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Synthesis of PMMA and PMMA Block Copolymers at Elevated Temperatures by Phosphor Ylide-Mediated Polymerizations

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SUMMARY: The MMA polymerization initiated by (1-naphthyl) triphenylphosphonium triphenylmethyl anion(TPM,NTPP) or the NTPP salt of the methylisobutyrate anion (MIB,NTPP) in THF at temperatures varying from 25 to 70^{0}C appears to be a living polymerization as indicatred by a linear M$_n$ vs. MMA conversion plot and by the narrow MW distributions. As indicated by the proton spectrum of MIB, NTPP in THF d$_8$ the predominant polymerization intermediate appears to be the ylide formed exclusively by addition of the MIB anion to the 4-carbon of the 1-naphthyl group. This ylide shows upfield shifts for the 3- proton of the cyclohexadienyl ring and of the 6- and 8--protons of the remaining aromatic ring.

The rates of the NTPP mediated polymerizations are reduced by factors of around 10^4-10^5 compared to that mediated by the corresponding ylides formed by addition of MIB to the phenyl ring of tetraphenylphosphonium ion. The reductions in rate in the presence of NTPP make it possible to carry out MMA polymerizations under conditions not normally accessible.

Introduction

There has been a great deal of interest in the controlled polymerization of (meth)acrylates at ambient conditions in recent years.[1,2] We have recently reported tetraphenylphosphonium carbanion initiators that polymerize MMA at temperatures between 0 and 25^0 C to give polymers of high molecular weights (MW • 50,000) and narrow polydispersities.[3,4] However these polymerizations were shown to be very rapid with monomer conversion half life times in the order of one second at 25^{0}C under typical reactions conditions and have the disadvantage that thermal control is limited due to the exothermicity of the polymerization.

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We now report the 1-naphthyltriphenylphosphonium triphenylmethyl anion (NTPP, TPM) initiated living anionic polymerization of MMA in THF at temperatures from 25 to 70^{0}C. These polymerizations are much slower then that in the presence of the tetraphenylphosphonium (TPP) ion and at 25^{0}C have half lives in the order of several hours. Because of the much lower rates these polymerizations can be carried out at or below 70^{0}C but all indications are that the polymerization temperatures can be increased further. Molecular weight distributions are narrow even at 70^{0}C with polydispersities of less than 1.20.

Experimental

Triphenylmethylpotassium (TPMK) was prepared from triphenylmethane and potassium metal in THF or from the reaction of the potassium dianion oligomer of alphamethylstyrene with triphenylmethane. Potassiomethylisobutyrate (KMIB) was synthesized by metalation of methylisobutyrate with hexamethyldisilazylpotassium. 1-Naphthyltriphenyl-phosphonium bromide (NTPPBr) was prepared by stirring $NiBr_2 \cdot 2Ph_3P$ and 1-bromonaphthalene overnight at 190°C under argon.[5] The removal of traces of water from the salt was carried out by titration with TPMK.[6] Thus a solution of Ph_3CK was added to the NTPPBr salt until a reddish color of the triphenylmethyl salt was clearly visible. The salt was then washed with THF until the red color had disappeared and was then dried overnight under high vacuum.

Initiators were prepared by addition of TPMK to a slurry of the NTTPBr in THF at or below room temperature using procedures similar to that reported previously.[3,4] A rapid formation of the NTPP carbanion could be observed by a slight change in color from bright red to a deep tomato red. The metathesis reaction could be observed by the precipitation of KBr that was not filtered off as it did not interfere with the polymerizations. The system was then warmed to the desired temperature and stirred for 15 minutes to allow complete cation exchange. The longer metathesis time was found to be necessary since the exchange reaction was slower than for the case of the tetraphenylphosphonium salt (TPPBr). The slower metathesis reaction is at least partially attributable to the statistical factor of four that favors the ylide formation in the TPP system.

Polymerizations were carried out by a one time addition of a THF solution of MMA through a teflon stopcock at or below room temperature followed by warming to the desired reaction temperature and the polymerization mixture was stirred for the specified reaction time (Table 1).

Alternatively the polymerization was carried out under inert gas. In one case (Table 1#12) the polymerization of MMA was carried out by a one time addition of MMA (10 mL) to the TPM, NTTP solution dissolved in THF to give a concentrated MMA solution (50 weight %). In this case the exothermic polymerization caused a rise in temperature to 76^{0}C causing the THF to reflux. The reaction in this case was complete in about 30 minutes and ,after addition of 50 mL of THF, was terminated by addition of 1 mL of methanol/acetic acid(1/1 V/V).

A PMMA -poly(t-butylmethacylate) block copolymer was synthesized by sequential addition of MMA (0.89M) and TBMA (0.62M)to the TPM, NTTP initiator at ambient conditions. In this case the reaction temperatures varied between 25 and 50^{0}C.

Polymer yields were determined gravimetrically in some cases by precipitation in hexane followed by drying.Polymer isolation, SEC, and NMR procedures have been described elsewhere.[3,4]

Results and Discussion

As was observed in the case of the TPP systems the initiation of MMA in the presence of the NTPP cation is indicated by a rapid change from deep red color to an orange brown the color of which is slightly different from that of the corresponding TPP ylide. The polymerizations of MMA in THF in the presence of NTPP counterion proceed in a controlled manner at temperatures from 20° up to 76°C. No upper limit for the polymerization was explored. The polymerization rates are *much* slower -on the order of 30 minutes to 24 hours- than observed for the TPP-mediated polymerizations that are typically complete in about one second. Clearly polymerization rates are four to five orders of magnitude lower than that determined in the TPP systems.[7]

The data shown in Table 1 are consistent with a living polymerization even at 70°C and good molecular weight control as indicated by a linear increase in M_n with conversion using a method by Penczek.[8] (Figure 1). Also relatively narrow MW distributions were obtained even at high temperatures (Table 1).

The termination reactions of the NTPP-mediated systems by water or alcohols typically can take up to several minutes or longer and are much slower than the TPP systems. Also upon opening the system to air, decoloration takes far longer than for the TPP systems.These observations are clearly related to the greater stability of the corresponding naphthyl ylide the stability of which is enhanced by the unperturbed aromaticity of the remaining benzene moiety (see below).

