Macromol. Symp. ***131,*** *115–125 (1998)*

(CO)POLYMERIZATION OF METAL-CONTAINING MONOMERS AS A WAY OF MMC SYNTHESIS

Anatolii D. Pomogailo
Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences, Chernogolovka, Moscow Region, 142432, Russia
e-mail: adpomog@icp.ac.ru

Abstract:

The principal advances and problems of the synthesis, of poly-, co- and graft- polymerization of metal-containing monomers (MCM) are analysed. The MCMs are classified on the type of the metal bond with the organic part of the molecule, *viz.* MCM with σ-, nv-, and π-bonds. The effect of a transition metal on both the polymerization and on the properties of the products formed is of special interest. The basic fields of application of metal-containing polymers have been summed up.

INTRODUCTION

Metal-containing monomers (MCM) are metal complexes with specific ligands. One of the main functions is their polymerization reactions. Their polymers are homogeneous or heterogeneous catalysts for numerous reactions such as polymerization, hydrogenation, oxidation, etc. In other words, such products are a variety of polymer-immobilized catalysts fixed on polymers as macroligands (Refs. 1-4). However, in contrast to the synthesis via macroligands, they can be obtained by a one-pot synthesis: polymerization and copolymerization of MCMs. In this case we avoid to obtain special polymers (such synthesis sometimes consists of several stages) the interaction of these polymers with metal complexes and the separation of chemically non-bonded components. Finally, the advantage

© 1998 Hüthig & Wepf Verlag, Zug CCC 1022-1360/98/$ 10.00

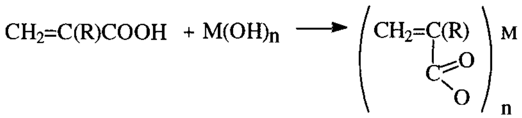
of such a method of MMC-synthesis is the possibility to obtain a more well-defined metal center structure with regard to the valence and electron state of the metal, its ligand environment, the geometry of the structure as well as the unique distribution of the structurally uniform metal complexes in the chain. In this report some possibilities of such approaches will be analysed.

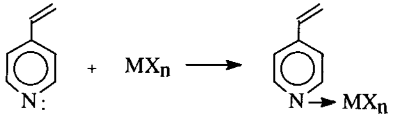
RESULTS AND DISCUSSION

Classification and the main route of synthesis of MCMs

In our opinion (Ref. 5), the most effective classification is based on the type of bond between the metal and the polymerizable group. By this principle MCMs can be classified into the following six major types (Tab. 1). Note the two general ways of synthesis of these compounds:

i) The interaction of traditional monomers with metal complexes:





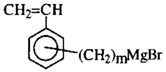
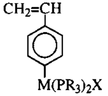
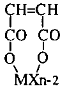
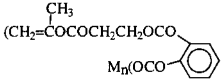
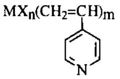
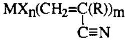
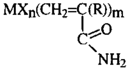
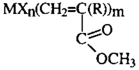
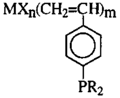
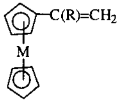
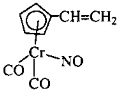
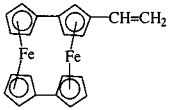
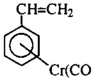
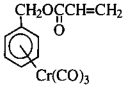
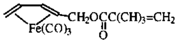
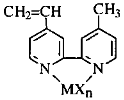
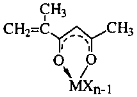
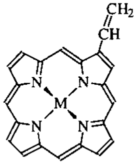
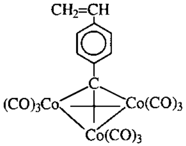
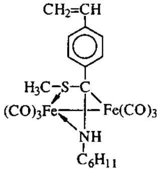
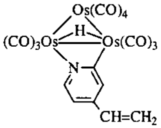
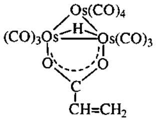
ii) In corporation of the polymerizable group in the ligand environment of metal complexes:

$$M(OR)_n + R'OH \longrightarrow M(OR')_m(OR)_{n-m} + ROH$$

$$MX_n + CH_2{=}CH\text{-}MgCl \rightarrow (CH_2{=}CH)_mMCl_{n-m} + MgClX$$

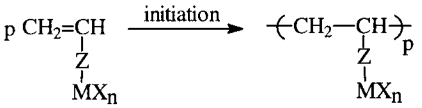
The typical examples of MCM under discussion are listed in Tab. 1.

