Atom transfer radical polymerisation with an immobilised $[RuCl_2(p\text{-cymene})]_2$ dimer

T. Opstal, K. Melis and F. Verpoort*

Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281 (S3), 9000 Ghent, Belgium
E-mail: Francis.Verpoort@rug.ac.be

Received 23 January 2001; accepted 7 May 2001

$[RuCl_2(p\text{-cymene})]_2$ has been immobilized on silica and mesoporous MCM-41 and used as a catalyst for the atom transfer radical polymerisation (ATRP) of styrene, (methyl)methacrylate and acrylonitrile. The heterogeneous catalyst has a comparable activity as the homogeneous analogues and showed no significant loss of catalytic activity when reused.

KEY WORDS: MCM-41 materials; heterogeneous catalysis; atom transfer radical polymerisation

1. Introduction

The investigation of heterogeneous hybrid catalysts has been driven by the vision of combining the positive aspects of homogeneous catalysis (high activity per site, high selectivity, reproducibility and efficiency) with those of heterogeneous catalysis (thermal stability, ease of separation, possibility of continuous working).

Atom transfer radical polymerisation (ATRP) is one of the most promising methods in the field of controlled/"living" radical polymerisation [3]. The basis of this technique is the reversible transfer of a halogen atom from a monomeric or polymeric alkylhalide (Pol–X) to a transition metal complex (LM_t^n), generating an organic radical ($Pol^\bullet$) and a transition metal complex with a higher oxidation state ($LM_t^{n+1}X$) (figure 1) [4,5]. The redox equilibrium between LM_t^n and $LM_t^{n+1}X$ is strongly shifted toward the LM_t^n complex; hence the concentration of propagating radicals is kept low, termination is reduced, and monomer addition is controlled. A range of systems have been described using different metal catalysts in conjunction with an activated alkyl halide initiator, *e.g.*, Ru(II) [6], Cu(I) [4,5,7], Ni(II) [8], Rh(I) [9] and Fe(II) [10].

Ruthenium ($RuCl_2(PPh_3)_3$) was first introduced by Sawamoto and co-workers [6] for the controlled polymerisation of methylmethacrylate (MMA) but requires the presence of a Lewis acid activator. Arene complexes coordinated with ruthenium have attracted significant interest in polymer chemistry. Dimeric $[RuCl_2(\text{arene})]_2$, more specific $[RuCl_2(p\text{-cymene})]_2$ in combination with a monophosphine (PR_3), exhibits an excellent catalytic activity in polymer synthesis. After the proper initiation, the complex acts as an extremely active catalyst for ring-opening metathesis polymerisation [11] (ROMP) or (ATRP) [12].

$$\mathrm{Pol{-}X} + LM_t^n \rightleftharpoons \mathrm{Pol}^\bullet + LM_t^{n+1}X$$

Figure 1. Redox dynamic equilibrium reaction.

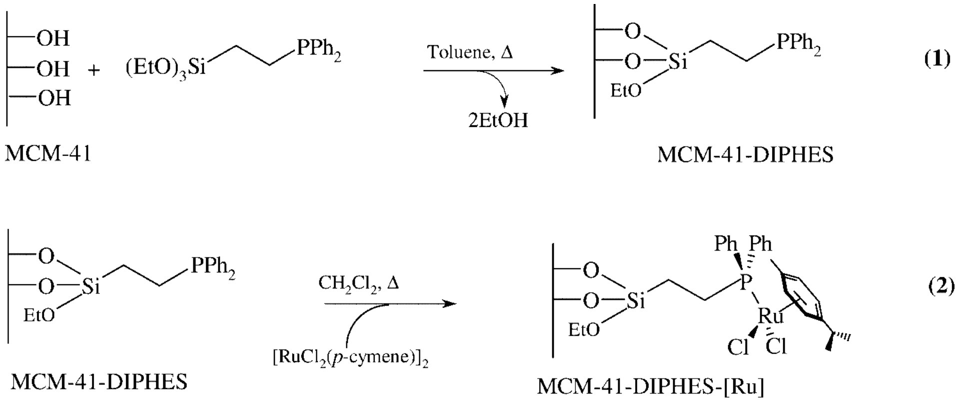
The Ru–arene complexes present a high functional group tolerance, which permits the polymerisation of monomer derivatives bearing acetal, ether, ester, epoxide and acid functions. This opens perspectives for the polymerisation of macromolecules with different topologies, architecture and functional groups. Demonceau and co-workers [11,12] exposed the efficacy of the Ru–arene complexes for ATRP in the absence of co-catalyst activation. The air-stable complexes are favourable compared to the most active ATRP catalysts reported to date. Although many advantages of this polymerisation technique have been disclosed so far, a few drawbacks remain. The use of this expensive transition metal catalyst and the polymer colouring effect limits any large scale application of this process. A number of strategies have been reported to alleviate this problem including immobilisation on insoluble organic and inorganic supports, *e.g.*, silicagel [13] and modified polystyrene [14], and the use of fluorous biphase reaction media [15] which allows for efficient catalyst separation.