Table 1. $NTPP^+,Ph_3C^-$ - Mediated Polymerization of MMA in THF at Various Temperatures.[f]

Run	Rxn Time[a]	Rxn Temp (°C)	Yield (%)	M_n (SEC)	PDI (SEC)	f[b]
1	28 min	25	-	1,250	1.05	-
2	28/19 min	25-70	-	2,500	1.03	-
3	28/49 min	25-70	-	3,800	1.11	-
4	70 min	70	40	5,700	1.06	0.26
5	3 hrs	70	50	9,300	1.17	0.25
6	20 hrs	70	> 95	19,000	1.17	0.25
7	3 hrs	25	80	8,300	1.08	0.40
8	12 hrs	70	> 95	9,900	1.07	0.40
9	4 hrs	70	> 95	15,000	1.12	0.24
10	20 hrs	70	> 95	17,000	1.14	0.23
11	18 hrs	25	> 95	7,300	1.24	0.36
12[d]	30 min	25-76[c]	> 95	24,100	1.23	0.66
13[e]	30 min	25-50	>95	9,500	1.14	-

a.Dual times indicate at 25 and 70°C respectively b) Initiator efficiency, M_n (Calc) / M_n by SEC using PMMA standards. c. Reaction temperature increase by adiabatic heating from 25 to 76°C. d. Syndiotactic content is 53%. e. Block copolymerization of MMA (0.89M) at 25-35°C and t-BuMA (0.62M) at 50°C for 24 hrs. f. MMA concentration is 0.16M

The initiator efficiencies for the NTPP,TPM system in THF ranged from 20% to 66%, regardless of reaction temperature. It is worth pointing out that these are calculated from the concentrations of the TPMK and similar precursor anions and not from the actual concentrations of the NTPP carbanion. Thus it is likely that these low values are apparent only and due to a combination of factors including traces of water present in the very hygroscopic phosphonium salts, to some TPMK decomposition and similar inadvertent loss of anion concentration prior to MMA addition.

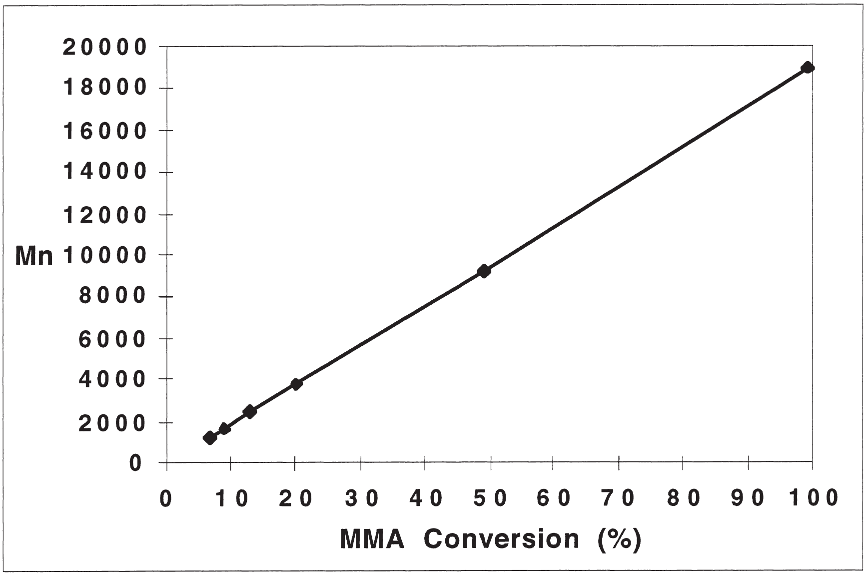


Figure 1. TPM,NTPP initiated polymerization of MMA. Number-average MW as a function of conversion.

The stereochemistry of the polymerizations is similar to that of anionic or radical polymerizations carried out at similar elevated temperatures.[9] Thus a predominantly syndiotactic stereochemistry was found but this does not provide a tool to elucidate the polymerization mechanism although in some cases this method was used to distinguish an ylide mediated polymerization from that in the presence of potassium ion.[6]

The occurrence of a living polymerization at very high monomer concentration (about 4.5M) and at relatively high temperatures is of interest (Table 1). For instance under these conditions for the case of run 12 the polymerization took only 30 minutes for completion and the heat of reaction gave a temperatures that caused the THF to start refluxing. Nevertheless the polymer had a relatively narrow distribution (Table 1). This would seem to indicate potential for industrial applications. The suitability of this NTPP mediated polymerization for the synthesis of PMMA-b-PTBMA block copolymers was demonstrated (Table 1,#12).

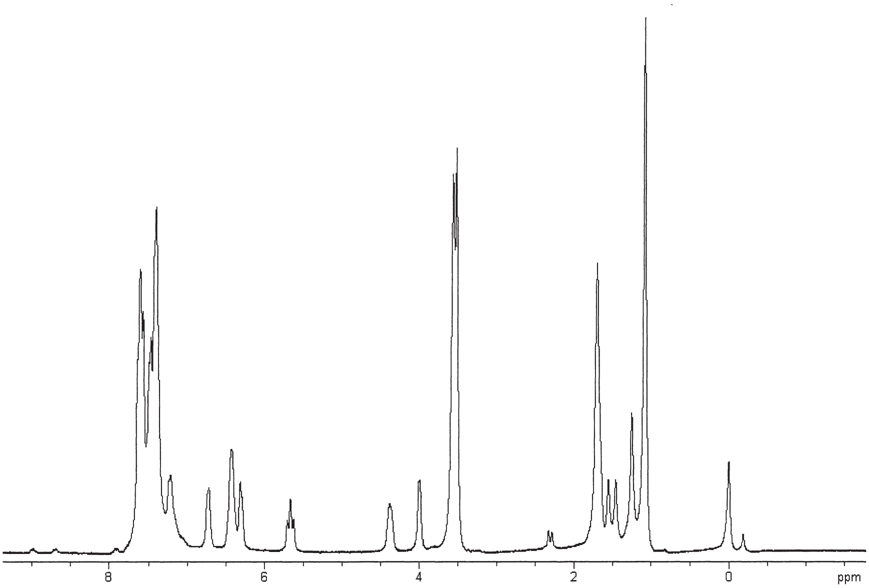
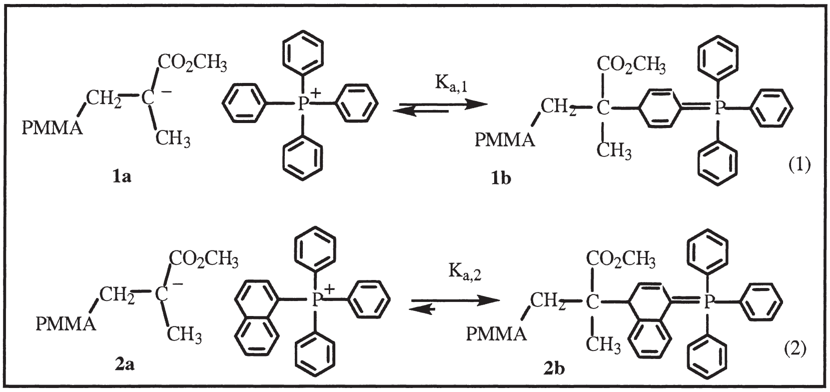


Figure 2. ^{1}H NMR (250 Mhz) spectrum of of MIB, NTPP (ylide 3) in d_8-THF).