Tab. 1. The main representatives of MCM

MCM σ -type	MCM ionic type	MCM nv-type	MCM π type	MCM chelate type	MCM cluster type
a) natural organometalic compounds $(CH_2=CH)_mMCl_{n-m}$;   M=Pt, Pd ; R=Et, Bu $Et_3Sn-CH=CH-C≡CR$; $RC≡C-M(PBu_3)_2-C≡CR$ (M = Pt, Pd, Ni; R = Ph, -C≡CR) b)organoelemental compounds $M(OR)_{n-m}(OR'CH=CH_2)_m$ $M(OR)_{n-m}(OR'C(R'')=CH_2)_m$ (M = Ti, V, Zr, Sn)	$M(OCOC(R)=CH_2)_n$ (R = H, CH_3); $(C_5H_5)_2M(OCOC(R)=CH_2)_2$ (M = Ti, V, Zr)  	    R = H, CH3 	 M = Fe, Os, Ru R = H, CH3     	a) intramolecular metallochelates  b) intracomplex compounds  c) macrocyclic complexes 	  $Rh_6(CO)_{15}(4\text{-}VPy)$ $Rh_6(CO)_{14}(4\text{-}VPy)_2$  

Polymerization of MCMs

The interval of reactivity of MCMs is extremely large. This means that the polymerizable monomers are already on the stage of synthesis of monomers incapable of polymerization even under sufficiently harsh conditions (high temperature, pressure, and concentration of the initiator). In principle, typical MCMs can be polymerized under the action of the known initiators of any types:



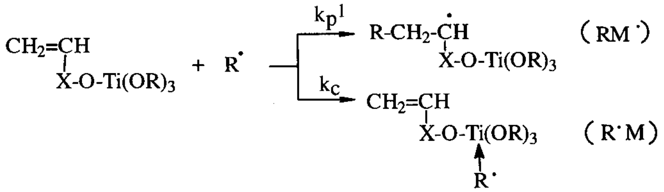
$$p\ \mathrm{CH_2{=}}\underset{\substack{|\\ \mathrm{Z}\\ |\\ \mathrm{MX_n}}}{\mathrm{CH}} \xrightarrow{\text{initiation}} \left(\mathrm{CH_2{-}}\underset{\substack{|\\ \mathrm{Z}\\ |\\ \mathrm{MX_n}}}{\mathrm{CH}}\right)_p$$

- radical initiation (the common initiators, γ - radiation, photo initiation),
- redox systems,
- ionic polymerization,
- anionic coordination polymerization (Ziegler-Natta catalysts).

The typical equation of the radical polymerization, when the polymerization rate (W_p) is proportional to the concentration of monomers (M) and to the square root of concentration of the initiators (I), $W_p = k\,[M]\,[I]^{0.5}$, is only realized with the polymerization of some types of MCM such as metal acrylates (Ref. 6), vinylferrocenes (Ref. 7), etc.

Usually, deviations from these regularities are observed. For example, with Ti-containing monomers the polymerization rate is proportional to the square root of concentration of the monomer (Ref. 8). For vinylcyclopentadienyl manganeze (cimantrene) the reaction order of the monomer is equal to 1.5 (Ref.9). An unusual kinetic ($W_p = k\,[M]^{0.8}[I]^{2.3}$) takes place at the polymerization of vinylcyclopentadienyltricarbonyl tungsten (Ref. 10).

During polymerization transformations of MCMs the occurrence of some processes affecting the reaction are possible. Among these are the coordination of the monomer with the initiator, the participation of the monomer in the initiation stage, the monomolecular chain termination. They are the reasons for the deviation from the canonical scheme of the radical polymerization. For example, this was shown by the polymerization of Ti-containing monomers (Ref. 8).