The discovery of a new family of ordered mesoporous inorganic materials has attracted considerable and still growing attention due to their remarkable structure and wide application perspectives [16]. This is not only because it has brought about a series of novel mesoporous materials with various compositions which may find applications in catalysis, adsorption and host–guest chemistry, but also it has opened a new avenue for creating zeotype materials [17,18]. These materials posses a regular pore diameter in the range of 2–10 nm and a specific surface area from at least 1000 m^2/g; besides the inner surface of MCM-41 is covered with silanol groups which enable the immobilisation of transition metal catalysts *via* spacer molecules, such

---

* To whom correspondence should be addressed.

1011-372X/01/0700-0155$19.50/0



Scheme 1. Preparation of MCM-41-DIPHES-[Ru].

as $(EtO)_3Si(CH_2)_nY$ (with $n = 1, 2, 3, \ldots$ and $Y = NH_2$, PR_2, halogen).

The reaction of spacer molecules has been proven to be a very flexible immobilisation technique for the preparation of heterogeneous catalysts [1,2]. In addition, the regular pore size of MCM-41 can provide shape selectivity not provided by silica. Here we present the immobilisation of a Ru dimer ($[RuCl_2(p\text{-cymene})]_2$) on a phosphine-modified MCM-41 and silica support.

2. Experimental

2.1. General

All reactions and manipulations were performed under an argon atmosphere by using conventional Schlenk-tube techniques. Argon gas was dried by passage through P_2O_5 (Aldrich, 97%). Methylmethacrylate, isobutylmethacrylate (Acros, 99%), methylacrylate, butylacrylate (Acros, 99+%) and acrylonitrile (Aldrich, 99+%) are all distilled from CaH_2 before use. The initiators: ethyl 2-bromoisobutyrate (Aldrich), 2-chloropropionitrile (Aldrich) and methyl 2-bromopropionate (Aldrich) are used as received. Diphenylphosphinoethyltrimethoxysilane (DIPHES, Gelest Organosilanes) was used as obtained. Silicagel 5–25 μm (Aldrich) was used as silica source

^{1}H-NMR spectra were recorded using $CDCl_3$ on a 500 MHz Bruker AM spectrometer. The chemical shifts (δ) are reported in ppm, referred to ^{1}H of TMSD. The anchoring of the dimer was characterised by a Bruker Equinox 55 Raman spectrometer. The loading of the hybrid catalyst was determined with a Varian Liberty ICP-AES spectrometer and an ARL 9400 Sequential XRF spectrometer. The number- and weight-average molecular weights (M_n and M_w) and molecular weight distribution (M_w/M_n) of the polymers were determined by gel permeation chromatography ($CHCl_3$, 25 °C) using a Waters Maxima 820 system equipped with a PL gel column (60 cm, $\varnothing = 7.5$ mm) and calibrated with polystyrene standards.

2.2. Preparation of MCM-41

MCM-41 was prepared following a procedure similar to previously described methods [19].

2.3. Preparation of [RuCl2(p-cymene)]2

The same procedure was followed as described in [20].