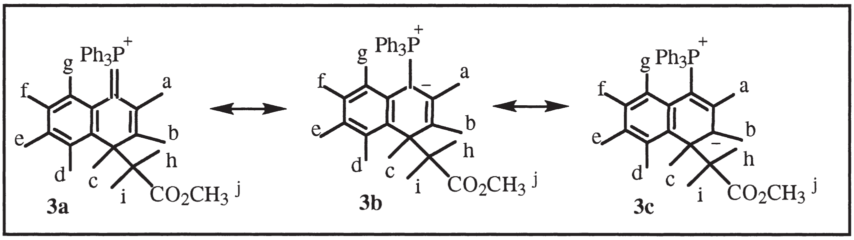
Surprisingly the polymerization of acrylates with the NTTP system were unsuccessful. In fact the MW the distributions and the control of the polymerization was less favorable than obtained with the TPP system where at least there was some indication for potential in the synthesis of PMMA- polybutylacrylate block copolymers.[6]

Characterization. The presence of ylides in the very similar TPP cation mediated MMA polymerization was demonstrated by NMR studies of the TPP MIB derivative that was synthesized by the reaction of the potassium MIB anion with TPP chloride in THF at low temperature and these studies indicated that essentially all of the MIB is in the ylide form.[3,4,6] This ylide is generated by the addition of the MIB anion to one of the four phenyl rings of the TPP cation (Scheme 1).[10]



Scheme 1. Ylide formation by addition of PMMA anion to TPP and NTPP cations.

The ^{1}H NMR of MIB,NTPP (**3**) that was synthesized by reaction of KMIB with NTPPBr in THFd8 displays a spectrum consistent with ylide formation by addition of the MIB anion exclusively to the 1-naphthyl ring of NTPP (Figure 2). As shown in the case of the TPP ylide the upfield shift of the cyclohexadienyl protons is consistent with the presence of the ylide. Thus proton (b) is present at about 4.4 ppm. The upfield shift of this proton is consistent with the expected negative charge on this carbon (Scheme-2). The upfield shifts of protons (e) and (g) are again consistent with the delocalization of negative charge into the aromatic ring as shown in Scheme -2. The upfield shifts of the remaining protons (a), d) and (f) are smaller consistent with Scheme 2.

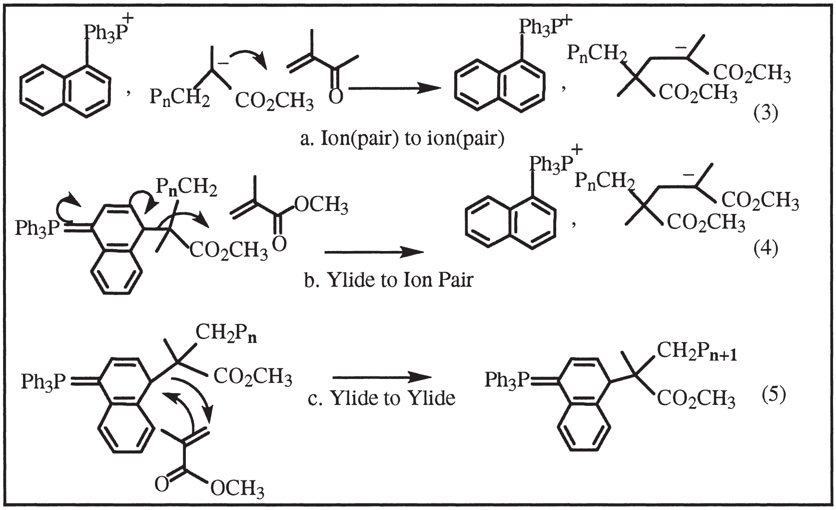


Scheme 2. Resonance structures of ylide, **3**.

Methine proton (c) is observed at about 4.0 ppm. The downfield resonance of this benzylic proton attributable boht to the diamagnetic shielding of the aromatic ring and to the deshielding and electron withdrawing effect of the ester group. Although the methyl groups would be expected to be diastereotopic only a single resonance for protons (i) and (j) is observed. The methoxy protons show a resonance at about 3.6 ppm. The other resonances at 1.3, 1.5 and 2.3 ppm appear to be due to solvent impurities or other sources unrelated to the ylide and but are not consistent with the presence of NTPPBr or of related species such as **2a.**

Although there is no NMR evidence thus far for the existence of the ion pairs **2a** or **1a**, their presence should not be ruled out. First the detection of small quantities of ionic species is difficult to showby NMR. Second, if the interconversion of the ion pairs and ylides is fast on the NMR time scale the direct observation of the ion pairs may only be possible at very low temperatures. This possibility can not be ruled out and is even likely that ions or ion pairs are involved inthe polymerization (see below).

Mechanism of the polymerization. The above and previous results on the ylide mediated polymerizations of MMA appear to be first documented cases of vinyl polymerizations mediated by ylides.[3,4,6] In these cases ylides appear to be the predominant intermediates. A previous report has documented the involvement of an ylide in the initiation step in an otherwise anionic polymerization.[11] It should also be pointed out that in the presence of small amounts of water the mechanism of the TPM,TPP initiated polymerization readily reverts to what was shown to be an anionic mechanism.[6]



Scheme 3. Possible MMA addition steps involving ylides and ion pairs.

The polymerization mechanism is of considerable interest particularly as it relates to that postulated for analogous polymerizations that are anionic or anion related.[1,2] The first question is the nature of the propagating species. It is clear that the predominant species in both the TPP and the NTPP systems is the ylide. In fact no other species could be shown conclusively by NMR to be present in addition to the NTTP ylide. As indicated above, this is not too surprising given the experimental limitations.