$$I \xrightarrow{k_i} 2R^{\bullet}$$

$$R^{\bullet} + M \xrightarrow{k_c} R^{\bullet}M$$

$$R^{\bullet} + M \xrightarrow{k_p^1} RM^{\bullet}$$

$$RM^{\bullet} + M \xrightarrow{k_p} RM_n^{\bullet}$$

$$RM^{\bullet} + RM^{\bullet} \xrightarrow{k_t} P$$

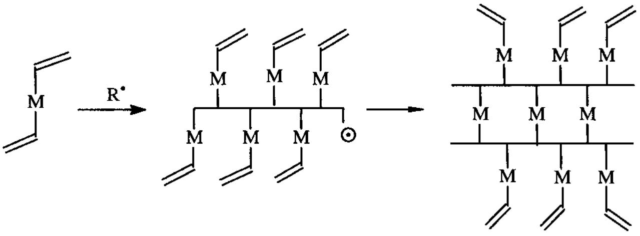
$$RM^{\bullet} + R^{\bullet} \xrightarrow{k_t'} P$$

$$R^{\bullet}M + RM^{\bullet} \xrightarrow{k_t''} P$$

Ti(IV) -coordinated radicals (R$^{\cdot}$M) take part both in chain growth and in chain termination, but in the later case they are more active.

One peculiarity of the radical polymerization of MCM is the possibility of obtaining stereoregular polymers. As known the difference between $\Delta F_{iso} - \Delta F_{syndio} = \delta\,\Delta F$ and iso- and syndioadditions for the polymerization of the vinyl monomers is small and equal to about 1 kcal/mol. The metal carboxyl groups present in MCMs promote inversion of the stereochemical configuration of the chain-growth center in each step of chain growth, which results in the formation of a predominantly syndiotactic polymer.

The polymerization of bifunctional acrylic monomers may be conceptually divided into two steps (Ref. 11):

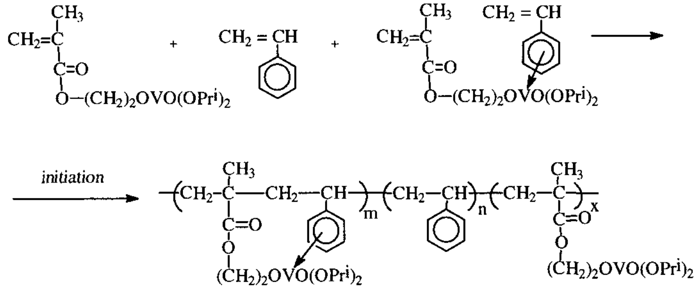


In the first step a stereoregular comb-like linear polymer is formed. The three-dimensional cross-linked structure itself is formed in the next stage. The C=C bonds in the side chains of the macroradicals are involved in the polymer chain-growth reactions. The growth of the chains in this stage proceeds under the conditions of strong steric hindrances and an increasing level of internal stresses, which result in the atactic structure of the chain. At the polymerization of metal acrylates the stereoregulation fraction makes up about 80 %.

Copolymerization of MCMs

The more interesting peculiarities are observed at the copolymerization of MCM and traditional monomers. Copolymerization of these monomers permits one to modificate the well-known polymers for giving them the required properties and evaluate the reaction activity of multiple bond of MCM (relative reactivity constants, Q - e parameters of the Alfrey-Price scheme, the monomer unit distribution etc.)

In the copolymerization system the complex donor-acceptor interactions with participation of π-electrons of the multiple bonds occur. In this case the vacant orbitals of transition metal play the significant role. This leads to the formation of the special zones - “stores”with the specific orientation of the monomer molecule. It results in the increasing of the polymerization rate and the formation of the more regular and long-chain macromolecules. For example, the copolymerization of monomethacrylic esters of ortovanadic acid with styrene is accompanied by such processes.



It's shown from the composition diagrams (Fig. 1), that the complex-bonded monomers enter the copolymerization first followed by MCM.

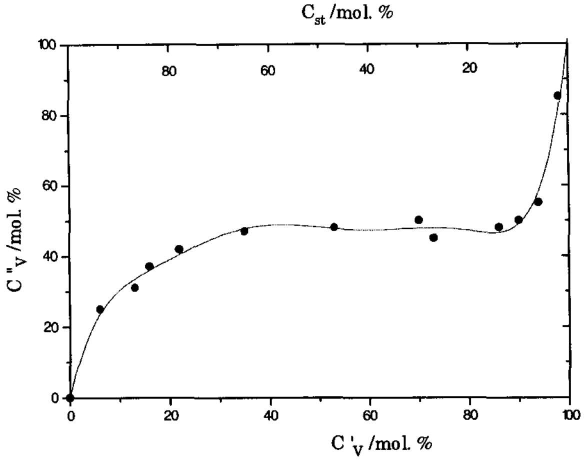
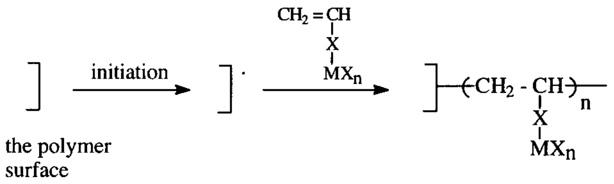