2.4. Preparation of MCM-41-[Ru]

The immobilisation of $[RuCl_2(p\text{-cymene})]_2$ on the mesoporous support (MCM-41) was carried out in two steps (scheme 1). The first step involved the drying of the support at 150 °C under vacuum for 24 h and the grafting of *di*phenyl*ph*osphino-*e*thyltrimethoxy*s*ilane (DIPHES) (2 mmol/g MCM-41) onto the siliceous support in toluene through condensation of the free silanol groups of the surface and the ethoxy functionalities of DIPHES. After continuous extraction with toluene for 5 h and drying of the MCM-41-DIPHES dichloromethane (15 ml) was added for the second step, the grafting of the Ru-complex. The immobilised complex was prepared by reaction of the dimer $[RuCl_2(p\text{-cymene})]_2$ with the PPh_2 functionalities of MCM-41-DIPHES. Subsequent filtration, washing until the filtrate is colourless and drying of the Ru-modified MCM-41 results in a deep orange powder. Elemental analysis gave a catalyst loading of 0.1627 mmol/g MCM-41, respectively.

2.5. Preparation of (EtO)3Si(CH2)3PCy2 (DICPS)

1 ml chloropropyltriethoxysilane (4.3 mmol) is added to 10 ml dry ether and cooled to −78 °C. Through a funnel 2.6 ml from a 1.6 M (4.3 mmol, in hexane) *n*-BuLi solution is added dropwise to the solution. After reaction 0.890 ml (4.3 mmol) dicyclohexylchlorophosphine is added. The reaction mixture is slowly warmed to room temperature and the LiCl is filtered off.

2.6. Preparation of MCM-41-DICPS-[Ru] and silica-DICPS-[Ru]

After removing the solvent the spacer is added to a suspension of 2 g MCM-41 in 20 ml toluene and the same procedure is followed as for MCM-41-DIPHES-[Ru]. This spacer is also added to 2 g dried silicagel resulting in the silica-DICPS-[Ru] system. A catalyst loading of 0.04700 mmol/g MCM-41 and 0.019 mmol/g silicagel was found.

2.7. Polymerisation procedure

The same reaction conditions as used by Simal *et al.* [12] were applied. Heterogeneous catalyst (1 eq.), monomer (800 eq.) and initiator (2 eq.) are transferred to a glass reaction tube under argon atmosphere and stirred in an thermostated oil bath. The initiators for MMA and styrene are, respectively, ethyl 2-bromoisobutyrate and (1-bromoethyl)benzene.

At timed intervals, the reaction tubes are opened and chloroform is added to dissolve the polymer. Then the catalyst is removed by filtration. Afterwards MMA or styrene are, respectively, precipitated in *n*-octane or methanol.

When the polymerisations are carried out in very diluted conditions (33 vol%) in toluene and catalyst/monomer/initiator = 1/100/2), the polymer remains dissolved in the reaction mixture and the catalyst can directly be filtered off and reused.

3. Results and discussion

FT-Raman study was used to check the immobilisation of the spacer molecule and the Ru-complex (figure 2). Comparison of the spectra of MCM-41 and the MCM-41-DIPHES clearly shows the superposition of the DIPHES vibrations on the MCM-41 baseline. Comparative study of the phosphinated MCM-41 and the heterogenised Ru-complex reveals new vibration bands at 800 cm^{-1}, 705 (ν Ru–P), 286 (ν Ru–Cl) and 177 (ν Ru–p-cymene) cm^{-1} which proves the chemical attachment of the [RuCl$_2$(p-cymene)]$_2$ on the modified mesoporous support. The far IR spectra of the [RuCl$_2$(p-cymene)]$_2$ shows two strong bands in the region of 290 and 250 cm^{-1} assigned to (ν Ru–Cl) modes of terminal and bridging chlorine atoms [21]. After the anchoring of the Ru-dimer one peak (286 cm^{-1}) remains, indicating that the bridging mode disappeared.

Porosity measurements of the three MCM-41 samples (pristine MCM-41, phosphinated MCM-41 and immobilised catalyst) all reveal type IV IUPAC adsorption–desorption isotherms. This means that the structure of the mesoporous material and accessibility of the mesopores is maintained after modification.

