Atom Transfer Radical Polymerization of Vinyl Monomers Mediated by Schiff Base Ruthenium−Alkylidene Catalysts and the Adventitious Effect of Water in Polymerizations with the Analogous Cationic Complexes

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ABSTRACT: Atom transfer radical polymerization (ATRP) of vinyl monomers mediated by Schiff base containing ruthenium−alkylidene catalysts was examined. The ATRP activity of the corresponding cationic complexes was also investigated using a water/toluene mixture and toluene as solvent. Our results show that both the counterion of the cationic complexes and the solvent used for the polymerization exert a remarkable effect on the reactivity of these complexes and the control over polymerization. These cationic ruthenium−alkylidene complexes are the first in their kind to perform the controlled radical suspension polymerization of methyl acrylate, methyl methacrylate, and styrene in water with good to excellent yields.

Introduction

Research on controlled/"living" radical polymerization has grown rapidly in recent years. Several new methods have been developed to gain control over the molecular weight and polydispersity of the polymer chains.[1] One of the most successful systems is atom transfer radical polymerization (ATRP), first reported in 1995 by Sawamoto et al.[2] and Matyjaszewski et al.,[3] who were both inspired by the landmark work of Otsu et al.[4] Controlled polymerization in ATRP is achieved by a reversible redox process catalyzed by a transition metal complex ($[M_t]^n$−Y/ligand, where Y may be another ligand or the counterion) which undergoes a one-electron oxidation with concomitant abstraction of a halogen atom, X, from a dormant species, R−X. As a result, this process generates oxidized metal complexes, X−M_t^{n+1}−Y/ligand, as persistent radicals and thereby minimizes the contribution of termination (Scheme 1).[1]

Recently, it has been demonstrated by Simal et al. that ruthenium benzylidene complexes of the general type $[RuCl_2({=}CHPh)(L)(L')]$ (L, L′ = PCy_3, PPh_3, and/or N-heterocyclic carbene) constitute a new class of catalysts for ATRP of vinyl monomers.[5] They promote the polymerization of various monomers with good to excellent yields and in a controlled way with methyl methacrylate and styrene.

In this study the controlled radical polymerization of some representative monomers is examined by using neutral and cationic Schiff base containing ruthenium−alkylidene catalysts in conjunction with an organic halide initiator R−X. The good activity of these complexes in ring-opening metathesis reactions (ROMP)[6] opens the possibility of making new interesting block copolymers by combining the ATRP and ROMP methodologies.

Results and Discussion

In a first set of experiments, the catalytic activity of the Schiff base substituted ruthenium benzylidenes **I.a−f (**Figure 1) is checked for ATRP with some representative vinyl monomers.

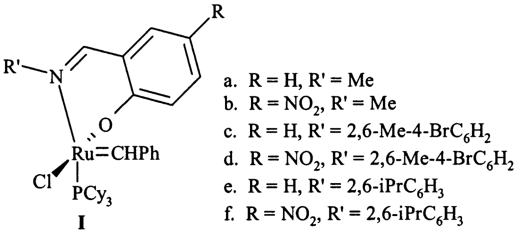

Figure 1. Structure of the neutral ruthenium−alkylidene complexes **I.a−f**.

Scheme 1. Schematic Representation of the Atom Transfer Radical Polymerization (ATRP) Process

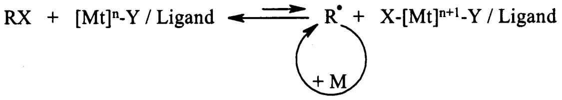

Table 1. Yield [%] for the ATRP of Some Representative Vinyl Monomers Catalyzed by I.a−f[a]

	catalyst					
substrate	**I.a**	**I.b**	**I.c**	**I.d**	**I.e**	**I.f**
methyl methacrylate	<5	< 5	11	28	7	10
isobutyl methacrylate	<5	< 5	9	19	<5	7
methyl acrylate	<5	<5	12	26	8	9
butyl acrylate	<5	<5	9	16	<5	7
styrene	10	16	74	88	56	65

[a] $[\text{Monomer}]_0:[\text{initiator}]_0:[\text{Ru}]_0 = 800:2:1$ (initiator, ethyl 2-methyl-2-bromopropionate for MMA and IBMA, methyl 2-bromopropionate for MA and BA, (1-bromoethyl)benzene for Styr; temperature, 85 °C for MMA, IBMA, MA, and BA and 110 °C for Styr; reaction time, 17 h).