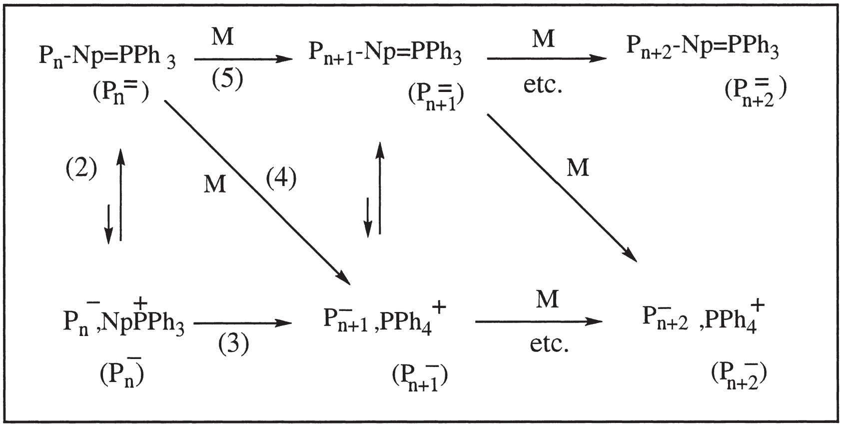
A key question in the mechanism of the polymerization is the nature of the propagating chain. As shown in Scheme-3 the propagation could be carried by ionic species (eqn.3) or by ylides (eqn.5). Another possibility is the addition of ylides to monomer giving ion pairs that could collapse back to ylides or react with monomer (eqn.4) (see below).

In the first (simplified) mechanism an unreactive ylide forms a NTPP ion pair in what could be called a tautomeric equilibrium (Scheme 1, eqn. (1)).[12] This ion pair would be expected to have a very high reactivity compared with the ylide first beacuse it is known that the major species is the ylide and second as the counterion in this case is known to be large. Thus the ion pair and the free ion would be expected to have similar reactivities.[9] If this situation prevails it would have to follow that the interconversion of ion pairs and ylides is fast compared to the polymerization time scale. This requirement is likely to be satisfied for the case of the NTPP ylides as polymerization half lives are on the order of hours. This situation may be different for the case of the TPP ylide where the polymerizations are much faster.

The enormous decrease (factor of 10^4- 10^5) in the value of the apparent polymerization rate constants compared to that of the corresponding TPP ylide-mediated polymerizations clearly reflects the much greater stability of the NTPP ylide. Thus the stability of ylide **2b** like that of its model, ylide **3**, is most likely due to the restoration of full benzene aromaticity in the naphthyl ylides upon addition of the enolate nucleophile to the naphthalene ring (Scheme -1). The TPP ylide **1b**, is expected to be less stable due to the disruption of the benzene aromaticity upon addition of the PMMA anion to the ring. Assuming an equilibrium between the ion pairs (**1a,2a**) and ylides (**1b, 2b**), the association constant $K_{a,2}$ is expected to be greater than $K_{a,1}$.

The less than full benzene aromaticity of the naphthyl rings is consistent with lower heats of hydrogenation and with the greater susceptibility of naphthalene toward nucleophilic attack.[13] As the resonance energies per ring in benzene and naphthalene are 36 and 61 Kcals, the restoration of full aromaticity to one of the two naphthalene rings is estimated as about 6 Kcal.[12] This is expected to add considerable driving force in the formation of the NTPP as opposed the TPP ylide. If the change in entropy is assumed to be the same for reactions (1) and (2) the decrease in free energy of of **2b** of 6 Kcals would increase the value of $K_{a,2}$ relative to $K_{a,1}$by a factor of about 2.10^4. Given equilibria (1) and (2) the concentrations of ionic species would be expected to increase linearly with the inverse of the association constants so that the concentration of **1a** would be expected to be about a factor of about 10^4 larger than that of **2a.** It is interesting that this increase is approximately equal to the increase in reactivity of the TPP relative to the NTPP system and this would seem to support the view that the propagation is carried by dissociated ionic species. The ion pairs because of their very low concentrations under the polymerization conditions are to be dissociated into free ions to a considerable extent. This free ion would be expected to have a reactivity close to, but somewhat greater than that of the ion pair.

The above does not necessarily exclude ylides as the reactive intermediates. However reaction (5) would not appear to be likely. Thus no precedent for such a reaction has been shown. Although an ylide to ylide type polymerization (eqn. 5) is possible this seems unlikely as high level *ab initio* calculations have shown this reaction to be too high in activation energy.[14]



Scheme 4. Possible polymerization mechanisms involving ylides as intermediates.

A more complicated situation would prevail for the cross-over reaction (4) that would lead to ylides and ion pairs that may both be contributing to the polymerization. This possibility should not be dismissed too readily but the corresponding polymerization is expected to be far more complicated. Because of its greater compexity experimental testing of this model would not be simple.

The corresponding mechanisms are summarized in Scheme -4. At this point it seems most likely that ionic species are the dominant if not the sole propagating species. First the ions (ion pairs) are higher in energy than the ylides for both of the ylide systems studied so far and are thus expected to be much more reactive than the ion pairs. Experiments to probe the mechanisms are underway.

Conclusions

The anionic polymerization of MMA in the presence of NTPP cation displays living character and is capable of producing PMMA of narrow polydispersity at temperatures up to 70°C and possibly higher. This polymerization is thought to be mediated through ylide formation between the NTPP cation and PMMA anion, as supported by ^{1}H NMR assignments using the model compound MIB. The PMMA, NTPP ylide stability is thought to be high, as seen by reaction times of hours as opposed to seconds for anionic MMA polymerizations. The NTPP-mediated polymerizations most likely proceed through free or ion paired enolates that are in rapid equilibrium with the predominant ylides.

This well controlled polymerization technique may allow the synthesis of PMMA polymers and block copolymers at elevated temperatures.

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Novel Segmented Copolymers by Combination of Controlled Ionic and Radical Polymerizations

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Summary. Transformation of different living and non-living polymerization mechanisms to controlled/"living" atom transfer radical polymerization (ATRP) in order to prepare block and graft copolymers is described. The synthesis and characterization of macroinitiators and the resulting segmented copolymers is discussed.