The bulk polymerisation was carried out with styrene, MMA, isobutylmethacrylate, methylacrylate, butylacrylate and acrylonitrile as the monomer and (1-bromoethyl)benzene, ethyl 2-bromoisobutyrate, methyl 2-bromopropionate and 2-chloropropionitrile as the, respectively, initiator. The results of ATRP with MCM-41-DIPHES-[Ru] and with MCM-41-DICPS-[Ru] are summarised in tables 1 and 2. In most cases an increase in the viscosity of the reaction mixture was observed after a couple of hours at elevated temperatures.

The best conversions were obtained for MMA and styrene; these polymers showed the highest molecular weights and the smallest polydispersities of all the investigated polymers. The catalytic activity of MCM-41-DICPS-[Ru] is

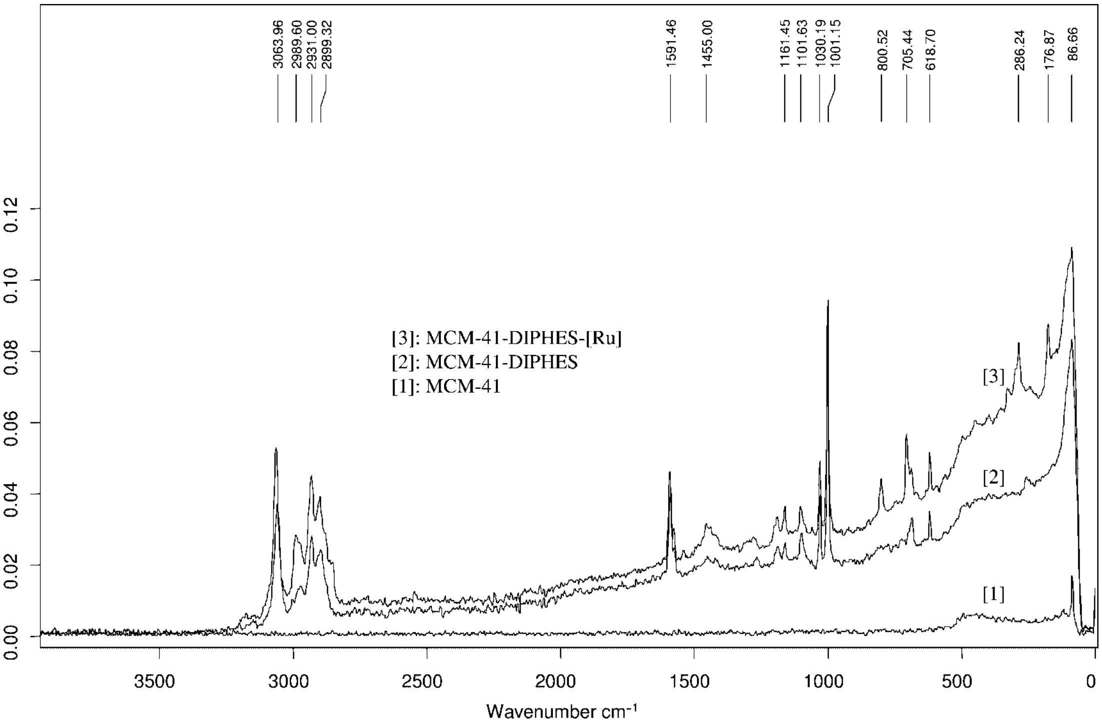


Figure 2. Immobilisation of [RuCl$_2$(p-cymene)]$_2$ followed by Raman spectroscopy.

Table 1
ATRP of different vinyl monomers with MCM-41-DIPHES-[Ru].[a]

Monomer	Temp. (°C)	Time (h)	Yield (%)	M_n $\times 10^3$	$M_{n,th}$[b] $\times 10^3$	M_w/M_n[c]
Methylmethacrylate	85	17	71	45.8	28.7	3.41
Isobutylmethacrylate	85	17	62	38.2	35.5	3.65
Styrene	110	17	81	40.2	34.0	3.21
Methylacrylate	85	17	5	15.7	1.7	4.21
Butylacrylate	85	17	5	12.8	2.6	4.46
Acrylonitrile	60	17	<5	–	–	–

[a] [Monomer] : [Ru] : [initiator] = 806 : 1 : 2 (for details see section 2). Catalyst MCM-41-DIPHES-[Ru].

