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Controlled Radical Polymerization of Methyl Methacrylate in the Presence of Palladium Acetate, Triphenylphosphine, and Carbon Tetrachloride

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Introduction. In contrast to anionic and cationic polymerization, radical processes are suitable for the polymerization of a wide range of monomers under not very demanding conditions. For instance, radical species can tolerate water, although water is usually a poison for ionic polymerization. Therefore, millions of tons of polymers are produced industrially each year in bulk and in aqueous emulsion or suspension. These advantages cannot, however, counterbalance the poor control imparted to the free radical polymerization by the facile coupling and disproportion reactions of the propagating species.

Since the pioneering work by Otsu[1] on iniferters, many research groups have devoted effort to eliminate these termination and transfer reactions. Under these "pseudoliving" conditions, polymers with controlled molecular weight and architecture can be now prepared.

A successful approach to pseudoliving radical polymerization consists of performing the polymerization in the presence of another much more stable radical, so as to generate a rapid exchange between the active propagating species and a dormant species. This reversible end-capping of the growing radical by the stable radical decreases the actual concentration of the propagating free radicals and, accordingly, limits the undesired coupling and disproportion reactions. This concept has, for instance, been exploited by Georges et al. by using TEMPO as an organic stable counter radical.[2]

As another example, Sawamoto et al.[3] have extended the well-known Kharasch reaction to the polymerization of MMA at 60−80 °C. The polymerization is initiated by a polyhaloalkane, e.g., CCl_4, and catalyzed by a ruthenium complex, $RuCl_2(PPh_3)_2$, and a Lewis acid activator, $MeAl(OAr)_2$ or $Al(OiPr)_3$. The latter compound is, however, very sensitive to water and unstable in air. Matyjaszewski et al.[4] have reported also recently on the polymerization of styrene and (meth)acrylates by phenylethyl chloride, a cuprous salt (CuCl), and 2,2′-dipyridyl, para-substituted or not, as a ligand. The polymerization, however, occurs at temperatures higher than 100 °C. The methodology used by Sawamoto and Matyjaszewki is based on the transfer radical addition, or ATRA, of alkyl halides to alkenes. By analogy, Matyjaszewski coined the name of atom transfer radical polymerization, or ATRP, for this novel process.[4] The organometallic plays the role of a halogen carrier through a series of consecutive reversible oxidation and reduction reactions, through monoelectronic transfers.

All the characteristics of this ATRP based on organometallic complexes are in favor of a "living" propagation, which allows polymers with controlled molecular weight and narrow molecular weight distribution to be prepared. However, it was a challenge until quite recently to perform the polymerization both in the presence of water and at temperatures lower than 100 °C,[5] which is a prerequisite for potential industrial applications. Very recently, some of us have studied a very efficient catalytic system for the controlled polymerization of MMA under very mild conditions.[5d] The Ni(II)-based catalyst, i.e., a bis(ortho-chelatedaryl)-nickel(II) complex, is active in organic solvent as well as in aqueous suspension at about 70 °C. However, the Ni(II) catalyst requires a multistep synthesis and is very sensitive to oxygen. In this communication, we report on a new class of palladium complexes able to control the polymerization of MMA at 70 °C, not only in organic solvents but also in the presence of water.

Table 1. MMA Polymerization Initiated by $Pd(OAc)_2$/PPh_3/CCl_4 in Toluene at 70 °C[a]

entry	$[MMA]_0$/ $[CCl_4]_0$	$[Pd]_0$/ $[CCl_4]_0$	conv (%)	$M_{n,th}$[b]	$M_{n,exp}$[c]	f[d]	M_w/M_n
1	186	5	75	14 000	41 500	0.30	2.3
2	0	5	traces				
3	186	2	87	16 200	52 000	0.30	2.6
4	186	10	64	11 900	16 000	0.70	1.8
5[e]	186	10	76	14 100	30 000	0.50	1.6

[a] Conditions: $[PPh_3]_0/[Pd(OAc)_2]_0 = 4$; $[MMA]_0 = 2.9$ mol/L; polymerization time = 24h. [b] $M_{n,th} = [MMA]_0/[CCl_4]_0 \times MW_{MMA} \times$ conv. [c] SEC calibrated with PMMA standards. [d] $f = M_{n,th}/M_{n,exp}$. [e] $[NaAc]_0/[Pd(OAc)_2]_0 = 40$.

