of the graft products can be predicted for a wide range by different graft conditions.

TABLE 3. Graft Copolymerization of Styrene (3.0 M) onto P([MVBzSO-co-TCEMA]-g-MMA) Initiated by $Cr(ac)_2$ (0.02 M) and MCH (0.02 M)

P([MVBzSO-co-TCEMA]-g-MMA)				
Chlorine content, wt%	$\overline{M}_n \times 10^{-3}$, g/mol	[Polymer backbone], wt%	% Conversion after 1.5 h	$\overline{M}_n \times 10^{-4}$, g/mol[a]
5.32[b]	n.d.	1.0	18.8	7.2
5.60[c]	29.4	0.5	11.8	6.6
5.60	29.4	1.0	18.7	7.4
5.60	29.4	1.5	24.3	9.0
6.60	25.0	1.0	19.9	7.1
7.59	40.3	1.0	24.2	7.9
8.92	n.d.	1.0	29.0	7.6
9.86	69.0	1.0	30.4	8.3
24.25[d]	4.4	1.0	33.4	4.8
8.89[e]	2.1	1.0	4.0	2.7

[a]Molecular weight of grafted polystyrene branches estimated by GPC.
[b]Synthesis conditions: cf. Fig. 1: $[MoCl_3]$ = 3.0 mmol/L, [polymer backbone] = 1.0 wt%.
[c]Synthesis conditions: cf. Fig. 1: $[MoCl_3]$ = 9.0 mmol/L, [polymer backbone] = 1.5 wt%.
[d]P(MVBzSO-co-TCEMA).
[e]P(MMA-co-TCEMA).

P([MVBzSO-co-TCEMA]-g-MMA) with similar chlorine contents undergoes the same monomer conversion. The graft products obtained are crosslinked due to the recombination of grafted polystyrene radicals. Furthermore, the gelation as well as the autoacceleration of the styrene polymerization caused by the increase in viscosity begins earlier than in grafting of styrene onto P(MMA-co-TCEMA). For instance, during the grafting of styrene onto P(MMA-co-TCEMA) with a chlorine content of 8.89 wt% ($\overline{M}_n$ = 2 100 g/mol), the gelation begins after 2 h, whereas for P([MVBzSO-co-TCEMA]-g-MMA) with a chlorine content of 5.60 to 9.86 wt% ($\overline{M}_n$ = 29 000 to 69 000 g/mol), it begins within a few minutes. Accordingly, in the first case the monomer conversion after 1.5 h is only 4.0%, starting from P(MVBzSO-co-TCEMA) grafted with MMA between 18.8 and 30.4%, respectively. Likewise, differ-