[b] $M_{n,th} = ([\text{monomer}]_0/[\text{initiator}]_0) \times M_w(\text{monomer}) \times \text{conversion}$.

[c] Determined with GPC (using PS standards) in chloroform at 25 °C.

Table 2
ATRP of different vinyl monomers with MCM-41-DICPS-[Ru].[a]

Monomer	Temp. (°C)	Time (h)	Yield (%)	M_n $\times 10^3$	$M_{n,th}$[b] $\times 10^3$	M_w/M_n[c]
Methylmethacrylate	85	17	90	105.7	36.3	2.30
Isobutylmethacrylate	85	17	69	62.7	39.4	2.51
Styrene	110	17	87	49.9	36.5	2.81
Methylacrylate	85	17	14	20.7	3.8	3.41
Butylacrylate	85	17	10	17.7	9.1	4.17
Acrylonitrile	60	17	<5	–	–	–

[a] [Monomer] : [Ru] : [initiator] = 806 : 1 : 2 (for details see section 2). Catalyst: MCM-41-DICPS-[Ru].

[b] $M_{n,th} = ([\text{monomer}]_0/[\text{initiator}]_0) \times M_w(\text{monomer}) \times \text{conversion}$.

[c] Determined with GPC (using PS standards) in chloroform at 25 °C.

Table 3
ATRP of different vinyl monomers with silica-DICPS-[Ru].[a]

Monomer	Temp. (°C)	Time (h)	Yield (%)	M_n $\times 10^3$	$M_{n,th}$[b] $\times 10^3$	M_w/M_n[c]
Methylmethacrylate	85	17	93	31.6	35.6	1.84
Isobutylmethacrylate	85	17	72	29.5	37.8	2.03
Styrene	110	17	90	28.9	37.8	1.69
Methylacrylate	85	17	18	20.7	6.1	2.11
Butylacrylate	85	17	14	30.2	7.3	2.38
Acrylonitrile	60	17	<5	–	–	–

[a] [Monomer] : [Ru] : [initiator] = 806 : 1 : 2 (for details see section 2). Catalyst silica-DICPS-[Ru].

[b] $M_{n,th} = ([\text{monomer}]_0/[\text{initiator}]_0) \times M_w(\text{monomer}) \times \text{conversion}$.

[c] Determined with GPC (using PS standards) in chloroform at 25 °C.

Table 4
Comparison of ATRP results between homogeneous and heterogeneous catalysts for MMA and styrene.

	Monomer	PPh_3-[Ru]		PCy_3-[Ru]	
		% Yield	PDI	% Yield	PDI
Homogeneous [12]	Styrene	39	1.8	64	1.3
	MMA	20	1.6	100	1.1
MCM-41	Styrene	81	3.2	87	2.8
	MMA	71	3.4	90	2.3
Silica	Styrene	–	–	90	1.7
	MMA	–	–	93	1.8

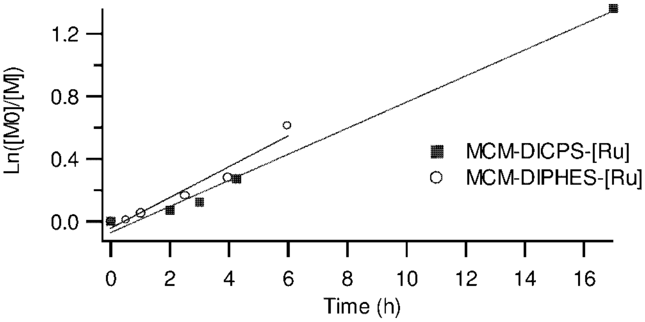


Figure 3. Time dependence of $\ln([M]_0/[M])$ at 85 °C where $[M]_0$ and [M] are the MMA concentration at times 0 and t ($y_{\text{DICPS}} = 0.0834x - 0.0724$, $r^2 = 0.9929$ and $y_{\text{DIPHES}} = 0.0983x - 0.0455$, $r^2 = 0.9622$).

higher due to the more σ-donation of the cyclohexyl group and more steric bulk capacity, *e.g.*, 90% conversion *versus* 71% in 17 h for MMA. Furthermore, it follows from tables 1 and 2 that only poor yields can be obtained for acrylates and acrylonitriles after 17 h.