Introduction

Block and graft copolymers represent valuable polymeric materials, as their properties can be designed by a proper choice of the monomers that form the polymeric segments. For example, impact resistant materials or thermoplastic elastomers can be obtained when the constituent blocks of the segmented copolymers are thermodynamically incompatible and microphase separation occurs. Also, amphiphilic copolymers with such applications as hydrogels, stabilizers, surface-modifying agents, compatibilizers in polymer blends, etc. have been prepared1,2).

Depending on the monomers involved, the segmented copolymers can be synthesized by employing the same polymerization mechanism for all blocks, or by using a combination of different mechanisms. In the former case the synthesis is accomplished by the appropriate sequential addition of the monomers if block copolymers are targeted. In the latter case, the most often used procedure involves the conversion of the functional end groups of the first block (in the case of block copolymers) or the groups distributed along the chain (in the case of graft copolymers) to initiating sites for the polymerization of the second monomer. This approach is employed when the monomers involved do not polymerize by the same mechanism, examples include conversion of vinyl polymerization to ring opening polymerization, cationic to anionic, condensation to radical polymerization, etc.3,4)

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The controlled/"living" polymerizations allow for the preparation of well-defined polymers, i. e. polymers with predetermined molecular weights and low polydispersities, and they have been extensively used for the preparation of segmented copolymers. Until lately, well-defined segmented copolymers could be obtained only by ionic polymerizations. Due to the lack of control of molecular weight and polydispersity, the free-radical methods led to ill-defined polymers, very often accompanied by a certain amount of homopolymer and/or crosslinked material(3,4). However, recently free-radical techniques have also became available for the preparation of well-defined polymers. The most important types of controlled radical polymerizations (CRP) are: i) stable free-radical polymerization (SFRP), which employs nitroxyl radicals(5); ii) atom transfer radical polymerization (ATRP), which uses complexes of transition metals in conjunction with alkyl halides(5); iii) reversible addition-fragmentation chain transfer polymerization (RAFT), which uses dithioesters together with a free-radical initiator(6) or other degenerative transfer processes(7). So far only SFRP and ATRP have been used to prepare segmented copolymers by combination with other polymerization mechanisms. Table 1 (block copolymers) and Table 2 (graft copolymers) summarize the results published on this subject.

In all the cases presented in Table 1, the block copolymer synthesis consists in at least 2 steps: the macroinitiator synthesis and the polymerization of the second monomer. A particular case is represented by the "one pot" synthesis, when a double-headed initiator is used to simultaneously initiate the formation of both blocks, by two different mechanisms. The method has been used to prepare a polyoxazoline - PSt block copolymer by simultaneous cationic ROP and SFRP(39), and PCL-PSt block copolymers by simultaneous anionic ROP and SFRP or ATRP(40).

In our continuing effort to develop new materials by ATRP, we addressed the field of block and graft copolymers by transformation reactions. The present paper aims to present our work concerning the preparation of segmented copolymers by using controlled/"living" atom transfer radical polymerization in conjunction with another polymerization mechanism, such as anionic, cationic, ROMP, conventional radical or step-growth polymerization. Detailed results are shown in Table 3 (block copolymers) and Table 4 (graft copolymers).

Table 1. Examples of block copolymers prepared by CRP using transformation reactions

Entry	Macroinitiator		Second block		Ref.
	Polymer	Polymn. mechanism	Monomer	Polymn. mechanism	
1	PSt, PBut	anionic	acrylates, St	SFRP	8,9)
2	PEO, PCL, PDMS	anionic ROP	St	SFRP	10-14)
3	PTHF, PCHO	cationic ROP	St	SFRP	15-17)
4	polycarbonate	condensation	St	SFRP	18)
5	PBA, PMMA, PIP	conv. radical	St	SFRP	19)
6	PSt	SFRP	CL	anionic ROP	12)
7	PSt	SFRP	phos + bph, aryleneX$_2$	condensation	18,20)
8	PSt, PEB	anionic	St, 4-acetoxySt MA, BA, MMA	ATRP	21,22)
9	PEO, PCL	anionic ROP	St, MMA, t-BA	ATRP	23-26)
10	PSt, PIb	cationic	St, 4-acetoxySt MA,MMA, IBA	ATRP	27-30)
11	PTHF, PDMS	cationic ROP	St,MA,MMA	ATRP	31,32)
12	PNB, PDCPD	ROMP	St, MA	ATRP	33)
13	PBA, PVDF, PSt, PVAc	conv. radical	St, BA	ATRP	34-36)
14	PMPSil, polyarylene, PSulfone	condensation	St, BA	ATRP	20,37,38)
15	PMMA	ATRP	CL	anionic ROP	12)

PBut - polybutadiene; PSt - polystyrene; PEO - poly(ethylene oxide); PCL - poly(e-caprolactone); PTHF - polytetrahydrofuran; PCHO - poly(cyclohexane oxide); phos - phosgene; bph - bisphenol A; PEB - poly(ethylene-*co*-butylene); PIb - polyisobutylene; PDMS - polydimethylsiloxane; PNB - polynorbornene; PDCPD - polydicyclopentadiene; PVAc - poly(vinyl acetate); PBA - poly(butyl acrylate); PVDF - poly(vinylidene fluoride); PMPSil - poly(methylphenylsilane); PSulfone - polysulfone; PMMA - poly(methyl methacrylate); aryleneX$_2$ - arylene dihalogen; MA - methyl acrylate; IBA - isobornyl acrylate

Table 2. Examples of graft copolymers prepared by CRP using transformation reactions

Entry	Macroinitiator		Second block		Ref.
	Polymer	Polymn. mechanism	Monomer	Polymn. mechanism	
1	PSt	conv. radical	St	SFRP	41)
2	PCL	anionic ROP	MMA	ATRP	42)
3	PIb	cationic	St, IBA	ATRP	43,44)
4	polysiloxane	cationic ROP	St	ATRP	32)
5	PEPDM	coordinative	MMA	ATRP	45)
6	CSPE, PE, PVC	conv. radical	St, MA, BA, MMA	ATRP	46-48)
7	PMPSil	cond.	St	ATRP	49)

PEDM - ethylene-propylene-diene terpolymer; CSPE - chlorosulfonated polyethylene; PE - polyethylene; PVC - poly(vinyl chloride).