The yields [%] and characteristics of the formed polymers are depicted in Table 1 and Table 2, respectively. Only the complexes **I.c** and **I.d** were found to catalyze the polymerization of acrylates and methacrylates. In contrast, all the complexes were able to convert styrene, although significant differences in their behavior were noticed. This is illustrated by the fact that the system with the lowest activity, namely system **I.a**, only reaches 10% conversion, whereas system **I.d** efficiently

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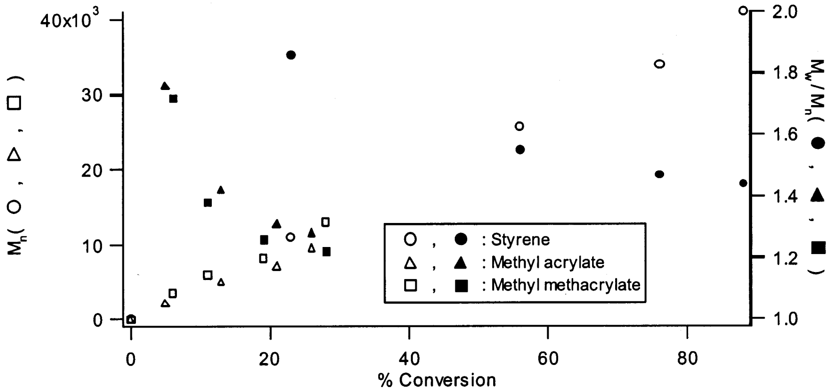

Figure 2. Dependence of the molecular weight M_n and M_w/M_n on monomer conversion for Styr, MA, and MMA and using catalytic system **I.d**.

Table 2. Characteristics of the Polymers Formed with Catalytic Systems I.c−f[a]

catalyst	monomer	M_n ($\times 10^3$)	PDI	f_i
I.c	methyl acrylate	5.7	1.31	0.72
	styrene	38	1.65	0.81
	methyl methacrylate	6.3	1.25	0.70
I.d	methyl acrylate	9.5	1.28	0.94
	styrene	41	1.44	0.89
	methyl methacrylate	13	1.22	0.87
I.e	methyl acrylate	4.5	1.52	0.61
	styrene	29	1.75	0.80
	methyl methacrylate	4.8	1.56	0.59
I.f	methyl acrylate	5.3	1.48	0.58
	styrene	32	1.71	0.85
	methyl methacrylate	6.6	1.51	0.61

[a] M_n, M_w, and the PDI's are determined by size-exclusion chromatography (SEC) with polyMMA (for MMA and MA) and polystyrene (for Styr) calibration. f_i = initiation efficiency = $M_{n,theor}/M_{n,exp}$ with $M_{n,theor}$ = ([monomer]$_0$/[initiator]$_0$) × MW(monomer) × conversion.

converts styrene in 88% yield. From Tables 1 and 2 it is clear that the polymers with the lowest polydispersities are formed by the most active systems.

For instance, the most performing system **I.d** reaches conversions of 26%, 88%, and 28% for respectively MA, Styr, and MMA, generating polyMA, polyStyr, and polyMMA with polydispersities of respectively 1.28, 1.44, and 1.22. **I.e**, the less performing system of which the characteristics of the formed polymers were determined, yields polyMA, polyStyr, and polyMMA in respectively 7% (PDI = 1.52), 56% (PDI = 1.75), and 8% (PDI = 1.56). This observation is not surprising as (i) the molecular weight distribution in ATRP decreases with conversion (a more active system reaches a higher conversion than a less active system for the same time period) and (ii) a more active system has a faster activation rate, but it can also have a faster deactivation rate (for example, Me_6tren/CuBr in the polymerization of acrylates). Moreover, when comparing the calculated number-average molecular weight (M_n) (assuming that one molecule of initiator generates one living polymer chain) and the measured M_n, it is clear that in this case the more active the catalytic system becomes, the more control over the molecular weights of the formed polymers can be obtained by adjusting the monomer to the initiator ratio ($DP_n = \Delta[M]/[I_0]$ and DP = degree of polymerization). For instance, the best ruthenium−alkylidene complex **I.d** possesses excellent initiator efficiencies (f_i's) of 0.94, 0.89, and 0.87 for respectively MA, Styr, and MMA.