Fig. 1. Composition diagram for the copolymerization of V-containing monomer with styrene. $C`_V$ and $C``_V$ are the concentrations of vanadium in the monomeric mixture and in the polymer, respectively, C_{st} is the concentration of styrene in the monomeric mixture

As a rule, MCMs are less active than the traditional monomers. As known the parameter *e* of the common vinyl monomers is in the range from -1 to +1.5 . It characterizes the extent of polar effect of the substituent at the multiple bond. For the series of monomers the correlation between the value of *e* parameter and the Gammet's constant is observed (Ref.13). We found that MCMs possess a high negative values of *e* parameter (Fig. 2, the shaded field). In other words, the metal group behaves as a strong electron donor, which is similar to amino group substituted aromatic compound. The electron density is shifted towards the C=C bond.

One variety of copolymerization is graft polymerization of MCM onto the surface of polymers. Such approach allows to fix a metallocenter onto the surface of a polymer carrier.

The surface undergoes initiation reaction in the presence of MCM:



The grafting degree is determined by the time and the nature of MCM (Fig. 3.).

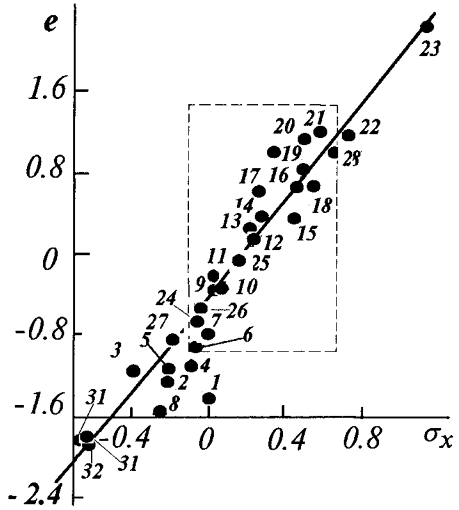


Fig. 2. Correlation of the polarity parameter (*e*) of the substituent X in $CH_2=CHX$ and its Hammet's constant (σ_x), where X equal 1 - $S\text{-}CH_3$; 2 - p-$C_6H_4N(CH_3)_2$; 3 - $-(CH_3)_2$; 4 - p-$C_6H_4OCH_3$; 5 - CH_3, C_6H_5; 6 - p-$C_6H_4CH_3$; 7 - C_6H_5; 8 - OC_2H_5; 9 - p-C_6H_4Cl; 10 - p-C_6H_4I; 11 - p-C_6H_4Br; 12 - Cl; 13 - p-C_6H_4CN; 14 - $C_6H_4NO_2$; 15 - CH_3, $COOCH_3$; 16 - Cl, Cl; 17 - CH_2Cl; 18 - $COOCH_3$; 19 - $CO(CH_3)$, 20 - CH_3, CN; 21 - CN, 22 - $SO(CH_3)$; 23 - CN, CN; 24 - $Co(OCOCH=CH_2)OCO$; 25 - $Cu(OCOCH=CH_2)OCO$; 26 - $(C_4H_9)_3SnOCO$; 27 - $(C_4H_9)_3SnOCO$, CH_3; 28 - $(CH_3)_3Sn$; 29 - $C_5H_3N(CH_3)ZnCl_2$; 30 - $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$; 31 - $(\eta^5\text{-}C_5H_4)Cr(CO)_2NO$; 32 - $(\eta^5\text{-}C_5H_4)Mn(CO)_3$

Only few examples of copolymerisations of MCMs are known. Here we note the copolymers of Ti(IV) - dicyclopentadienyl-dimethacrylate and Ni(II) acrylate (Ref. 15), benzyltricarbonylchromiumacrylate with ferrocenylacrylate, vinylcyclopentadienyltricarbonyl manganese and vinylcyclopentadienyldicarbonylnitrosyl chromium (Ref. 16). Also copolymers based on the same metal in the different valence states can be referred to this type.