Results and Discussion. Otsu showed that a combination of carbon tetrachloride and metallic palladium adsorbed on carbon black was able to polymerize MMA, although with a low monomer conversion.[6] Stille et al.[7] synthesized PMMA-*co*-PS copolymers in low yield using $Pd(PPh_3)_4$ and bromofluorene. A very active catalyst was prepared from palladium acetate, $Pd(OAc)_2$, and triphenylphosphine, PPh_3, by Tsuji et al.[8] and used for the ATRA of carbon tetrachloride to olefins. The monoadduct was obtained in high yield even at room temperature. It is worth noting that both $Pd(OAc)_2$ and PPh_3 tolerate the presence of water. For these reasons, we decided to investigate the potential of this system for the polymerization of MMA.

The first polymerization experiments were carried out in toluene at 70 °C by using a MMA/CCl_4 molar ratio of 186, in the presence of an excess of palladium acetate with respect to CCl_4.[9] The results are summarized in Table 1 and show that high MMA conversions can be reached. Only polymer traces are served in the absence of carbon tetrachloride, which indicates that this halogeno compound plays a key role in the initiation step (entry 2; Table 1). The MMA polymerization has been studied in relation to the $Pd(OAc)_2$/CCl_4 molar ratio. The best correlation between theoretical and experimental molecular weight is observed when the palladium acetate is used in a 10-fold molar excess with respect to CCl_4. The necessity to use so large an excess of palladium acetate can be due to a low turnover of the palladium complex. According to Tsuji et al. the yield in the monoaddition of the halogeno compound is improved by the addition of sodium acetate, NaOAc.[8] Nevertheless, in our case, the monomer conversion and the initiator efficiency are not significantly improved by the addition of sodium acetate (entry 5; Table 1).

The role of PPh_3 is illustrated in Table 2. In the absence of this ligand, the formation of a black slurry of metallic palladium leads to an ill-controlled polymerization (entry 1; Table 2). When 4 equiv of PPh_3 is added to the polymerization mixture, a yellow species

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Table 2. Influence of the Amount of Phosphine on the MMA Polymerization Initiated by CCl_4 in the Presence of $Pd(OAc)_2$[a]

entry	$[PPh_3]_0/[Pd]_0$[b]	conv (%)	$M_{n,th}$[b]	$M_{n,exp}$[c]	f[d]	M_w/M_n
1	0	31	5 800	195 000	0.03	3.2
2	4	74	13 800	16 000	0.85	1.8
3	10	66	12 300	52 500	0.20	1.3

[a] Conditions: $[MMA]_0/[CCl_4]_0 = 186$; $[Pd]_0/[CCl_4]_0$ molar ratio $= 10$; $[MMA]_0 = 2.92$ mol/L toluene; polymerization time = 24 h; $T = 70$ °C. [b] $M_{n,th} = [MMA]_0/[CCl_4]_0 \times MW_{MMA} \times$ conv. [c] Determined by SEC calibrated with PMMA standards after precipitation in methanol. [d] $f = M_{n,th}/M_{n,exp}$.

Table 3. MMA Polymerization at Different Temperatures[a]

entry	T (°C)	conv (%)	$M_{n,th}$[b]	$M_{n,exp}$[c]	f[d]	M_w/M_n
1	20	54	10 000	37 500	0.25	1.80
2	70	74	13 800	16 000	0.85	1.80
3	90	46	8 600	23 500	0.35	1.35

[a] Conditions: $[MMA]_0/[CCl_4]_0 = 186$; $[CCl_4]_0/[Pd]_0/[PPh_3]_0 = 1/10/40$; $[MMA]_0 = 2.92$ mol/L; toluene; polymerization time = 24 h. [b] $M_{n,th} = [MMA]_0/[CCl_4]_0 \times MW_{MMA} \times$ conv. [c] Calculated by SEC (PMMA standards). [d] $f = M_{n,th}/M_{n,exp}$.

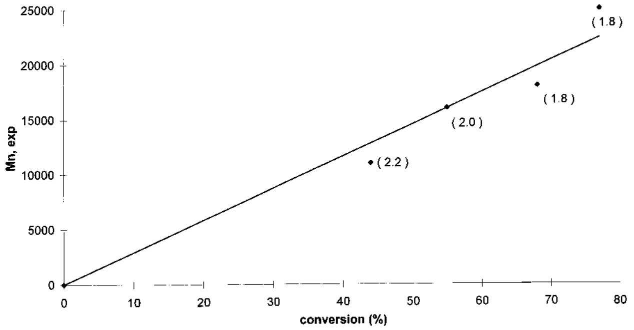

Figure 1. Dependence of experimental M_n on the monomer conversion. $[CCl_4]_0/[Pd]_0/[PPh_3]_0 = 1/10/40$; $[MMA]_0 = 2.92$ mol/L; $M_{n,th} = [MMA]_0/[CCl_4]_0 \times MW_{MMA} \times$ conv. $M_{n,exp}$ is calculated from SEC, and PMMA standards. M_w/M_n is indicated in parentheses.