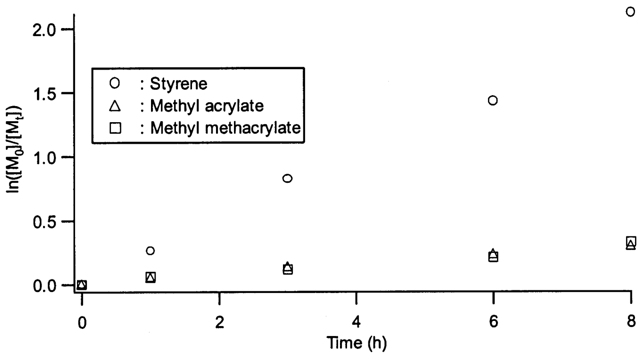

Figure 3. Time dependence of ln([M$_0$]/[M$_t$]) for the ATRP of Styr, MA, and MMA using catalytic system **I.d**. [M$_0$] and [M$_t$] are the monomer concentrations at times 0 and t. Styrene: $y = 0.2562x + 0.0035$; $r^2 = 0.9934$. Methyl acrylate: $y = 0.037x + 0.0122$; $r^2 = 0.9926$. Methyl methacrylate: $y = 0.0381x + 0.0065$; $r^2 = 0.9813$.

For the most performing ruthenium−alkylidene complex **I.d**, the monomer conversion and the number-average molecular weight (M_n) were followed as a function of time. The dependence of molecular weight and polydispersity on the monomer conversion is illustrated in Figure 2. The linear dependence observed for M_n is in agreement with a controlled process with a constant number of growing chains. In addition, a significant decrease of the polydispersity is observed as the polymerization proceeds, reaching 1.28, 1.44, and 1.22 for respectively MA, Styr, and MMA at respectively 26%, 88%, and 28% conversion. This indicates that the radicals are long-lived. The first-order kinetic plots for all three monomers are linear, indicating that termination reactions are almost completely excluded (Figure 3).

In a second set of experiments, the catalytic activity of the cationic ruthenium−alkylidene species **II.a−f** was tested in ATRP with some representative vinyl monomers. To assess the influence of the counterion on the catalytic activity, three different salts (silver tetrafluoroborate, silver tosylate, and trimethylsilyltriflate) were used for an in situ abstraction of chloride from the complexes **I.a−f** (Figure 4). Moreover, the polymerizations were performed in both toluene and a water/toluene mixture as solvent.

The cationic catalysts **II.a−f** were prepared in situ by adding 1 equiv of the appropriate silver salt to a solution of the neutral catalytic systems **I.a−f** in toluene. For the polymerizations in toluene, the monomer and the initiator were dissolved in a small amount

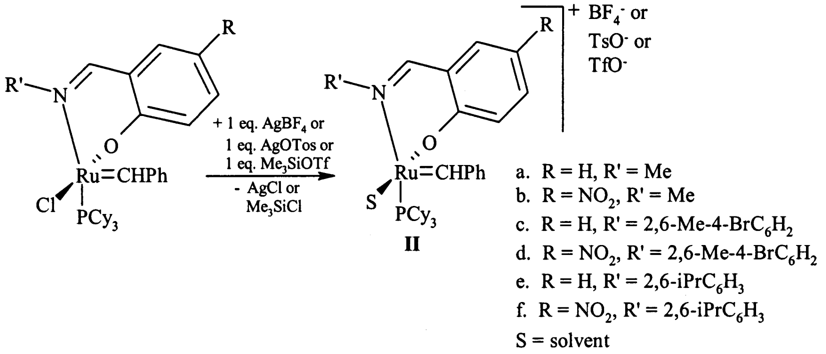

Figure 4. Structure of the cationic ruthenium–alkylidene complexes **II.a–f**.