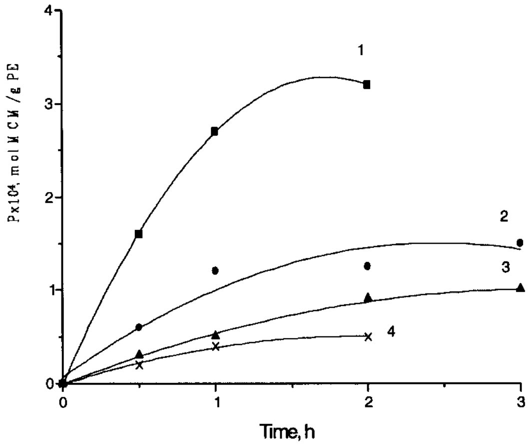


Fig. 3. Kinetic curves for yield of polymers resulting from grafting of acrylamide (AAm) complexes onto PE: $Cr(AAm)_4Cl_3$ (1), $Co(AAm)_4Cl_2$ (2), $Ni(AAm)_4Cl_2$ (3), $Co(AAm)_4(NO_3)_2(H_2O)_2$ (4)

Basic Applications of Metal-Containing Polymers

Modifications of traditional polymers are interesting as applications of such products in metal complex catalysis and as biological active additives, which has recently been summarized in a monograph (Ref. 17.).

CONCLUSION

Finally, we like to print out new trends in the synthesis and polymerization transformations of MCM. Among them is synthesis and polymerization of optical active, chelate and macrocycle types of MCMs. Also cluster-containing monomers are of essential interest. One should expect advances in the study of structural and supramolecular organization of metal-containing polymers. The investigation of the multiple bond reactivity of MCMs not only in polymerization, but in other reactions such as hydrogenization, hydroformylation, epoxidation etc. are also basic problems.

REFERENCES

(1) J. E. Sheats, *J. Macromol. Sci.-Chem.* A**15**, 1173 (1981)

(2) C. E. Carraher, J. E. Sheats, C. U. Pittman, (Eds) *"Metal-containing Polymer Systems"*, Plenum Press , N. Y. (1985)

(3) A. D. Pomogailo, V. S. Savost'yanov, *"Metal-containing monomers and their polymers"*, Khimiya, Moscow. (1988) (in Russian)

(4) A. D. Pomogailo, *"Immobilized Polymeric Metallo-Complex Catalysts"*, Nauka, Moscow (1988) (in Russian)

(5) A. D. Pomogailo, V. S. Savost'yanov, *J. Macromol. Sci. Rev.* **25**C, 375 (1985)

(6) G. I. Dzhardimalieva, A. D. Pomogailo, S. P. Davtyan, V. I. Ponomarev, *Izv. Akad. Nauk SSSR, Ser. Khim.*,1531 (1988) (*Bull.Acad Sci USSR, Div Chem.Sci.*, **37**,1352 (1988)

(7) C.U.Pittman, Jr., T.D.Rounsefell, E.A.Lewis et al., *Macromolecules,* **11**, 560 (1978)

(8) G. I. Dzhardimalieva, A. Tonoyan, A. D. Pomogailo, S. P. Davtyan, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1744 (1987)

(9) C.U.Pittman, Jr., C.C.Lin, T.D.Rounsefell, *Macromolecules*, **11**, 1022 (1978)

(10) C.U.Pittman, Jr., R.D.Priester,Jr., T.V.Jayaraman, *J.Polymer Sci.: Polym.Chem.Ed.,* **19,** 3351 (1981)

(11) B. S. Selenova, G. I. Dzhardimalieva, M. V. Tsikalova, S. V. Kurmaz, V. P. Roschupkin, I. Ya. Levitin, A. D. Pomogailo, M. E. Vol'pin, *Russ. Chem. Bull.*, **42**, 453 (1993)

(12) A. D. Pomogailo, N. D. Golubeva, *Russ. Chem. Bull.,* **43**, 2020 (1994)

(13) J. Furukawa, T.Tsuruta, *J.Polymer Sci.,***36**, 275 (1959)

(14) V. S. Savost'yanov, A. D. Pomogailo, D. A. Kritskaya, A. N. Ponomarev, *J. Polym. Sci.: Polym. Chem.*, **32**A (1994)

(15) G. I. Dzhardimalieva, A. D. Pomogailo, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 352 (1991).

(16) C.U.Pittman, Jr. *"Organometallic Reactions"*, Marcel Decker, N.Y. **6**, 1 (1977)

(17) A. D. Pomogailo, V. S. Savost'yanov, *"Synthesis and Polymerization of Metal-Containing Monomers"* CRC Press, Boca Raton 1994, 164 p.