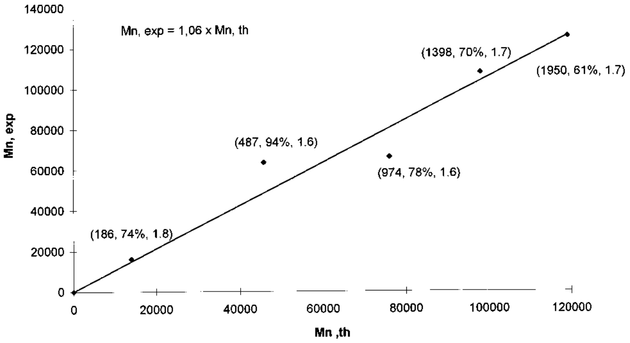

Figure 2. Dependence of experimental M_n on theoretical values. $[CCl_4]_0/[Pd]_0/[PPh_3]_0 = 1/10/40$; $[MMA]_0 = 2.92$ mol/L; polymerization time = 24 h; $T = 70$ °C; $M_{n,th} = [MMA]_0/[CCl_4]_0 \times M_{WMMA} \times$ conv. $M_{n,exp}$ is calculated from SEC and PMMA standards samples. $[MMA]_0/[CCl_4]_0$, the monomer conversion, and M_w/M_n are indicated in parentheses.

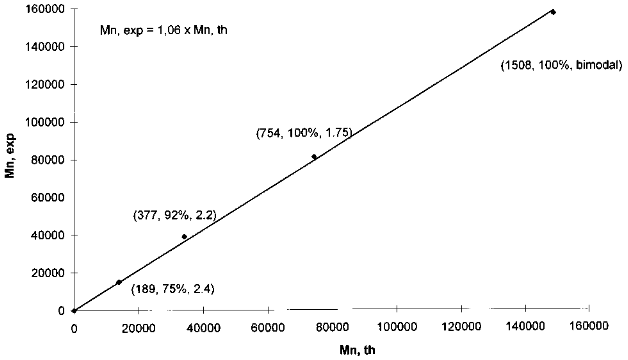

Figure 3. Effect of the $[MMA]/[CCl_4]$ molar ratio on the MMA polymerization in water. $[CCl_4]_0/[Pd]_0/[PPh_3]_0 = 1/10/40$; MMA content = 17 wt %; polymerization time = 24 h; $T = 70$ °C; $M_{n,th} = [MMA]_0/[CCl_4]_0 \times MW_{MMA} \times$ conv. M_n, exp is calculated from SEC and PMMA standards. $[MMA]_0/[CCl_4]_0$, the monomer conversion, and M_w/M_n are indicated in parentheses.

is formed, which is poorly soluble in toluene. Interestingly enough, the control of the polymerization is then substantially improved (higher conversion, higher initiation efficiency, and narrower molecular weight distribution, as shown by entries 1 and 2 in Table 2). Nevertheless, too large an excess of ligand is undesirable, more likely due to the saturation of the transition metal coordination sites (entry 3; Table 2).

Polymerization experiments have been conducted at different temperatures as shown in Table 3. Polymerization still occurs at a temperature as low as 20 °C (entry 1; Table 3), even though the initiator efficiency is much smaller and the control of the molecular parameters is not as good as at 70 °C. Similarly, low monomer conversion and initiation efficiency are observed when the polymerization temperature is too high (90 °C) and the palladium complex becomes unstable (entry 3; Table 3).

That the MMA polymerization is well controlled is confirmed by a linear dependence of the experimental M_n on the monomer conversion (Figure 1) and by a linear relationship between experimental M_n and theoretical values calculated for various MMA/CCl_4 molar ratios (Figure 2). Linearity of Figure 2 is observed at least up to a molecular weight of 10^5, with a slope close to unity that indicates a very high initiation efficiency. The narrowing of the molecular weight distribution with conversion (Figure 1) and the absence of low molecular weight PMMA chains (Figure 2) indicate that the high polydispersity is not caused by the formation of dead polymer but more probably by a slow initiation or a too slow exchange between active and dormant species.

The substitution of the aromatic ring is a tool for stabilizing the palladium complex. Under otherwise unchanged conditions, the substitution of tris(4-methoxyphenyl)phosphine for triphenylphosphine allowed the polymerization of MMA to be performed under homogeneous conditions. After 24 h at 70 °C in toluene, the monomer conversion is quantitative and the initiatior efficiency close to unity (conversion, 100%; $M_n = 36\,500$; "f" $= 0.98$; $M_w/M_n = 1.8$).