The molecular weight analyses for all reactions show much higher molecular weights than predicted based on quantitative initiation ($DP_n = \Delta[M]/[I]_0$), and the polydispersities are high ($M_w/M_n > 2$). This can be explained by the fact that the propagation is faster than the initiation or by a slow deactivation, both resulting in an incomplete initiation. The growing radicals cannot easily approach the deactivator ($LM^{n+1}X$) and thus polymerise in a less controlled manner in the initial stage of the reaction. When enough deactivator ($LM^{n+1}X$) is generated by irreversible termination, controlled polymerisation then proceeds.

The results of the different vinyl monomers for ATRP with the silica-DICPS-[Ru] catalyst are shown in table 3.

From table 3 it is clear that the influence of diffusion is smaller compared to the MCM-based Ru systems, resulting in smaller polydispersities. Also the yields are higher for the silica-based systems except for acrylonitrile for which the yield is still lower than 5%.

The results obtained for MMA and styrene are compared with the homogeneous analogues and the heterogeneous silica and MCM-41 catalyst in table 4.

From table 4 it follows that the yields obtained *via* the heterogeneous catalysts for the polymerisation of styrene are higher in comparison with the yields obtained in a homogeneous way. Unfortunately, the polydispersity has also increased especially when MCM-41 is used as support. With silica as support the PDI values are slightly increased compared with the PDI values of the homogeneous systems. For MMA the same trend is observed, except for the homogeneous PCy_3-catalyst were the yield was 100%.

Comparing of the homogeneous PPh_3 and PCy_3 system, a drastic increment of the yield is observed for both monomers. This increment is far less pronounced when the PPh_3 and PCy_3 heterogeneous systems are compared.

Evidence for a controlled polymerisation is given by a linear increase of M_n *versus* conversion (figure 3) and a linear first-order rate plot for the reaction (figure 4).

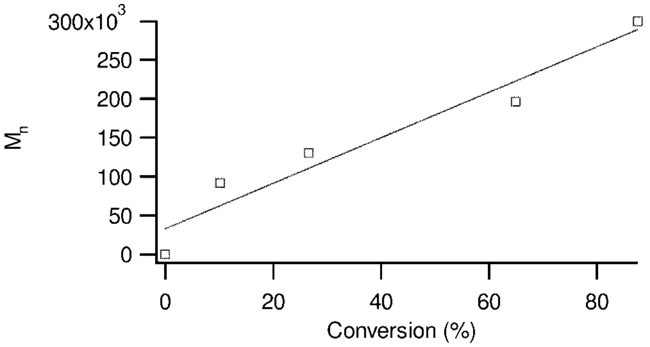


Figure 4. Dependence of the PMMA molecular weight M_n with DIPHES-MCM-41 on monomer conversion ($y_{\mathrm{DIPHES}} = 2923.6x + 32507$, $r^2 = 0.94$).

The linear time dependence of $\ln([M]_0/[M])$ indicates that the concentration of the active species remains constant during polymerisation. The lack of transfer reactions is supported by the linearity of the plot of M_n *versus* conversion. The polymerisation runs to seed through a radical mechanism as the PMMA tacticity (typically rr : rm : mm = 58, 37, 5, $\rho = 0.99$) fits the tacticity known for a radical polymerisation reaction. The radical mechanism is proven by adding a radical inhibitor such as galvinoxyl which inhibits the reaction completely. Furthermore, control of MMA polymerisation was confirmed by the addition of a second amount of MMA to the polymerised system generating a polydispersity increase from 3.41 to 3.50.

In order to evaluate the possibility of leaching, the catalysts were filtered from the polymer (see polymer procedure). ICP-AES measurements of the filtrates of the different heterogeneous systems showed no ruthenium. This confirms the absence of lost Ru.