Table 3. Yield [%] for the ATRP of Some Representative Vinyl Monomers in a Water/Toluene Mixture and Toluene and Catalyzed by the Cationic Ruthenium–Alkylidene Complexes II.a–f with Three Different Counterions[a]

		water/toluene			toluene		
catalyst	monomer	X = BF_4^-	X = TsO^-	X = TfO^-	X = BF_4^-	X = TsO^-	X = TfO^-
II.a	methyl acrylate	6	<5	<5	11	8	<5
	styrene	16	8	<5	22	15	9
	methyl methacrylate	<5	<5	<5	8	<5	<5
II.b	methyl acrylate	6	<5	<5	14	12	8
	styrene	17	11	8	26	21	14
	methyl methacrylate	<5	<5	<5	11	7	<5
II.c	methyl acrylate	64	51	21	78	64	36
	styrene	85	69	53	95	86	72
	methyl methacrylate	61	43	14	71	59	32
II.d	methyl acrylate	68	62	36	81	71	51
	styrene	91	84	69	98	92	87
	methyl methacrylate	67	55	32	77	68	48
II.e	methyl acrylate	11	9	<5	16	16	11
	styrene	49	40	36	66	61	57
	methyl methacrylate	7	<5	<5	12	11	8
II.f	methyl acrylate	13	13	<5	21	16	11
	styrene	53	46	41	74	70	67
	methyl methacrylate	11	8	<5	18	13	9

[a] The reaction conditions for the polymerization in toluene:monomer/toluene = 1/1 v/v. For the polymerizations in water:monomer/toluene = 1/3.5 v/v, water/organic phase = 1/1 v/v. The other reaction condition parameters are the same as in Table 1.

of toluene and added to the cationic catalyst so that the monomer/toluene ratio was 1/1 v/v. For the suspension polymerization in a water/toluene mixture, the monomer, the initiator, toluene, and distilled water were added so that the monomer/toluene ratio was 1/3.5 v/v and the water/organic phase ratio was 1/1 v/v. Unlike conventional suspension or dispersion polymerizations, no dispersants or surfactants (particle stabilizers) were added. Thus, in a strict sense, these polymerizations may not be called “suspension polymerizations”.

When the water/toluene mixture was used as a solvent, the initially two-layered heterogeneous mixture was vigorously stirred and kept at the reaction temperature to initiate polymerization, while magnetic stirring continued throughout the reaction. Under these conditions, the stirred mixture stayed a brown suspension that consisted of a continuous aqueous phase and finely suspended droplets of the organic phase where monomer polymerized. At the appropriate time, stirring was stopped, and the mixtures were allowed to cool to room temperature, to regenerate a two-layered mixture. From the upper organic phase the resulting polymers were isolated. Visual inspection of batches for different reaction times indicated that the higher the conversion (or polymer content), the more stable the suspension (slower phase separation), due to an increase in viscosity of the organic phase.

The polymerization yields [%] of MA, Styr, and MMA with the 18 different cationic ruthenium–alkylidene complexes using both a water/toluene mixture and toluene as solvent are summarized in Table 3. The characteristics of the polymers obtained with the best catalytic system, namely system **II.d**, are depicted in Table 4. The first thing one observes from Table 3 is that, irrespective of the counterion used, the cationic complexes give higher polymerization yields than the neutral alkylidene analogues discussed earlier. Furthermore, Table 3 shows that for a certain catalytic system the polymerization yields are systematically higher in toluene than in the water/toluene mixture. For example, the best system **II.d** with counterion BF_4^- converts MA, Styr, and MMA in toluene in respectively 81%, 98%, and 77% yield, whereas in the water/toluene mixture the conversion decreases to respectively 68%, 91%, and 67%. In both the water/toluene mixture as in toluene, the conversion depends dramatically upon the counterion used. In both cases the activity decreases from BF_4^- to TsO^- to TfO^- and this for all the catalytic systems used. The data gathered in Table 4 (giving the results for system **II.d**) reveal another interesting feature: despite the fact that the conversions are higher in toluene in comparison with the water/toluene mixture, the polymerization is less controlled. This is indicated by the broader polydispersities and lower initiator efficiency values when using toluene as a solvent. For example, when using BF_4^- as a counterion and the water/toluene mixture as solvent, the polydispersities are 1.37, 1.48, and 1.34 with f_i's of 0.81, 0.88,