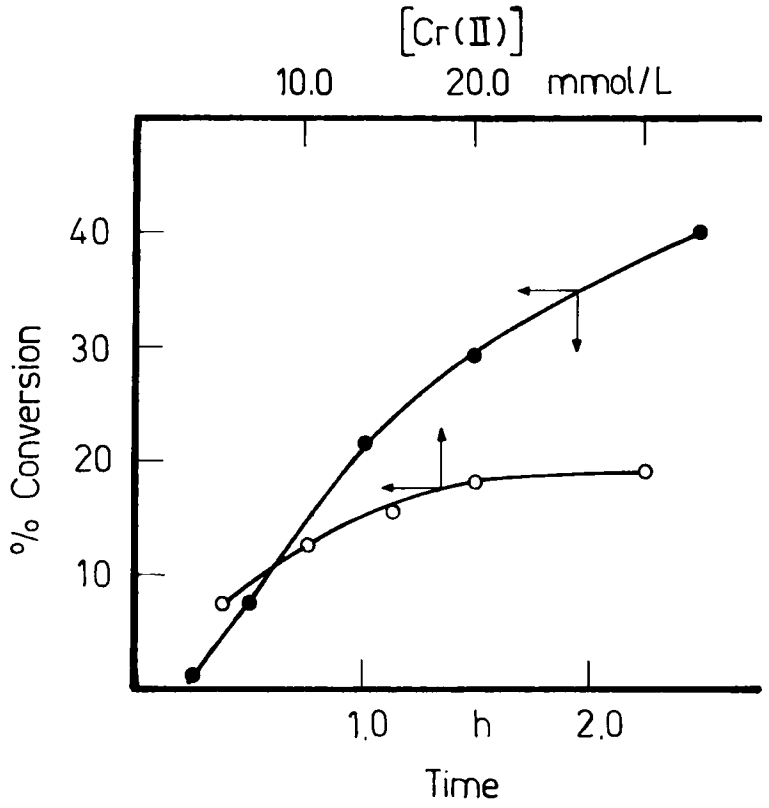

FIG. 5. Grafting of styrene (3.0 M) onto P([MVBzSO-co-TCEMA]-g-MMA] (1.0 wt%) initiated by $Cr(ac)_2$/MCH. (•) $[Cr(ac)_2]/[MCH]$ = 1/1; time, 1.5 h; polymer backbone with chlorine content of 5.60 wt%. (○) $[Cr(ac)_2] = [MCH] = 2 \times 10^{-2}$ M, chlorine content of starting polymer, 8.92 wt%.

ences in the molecular weight of grafted polystyrene branches are obvious. The grafting onto P(MMA-co-TCEMA) results in lower $\overline{M}_n$ (27 000 to 43 000 g/mol) than the grafting onto P(MVBzSO-co-TCEMA]-g-MMA) ($\overline{M}_n$ = 66 000 to 90 000 g/mol).

These results may be explained on the basis of the gelation theory [13]. Accordingly, it can be concluded that for a similar chlorine content of the polymer backbone, the differences may be attributed to the significantly higher molecular weights of P([MVBzSO-co-TCEMA]-g-

TABLE 4. Graft Copolymerization of Styrene (3.0 M) onto P([MVPhSO-co-TCEMA]-g-MMA) (1.0 wt%) Initiated by $Cr(ac)_2$ (0.02 M) and MCH (0.02 M)[a]

Chlorine content of the polymer backbone, wt%	Conversion, %
5.67	16.1
6.21	17.7
7.03	18.3
9.20	21.2

[a]Time: 1.0 h.

MMA) compared to P(MMA-co-TCEMA). Analogous results were observed in the graft copolymerization of styrene onto P([MVPhSO-co-TCEMA]-g-MMA) (Table 4).

CONCLUSIONS

The reaction of $MoCl_3$ and, consecutively, of $Cr(ac)_2$ with polymers containing sulfoxide and trichloroethyl groups initiate the selective two-step synthesis of graft copolymers. Because of the high selectivity of the reduction of the sulfoxide groups by $MoCl_3$ and the trichloroethyl groups by $Cr(ac)_2$, respectively, as well as the reducing power of the metal compounds, this graft copolymer synthesis is distinguished by high efficiency and wide variability of attainable composition of graft products. Hence this technique is especially suitable for making polymers with tailormade properties.

REFERENCES

[1] M. Hüller, M. Hartmann, and M. Gerth, Acta Polym., 30, 760 (1979).
[2] N. Moszner and M. Hartmann, Ibid., 32, 19 (1981).
[3] N. Moszner and M. Hartmann, Ibid., 33, 523 (1982).
[4] N. Moszner and M. Hartmann, Eur. Polym. J., 20, 501 (1984).
[5] N. Moszner and M. Hartmann, Ibid., 21, 329 (1985).
[6] N. Moszner and M. Hartmann, Acta Polym., 37, 304 (1986).
[7] N. Moszner and M. Hartmann, Ibid., 35, 616 (1984).
[8] N. Moszner and M. Hartmann, J. Prakt. Chem., 327, 595 (1985).

[9] Y. Akita, M. Inaba, H. Uchida, and A. Ohta, Synthesis, 1977, 792.
[10] M. Lee and Y. Minoura, Nippon Kagaku Kaishi, p. 167 (1972); Chem. Abstr., 76, 15480c (1972).
[11] M. Lee and Y. Minoura, J. Polym. Sci., Polym. Chem. Ed., 13, 1427 (1975).
[12] G. P. Gladyshev and V. A. Popov, Radikalische Polymerisation bis zu hohen Umsätzen, Akademie-Verlag, 1978, p. 38.
[13] C. H. Bamford, R. W. Dyson, and G. C. Eastmond, J. Polym. Sci., Part C, 16, 2425 (1967).
[14] K. Ogura, K. Itoh, S.-I. Isogai, S. Kondo, and K. Tsuda, J. Macromol. Sci.–Chem., A17, 1371 (1982).

Received June 19, 1985
Revision Received September 30, 1985