4. Conclusions

It is possible to carry out ATRP with a $[RuCl_2(p\text{-cymene})]_2$ complex immobilised on a phosphine-modified MCM-41 and silica support. Two phosphane spacer molecules were use to anchor the Ru dimer: a dicyclohexylphosphine spacer and a diphenylphosphine spacer. Good yields are obtained for MMA and styrene with both supports after 17 h. Higher conversions were obtained with the heterogeneous systems compared to the homogeneous analogues. $[RuCl_2(p\text{-cymene})]_2$ in combination with the cyclohexylphosphine-modified silica is the most promissing system, high yields and PDI < 2 for MMA (1.8) and styrene (1.7) are obtained. The reactions showed that the abstraction of halogen atoms from the chain end is successful, but deactivation of the growing radical was slow due to diffusion. This results in quiet broad polydispersities especially for the MCM-41-based systems.

Improvements in the degree of control are under investigation.

Acknowledgement

FV is indepted to the FWO-Flanders (Fonds voor Wetenschappelijk Onderzoek Vlaanderen) for a financial support. TO and KM are indebted to the BOF (Bijzonder Onderzoeksfonds) of Ghent University for a research grant. M. Van Driessche (Texaco Technology, Belgium) is acknowledged for the elemental analysis.

References

[1] P. Sutra and D. Brunel, J. Chem. Soc. Chem. Commun. (1997) 2485.
[2] Y.V.S. Rao, D.E. De Vos, T. Bein and P.A. Jacobs, J. Chem. Soc. Chem. Commun. (1997) 355.
[3] K. Matyjaszewski, in: *Controlled Radical Polymerisation*, Vol. 685, ACS Symp. Ser. (Am. Chem. Soc., Washington, DC, 1998).
[4] J.S. Wang and K. Matyjaszewski, J. Am. Chem. Soc. 117 (1995) 5614.
[5] J.S. Wang and K. Matyjaszewski, Macromolecules 28 (1995) 7901.
[6] M. Kato, M. Kamigaito, M. Sawamoto and T. Higashimura, Macromolecules 28 (1995) 1721.
[7] J. Xia and K. Matyjaszewski, Macromolecules 30 (1997) 7697.
[8] C. Granel, P. Dubois, R. Jerome and P. Teyssie, Macromolecules 29 (1996) 8576.
[9] G. Moineau, C. Granel, P. Dubois, R. Jerome and P. Teyssie, Macromolecules 31 (1998) 542.
[10] T. Ando, M. Kamigaito and M. Sawamoto, Macromolecules 30 (1997) 4507.
[11] A. Demonceau, A.W. Stumpf, E. Saive and A.F. Noels, Macromolecules 30 (1997) 3127.
[12] F. Simal, A. Demonceau and A.F. Noels, Angew. Chem. Int. Ed. Engl. 38 (1999) 538.
[13] G. Kickelbick, H.J. Paik and K. Matyjaszewski, Macromolecules 32 (1999) 2941.
[14] D.M. Haddleton, D. Kukulj and A.P. Radigue, J. Chem. Soc. Chem. Commun. (1999) 99.
[15] D.M. Haddleton, S.G. Jackson and S.A.F. Bon, J. Am. Chem. Soc. 122 (2000) 1542.
[16] J. Beck, J. Vartuli, W. Roth, M. Leonowicz, C. Kresge, K. Schmitt, C. Chu, D. Olson, E. Sheppard, S. McCullen, J. Higgins and J. Schlenker, J. Am. Chem. Soc. (1992) 10834.
[17] A. Corma, Chem. Rev. 97 (1997) 2373.
[18] U. Ciesla and F. Schütz, Micropor. Mesopor. Mater. 27 (1999) 131.
[19] G. Schulz, J. Rathousky and A. Zukal, Int. J. Int. Mat. (1999) 97.
[20] M.A. Bennett and A.K. Smith, J. Chem. Soc. Dalton Trans. (1974) 233.
[21] G. Winkhaus and H. Singer, J. Organomet. Chem. (1967) 487.