Table 4. Characteristics of the Polymers Formed with the Catalytic System II.d in a Water/Toluene Mixture and Toluene and Using Three Different Counterions[a]

		catalyst **II.d**					
		water/toluene			toluene		
		$AgBF_4$	AgOTs	Me_3SiOTf	$AgBF_4$	AgOTs	Me_3SiOTf
methyl acrylate	M_n ($\times 10^3$)	29	27	16.5	42	39	28
	PDI	1.37	1.52	1.64	1.66	1.73	1.77
	f_i	0.83	0.79	0.75	0.66	0.63	0.63
styrene	M_n ($\times 10^3$)	43	41	36	56	54	61
	PDI	1.48	1.56	1.65	1.71	1.81	1.86
	f_i	0.88	0.85	0.80	0.73	0.71	0.59
methyl methacrylate	M_n ($\times 10^3$)	30	26	17.6	46	43	32
	PDI	1.34	1.45	1.58	1.46	1.54	1.64
	f_i	0.89	0.85	0.73	0.67	0.64	0.61

[a] M_n, M_w, and the PDI's are determined by size-exclusion chromatography (SEC) with polyMMA (for MMA and MA) and polystyrene (for Styr) calibration. f_i = initiation efficiency = $M_{n,theor}/M_{n,exp}$ with $M_{n,theor}$ = ([monomer]$_0$/[initiator]$_0$) × M_w(monomer) × conversion.

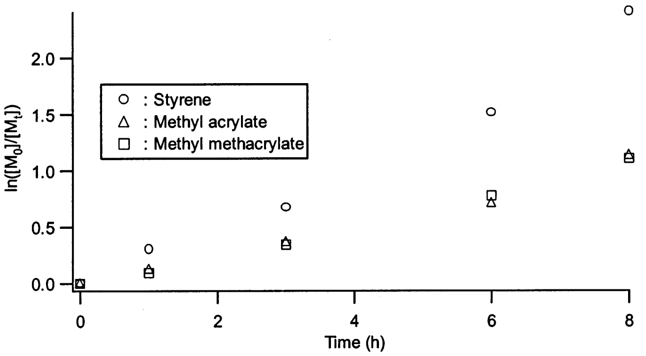

Figure 5. Time dependence of ln([M$_0$]/[M]$_t$) for the ATRP of Styr, MA, and MMA using catalytic system **II.d** with BF_4^- as a counterion and using a water/toluene mixture as solvent. [M$_0$] and [M$_t$] are the monomer concentrations at times 0 and t. Styrene: $y = 0.3003x + 0.0896$; $r^2 = 0.9891$. Methyl acrylate: $y = 0.1325x + 0.0265$; $r^2 = 0.9944$. Methyl methacrylate: $y = 0.1329x + 0.0316$; $r^2 = 0.9912$.

and 0.89 for respectively polyMA, polyStyr, and polyMMA. With the same counterion and applying the same reaction conditions, but using toluene as solvent, the polydispersities increase to 1.66, 1.71, and 1.46 with f_i's of 0.66, 0.73, and 0.67 for respectively polyMA, polyStyr, and polyMMA. Thus, when toluene is used as solvent, the initiation process is less efficient. Furthermore, it is clear from Table 4 that not only the activity decreases from BF_4^- to TsO^- to TfO^-, but also the control over polymerization, irrespective the solvent used for the polymerization. This decrease in control over polymerization is nicely illustrated by the PDI's that increase from BF_4^- to TsO^- to TfO^- and the f_i's that decrease from BF_4^- to TsO^- to TfO^-, irrespective of the solvent used.

For the best system, namely **II.d** with BF_4^- as counterion and using the water/toluene mixture as solvent, the time course of the polymerization was followed for the three different monomers. The results of these experiments are depicted in Figures 5 and 6.

Under the reaction conditions used, the kinetics were first order in monomer and this for all three monomers (Figure 5), and the number-average molecular weight (M_n) of the polymers increased linearly with monomer conversion (Figure 6), although they were slightly lower than the calculated values (this is indicated by the f_i's in Table 4). Furthermore, the decrease of the molecular weight distribution (M_w/M_n) as the polymerization proceeds (Figure 6) confirms the "living" character of the polymerization.