Results and discussion

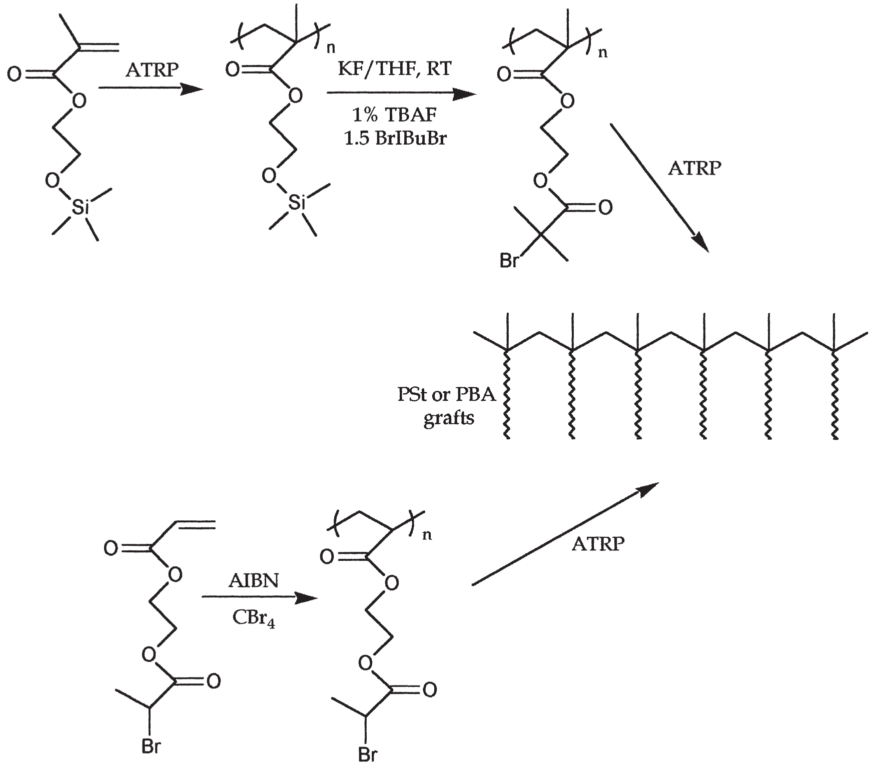
Almost all polymerization mechanisms were combined with ATRP in order to prepare block copolymers. Whenever possible, the first block was prepared in a living manner (Table 3, entries 1-12, 14-17), which allowed a better control of the molecular weights, polydispersities and end functionalities. Thus, “living” anionic polymerization of styrene was terminated with styrene oxide/2-bromoisobutyryl bromide, and after isolation, the polymer was used to initiate ATRP of (meth)acrylates (Table 3, entries 1-3). “Living” cationic polymerizations of styrene and isobutene were also used to prepare ATRP macroinitiators (Table 3, entries 4-9). In the latter case a difunctional polyisobutene terminated with several units of styrene was employed in order to prepare ABA-type block copolymers. In both cases no transformation chemistry was needed because the ATRP initiating sites naturally resulted due to the polymerization characteristics. Mono- (Table 3, entries 10, 11) and difunctional (Table 3, entry 12) PTHF macroinitiators were synthesized by initiating THF polymerization with 2-bromopropionyl bromide/silver triflate or by deactivating a difunctional “living” PTHF with sodium 2-bromopropionate, respectively.

ROMP was also successfully employed to prepare block copolymers in conjunction with ATRP (Table 3, entries 14-17). Polynorbornene and polydicyclopentadiene were synthesized in a "living" manner by using the Schrock catalyst, followed by deactivation with p-(bromomethyl)benzaldehyde to provide a bromobenzyl terminated macroinitiator.

Poly(dimethylsiloxane), commercially available with Si-H end groups and a polysulfone with hydroxy end groups, prepared by the condensation polymerization of bisphenol A and 4,4'-difluorosulfone, were converted to ATRP macroinitiators by reacting the terminal groups with vinylbenzyl chloride in the presence of a Karstedt catalyst or with 2-bromopropionyl bromide, respectively (Table 3, entries13, 19).

Conventional radical polymerization was combined with ATRP in both ways in order to prepare block copolymers. When the first block was prepared by conventional radical polymerization, the macroinitiator resulted directly by using either a thermal initiator containing the ATRP initiating group (Table 3, entry 19) or CCl_4 as a telogen (Table 3, entry 18). The other way involves the preparation of the first block by ATRP initiated by an initiator containing an thermolabile azo group, which can be decomposed later, at a higher temperature, to initiate the polymerization of a second monomer by conventional radical polymerization (Table 3, entry 22). Because of the lack of control in the conventional radical polymerization step, the synthesized block copolymers had higher polydispersities.

Commercially available polymers were used as macroinitiators or precursors in almost all graft copolymer syntheses. Thus, brominated poly(isobutene-co-p-methylstyrene) with 1.2 mole-% bromobenzyl groups (PIb-Br), chlorosulfonated polyethylene with sulfonyl chloride groups as ATRP initiating sites and a statistical copolymer of vinyl chloride with 1 mole-% vinyl chloroacetate (PVCA) have been used as macroinitiators without any further transformation (Table 4). In other cases, transformation reactions were carried out in order to convert the functional groups of the precursor into initiating sites for ATRP. Thus, the vinyl groups of poly(dimethyl-co-vinylmethylsiloxane) (PSilox) were reacted with 2-(4-chloromethylphenyl)ethyldimethylsilane to produce a polymer with pendant benzyl chloride functionalities, which was used to initiate ATRP of styrene (Table 4, entry 3). Similarly, commercially available poly(ethylene-co-glycidyl methacrylate) (PEGM) was converted to a macroinitiator by reacting the epoxy groups with chloroacetic acid in the presence of tetrabutylammonium hydroxide in xylene at 115°C (Table 4, entry 6).



Scheme 1

Acknowledgment

Financial support form the Industrial Members of the ATRP Consortium at CMU is greatly appreciated.