These very encouraging results reported in toluene have prompted us to investigate the MMA polymerization in the presence of water. The first experiments conducted in water but in the absence of any surfactant (Figure 3) indicate again a good control of the molecular weight, which agrees with the MMA/CCl_4 molar ratio. It is worth pointing out that a bimodal molecular weight distribution is observed for the high molecular weight PMMA sample ($M_n = 150\,000$), more likely as result of a poorly efficient stirring of the settled down material.

In order to overcome this drawback, "suspension" polymerization has been carried out in the presence of sorbitane monooleate poly(ethylene glycol) (Tween 80, 5 wt %) as a surfactant, all the other experimental conditions being unchanged. The good control of the molecular parameters is very promising (conversion = 100%; M_n, exp $= 32\,500$; $f = 0.55$; $M_w/M_n = 1.55$). It must, however, be noted that the aqueous suspension

Table 4. Modification of the Palladium Source[a]

entry	palladium source	$[Pd]_0/[CCl_4]_0$	conv (%)	$M_{n,th}$[b]	$M_{n,exp}$[c]	f[d]	M_w/M_n
1	$Pd(OAc)_2 + 4PPh_3$	5	75	14 000	41 500	0.30	2.3
2	$Pd(PPh_3)_4$	5	41	7 700	25 000	0.30	1.5
3	$Pd(PPh_3)_4$	1	35	6 600	41 000	0.15	1.4
4	$Pd(PPh_3)_4$	0.5	31	5 800	70 000	0.08	2.4

[a] Conditions: $[MMA]_0 = 2.92$ mol/L; toluene; polymerization time = 24 h; $T = 70$ °C. [b] $M_{n,th} = [MMA]_0/[CCl_4]_0 \times MW_{MMA} \times$ conv. [c] Calculated by SEC (PMMA standards). [d] $f = M_{n,th}/M_{n,exp}$.

does not remain stable until the monomer conversion is complete.

Polymerization Mechanism. Tsuji et al.[8] and Amatore et al.[10] have suggested that the poorly soluble yellow species formed by the "in situ" reaction of $Pd(OAc)_2$ with PPh_3 consists of Pd(0) complexed with the ligand. In order to clear up that point, MMA polymerization has been catalyzed by $Pd(PPh_3)_4$ as the palladium source under otherwise unchanged experimental conditions. Whatever the palladium origin, the polymerization occurs with a good initiator efficiency if an excess of palladium complex is used with respect to CCl_4 (Table 4).

Although a detailed analysis of the intimate mechanism has to be undertaken, some experimental observations are in favor of a radical pathway. Even if recovered within very limited yields, the random poly(MMA-*co*-styrene) copolymer prepared by Stille et al. by using $Pd(PPh_3)_4$ and bromofluorene has a ^1H NMR spectrum[7] typical of the copolymers prepared by conventional free radical copolymerization of MMA and styrene mixtures. The tacticity of PMMA prepared in this work is also in line with the tacticity usually reported for poly(methyl methacrylate) initiated by AIBN at the same temperature, i.e., ca. 60−65% syndiotactic triads. The persistence ratio [$r = 2(m)(r)/(mr)$] is close to unity, in accordance with a Bernoullian addition process, where (m), (r), and (mr) stand for meso diads, racemic diads, and isotactic triads, respectively. Furthermore, radical scavengers, such as diphenylpicrylhydrazyl (DPPH) or galvinoxyl, completely inhibit the polymerization.

Nevertheless, other synthetic pathways, e.g., oxidative addition followed by reductive elimination, cannot be ruled out. For instance, a mechanism that does not involve radical species has been proposed for the parent Heck reaction.[11] A detailed mechanistic study is thus required, which will be completed by the investigation of the effect of the palladium complexes on the control of the polymerization reaction.

As a short conclusion, PMMA chains with a number-average molecular weight up to ca. 150 000 can be synthesized by tuning up the monomer to initiator molar ratio. The commercial availability of the starting materials together with their possible handling in air atmosphere and in the presence of water pave the way to the well-tailored polymerization of methacrylic derivatives in aqueous suspension and emulsion.

Others monomers have been tested under the above mentioned experimental conditions. The control for ethyl acrylate and styrene is poor, while no control of the vinyl acetate polymerization has been observed. A deeper study of the polymerization mechanism will allow a comparison of the present results with those reported for other metal-mediated ATRP polymerizations. Such a study will be developed in a forthcoming paper.

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