In conclusion, we showed that the Schiff base containing ruthenium−alkylidene catalysts **I.a**−**f** exhibit moderate activity in ATRP reactions. However, the activity of the neutral Ru systems increases dramatically when a chloride is abstracted from the metal center, giving rise to cationic Ru−alkylidene complexes. The results show that the control over polymerization and the polymerization yields are very dependent on the counterion and solvent used. Moreover, these cationic systems are the first ruthenium−alkylidene complexes reported so far that allow a controlled radical suspension polymerization of vinyl monomers in water in very good yields. Furthermore, the fact that these catalysts also exhibit promising activities in ring-opening metathesis polymerization (ROMP) reactions[6] allows them to combine the ROMP and the ATRP methodologies to make

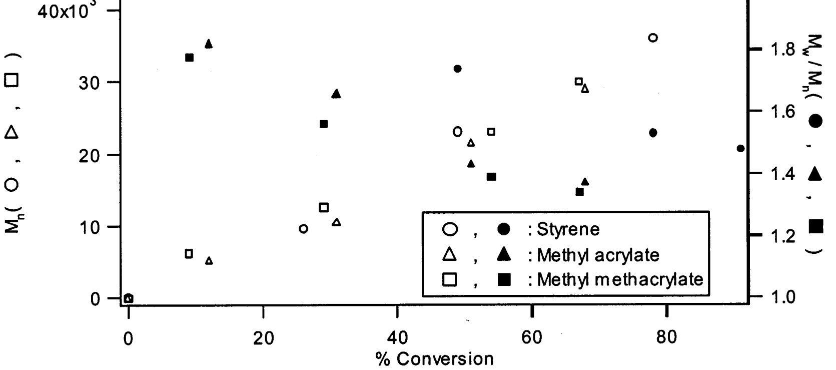

Figure 6. Dependence of the molecular weight M_n and M_w/M_n on monomer conversion for Styr, MA, and MMA and using catalytic system **II.d** with BF_4^- as a counterion and using a water/toluene mixture as solvent.

block copolymers with interesting properties by using new monomer combinations.

Further studies concerning this last point are currently under investigation.

Experimental Section

All reactions and manipulations were performed under an argon atmosphere by using conventional Schlenck tube techniques. All reagents and solvents used were purchased from Aldrich Chemical Co. All reagents and solvents were dried, distilled, and stored under nitrogen at −20 °C with conventional methods. ATRP of methacrylates (methyl methacrylate, isobutyl methacrylate), acrylates (methyl acrylate, butyl acrylate), and styrene was carried out with respectively ethyl 2-methyl-2-bromopropionate, methyl 2-bromopropionate, and (1-bromoethyl)benzene as initiator. The catalytic systems **I.a**−**f** were prepared using well-established procedures[6] and were fully characterized by Raman, IR, ^{1}H NMR, ^{13}C NMR, and elemental analysis.[7] The catalytic systems **II.a**−**f** were prepared in situ by adding 1 equiv of the appropriate silver salt to catalysts **I.a**−**f**.

The polymerizations were carried out under an argon atmosphere in sealed glass vials. For the neutral alkylidene−ruthenium complexes **I.a**−**f** a typical ATRP experiment is given below: 0.0117 mmol of catalyst was placed in a glass tube (in which the air was expelled by three vacuum−nitrogen cycles) containing a magnet bar and capped by a three-way stopcock. Then the monomer and initiator were added so that the molar ratios [catalyst]/[initiator]/[monomer] were 1/2/800. All liquids were handled under argon with dried syringes. The reaction mixture was then heated for different time periods at the reaction temperature that was 85 °C for the acrylates and methacrylates and 110 °C for styrene. After cooling, it was diluted in THF and poured in 50 mL of *n*-heptane (for the acrylates, methacrylates) or 50 mL of methanol (for styrene) under vigorous stirring. The precipitated polymer was filtered and dried in a vacuum overnight. For the polymerization reactions with the cationic ruthenium−alkylidene complexes, the same procedure was followed with this difference that the appropriate solvent was added before heating the reaction mixture. For the polymerizations in toluene, the monomer, the initiator, and the catalyst were dissolved in a small amount of toluene so that the monomer/toluene ratio was 1/1 v/v. For the suspension polymerization in water/toluene mixtures, the monomer, the initiator, and the catalyst were dissolved in a small amount of toluene, and distilled water was added to the organic solution so that monomer/toluene ratio was 1/3.5 v/v and the water/organic phase ratio 1/1 v/v.

Measurements. The number- and weight-average molecular weights (M_n and M_w) and polydispersity (M_w/M_n) of the polymers were determined by gel permeation chromatography ($CHCl_3$, 25 °C) using polyMMA (for the polyacrylates and polymethacrylates) or polystyrene (for polystyrene) standards. The GPC instrument used is a Waters Maxima 820 system equipped with a PL gel column.

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