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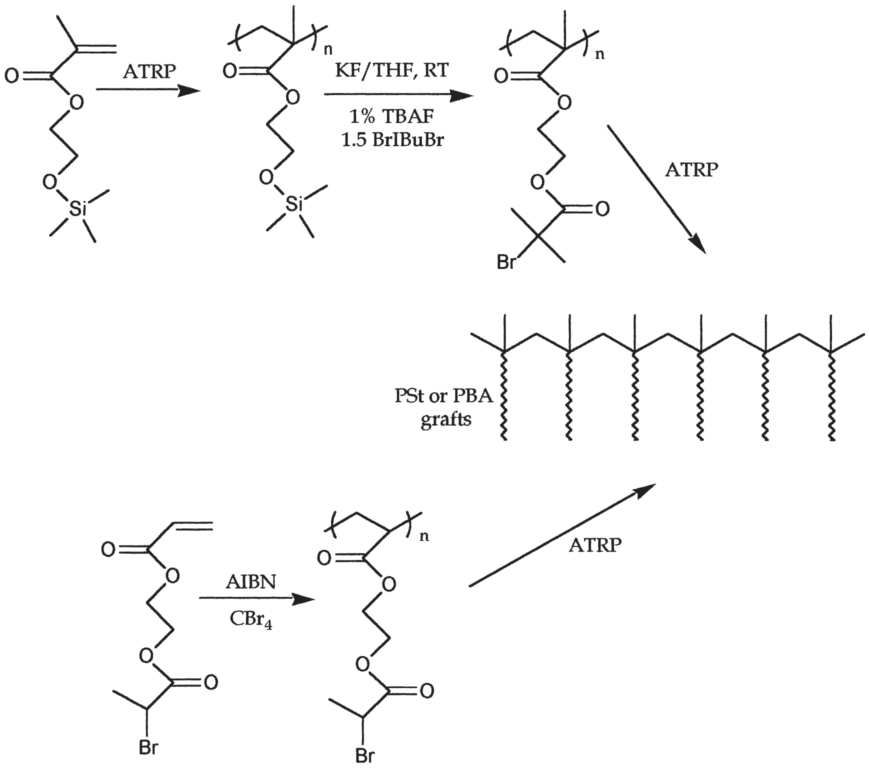
Table 4. Graft copolymers by combining different polymerization mechanisms with ATRP

No	Macroinitiator					Mon.	Graft copolymer				Ref
	Polym	Polymn mech.	M_n (10^{-3})	M_w/ M_n	T_g /°C		Mon. /wt-%	M_n (10^{-3})	M_w/ M_n	T_g /°C	
1	PIb-Br	cationic	108	2.3	-60	St	69	250	2.4	-60/98	43)
2	“	“	“	“	“	IBA	21	181	2.5	-10	“
3	PSilox	CROP	6.6	1.8	-	St	54	14.8	2.1	-	32)
4	CSPE	radical	14.9	2.32	-15	St	-	85.6	1.78	-10/87	46)
5	“	“	“	“	“	MMA	-	26.3	1.75	-2	“
6	PEGM	“	-	-	-15	St	69	-	-	-15/108	48)
7	PVCA	“	47.4	2.66	83	St	80	99.5	3.72	80	47)
8	“	“	“	“	“	MA	50	57.7	2.40	21	“
9	“	“	“	“	“	MMA	60	83.6	4.94	111	“
10	“	“	“	“	“	BA	65	81.4	2.44	-19	“
11	PBPEA	“	27.3	2.3	-	BA	-	1,500	1.5	-	-

A particular case of graft copolymers is represented by densely grafted or “brush” copolymers. They were synthesized using macroinitiators with ATRP initiating sites at each repeating unit along the backbone, prepared either by free radical polymerization of 2-(2-bromopropionoxy)ethyl acrylate (BPEA) (Table 4, entry 11) or by esterification with 2-bromoisobutyryl bromide of well-defined poly(2-trimethylsilyloxyethyl methacrylate), which has already been prepared by ATRP (Scheme 1)50).

Conclusions

Atom transfer radical polymerization (ATRP) has been successfully used in combination with other living and non-living polymerization mechanisms to prepare block and graft copolymers.



Scheme 1

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Macromol. Symp. ***157**, 193–200 (2000)*

Ru(II)-Mediated Living Radical Polymerization: Block and Random Copolymerizations of *N*,*N*-Dimethylacrylamide and Methyl Methacrylate

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SUMMARY: $RuCl_2(PPh_3)_3$ led to living radical copolymerization of *N*,*N*-dimethylacrylamide (DMAA) and methyl methacrylate (MMA) in conjunction with a halide-initiator (R–X; $CHCl_2COPh$, CCl_3Br) and $Al(Oi\text{-}Pr)_3$ in toluene at 80°C. Both the monomers were polymerized at almost the same rate into random copolymers, where the number-average molecular weights (M_n) increased in direct proportion to weight of the obtained polymers, and the molecular weight distributions (MWDs) were narrow throughout the reactions ($M_w/M_n = 1.2–1.6$). MMA was consumed faster in the copolymerization than in the homopolymerization, which was due to the interaction of DMAA with the ruthenium complex. The Ru(II)-based initiating system was also effective in block copolymerization of DMAA and MMA.

Introduction

Extensive efforts have been directed towards developing living polymerizations[1]. Although it is increasingly important to develop such precision processes applicable to polar functional monomers, not many living polymerizations are tolerant to polar groups. One of the most significant features of radical polymerizations is their versatility, as indicated by the wide variety of applicable monomers and their facile copolymerizability, in contrast to ionic counterparts, where polar functional groups often deactivate ionic growing species and the monomer reactivity greatly changes with electronic nature of their substituents.

We have developed living radical polymerizations of methacrylates and styrenes catalyzed by transition metal complexes such as ruthenium[3], iron[4], nickel[5], and rhenium[6] (Eq. 1). These living polymerizations proceed via the metal-assisted reversible activation of carbon–halogen terminals derived from a halide initiator, where the metal center undergoes one-electron redox reaction. A key to these living polymerizations is an equilibrium between the dormant and

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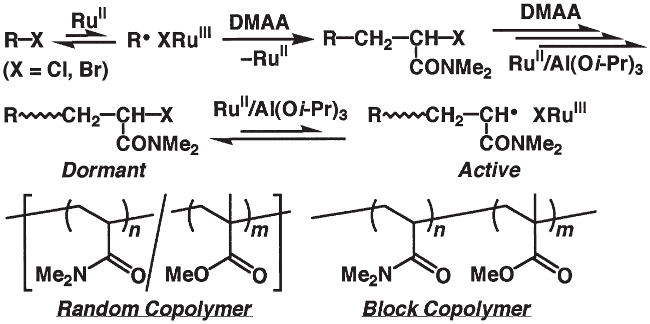
the active species, where the equilibrium is shifted to the former[2f, 2g]. This methodology has proved effective because the growing radical species is kept at low concentrations to diminish bimolecular termination reactions[2], the most serious chain breaking processes in free radical polymerization.



(1)

More recently, we have found that a ruthenium(II)-complex, $\mathrm{RuCl_2(PPh_3)_3}$, induced living radical polymerization of a polar monomer, *N*,*N*-dimethylacrylamide (DMAA), in conjunction with a halide initiator (R–X) and $\mathrm{Al(O}i\mathrm{\text{-}Pr)_3}$ to give polymers of controlled molecular weights and narrow molecular weight distributions (MWDs)[7]. This study deals with the living radical, statistic (or random) copolymerization of DMAA and methyl methacrylate (MMA) with the Ru(II)-based initiating system and the synthesis of their block copolymers by sequential living polymerization.

Living Random Copolymerization of MMA and DMAA

An equimolar mixture of MMA and DMAA was polymerized with $\mathrm{CHCl_2COPh/RuCl_2(PPh_3)_3/Al(O}i\mathrm{\text{-}Pr)_3}$ in toluene at 80°C. As shown in Fig. 1, both monomers were polymerized almost simultaneously. MMA was consumed much faster than in the homopolymerization where it takes over 4 days to reach 90% conversion under the same conditions[8], while such a dramatic acceleration was not seen for DMMA in its homo- and copolymerizations. The fast consumption of MMA is due to some interaction between $\mathrm{RuCl_2(PPh_3)_3}$ and the amide group of DMAA or of the DMAA unit in the polymers, similarly to added amines, which also accelerate the Ru(II)-catalyzed polymerization of MMA[9]. A bromide-initiator, $\mathrm{CCl_3Br}$, also induced random copolymerization of the two monomers in conjunction with $\mathrm{RuCl_2(PPh_3)_3}$ and $\mathrm{Al(O}i\mathrm{\text{-}Pr)_3}$.

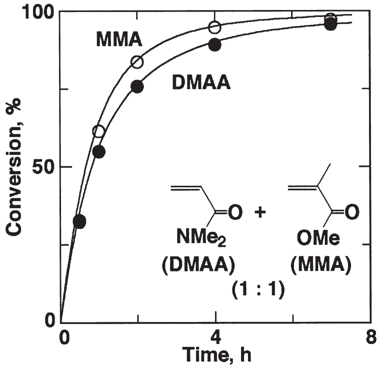


Fig. 1: Polymerization of mixture of DMAA (●) and MMA (O) with $CHCl_2COPh/RuCl_2(PPh_3)_3/Al(Oi\text{-}Pr)_3$ in toluene at 80°C: $[DMAA]_0 = [MMA]_0 = 1.0$ M; $[CHCl_2COPh]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(Oi\text{-}Pr)_3]_0 = 40$ mM.

Fig. 2 plots the number-average molecular weights (M_n) and MWDs of the polymers. Irrespective of the halogens in the initiators, the size-exclusion chromatograph (SEC) curves shifted to higher molecular weights as the reaction proceeds, keeping unimodal and narrow MWDs. With CCl_3Br, the M_n increased with polymer yield and was very close to the calculated value assuming that one molecule of the initiator generates one living polymer chain. The M_n were higher with $CHCl_2COPh$ similarly to the homopolymerization$^{7)}$. These are due to the low reactivity of the C–Cl bonds relative to C–Br, which results in slower initiation as well as slower interconversion between the dormant and the radical species (cf. Eq. 1).

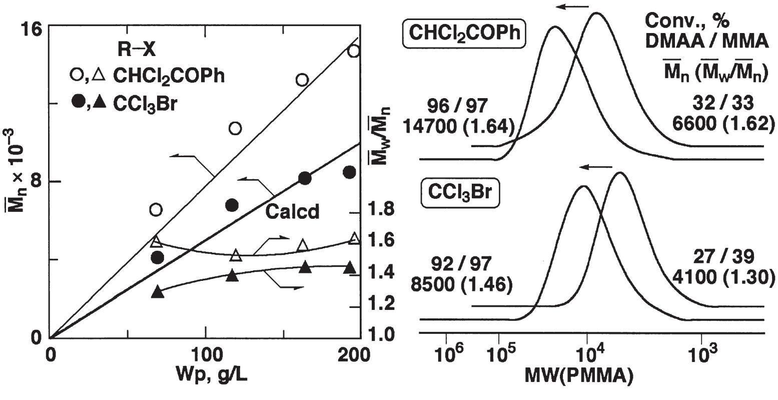


Fig. 2: M_n, M_w/M_n, and SEC curves of copolymers of DMAA and MMA obtained with $R\text{–}X/RuCl_2(PPh_3)_3/Al(Oi\text{-}Pr)_3$ in toluene at 80°C: $[DMAA]_0 = [MMA]_0 = 1.0$ M; $[R\text{–}X]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(Oi\text{-}Pr)_3]_0 = 40$ mM. R–X: (O, △) $CHCl_2COPh$; (●, ▲) CCl_3Br.

Another copolymerization at a feed ratio DMAA/MMA = 1/9 also gave similar results; both monomers were polymerized almost simultaneously to give polymers whose molecular weights increased with conversion (Fig. 3). The MWDs were unimodal throughout the reactions and narrower than those obtained in the copolymerization of the equimolar mixture. This is due to the lower content of DMAA, which results in broader MWDs when polymerized with the Ru(II)-based system.

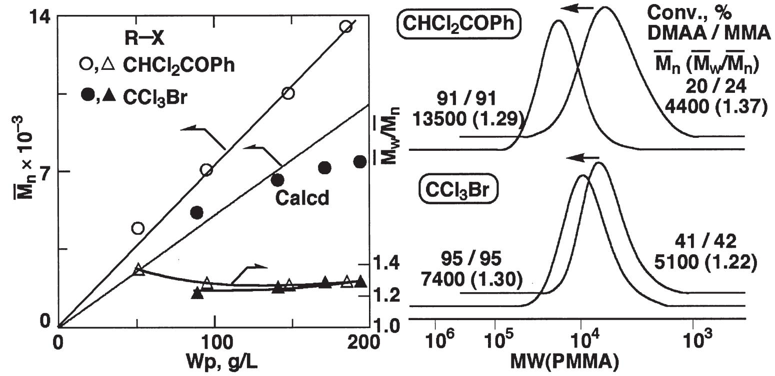


Fig. 3: M_n, M_w/M_n, and SEC curves of copolymers of DMAA and MMA obtained with R–X/ $RuCl_2(PPh_3)_3/Al(Oi\text{-}Pr)_3$ in toluene at 80°C: $[DMAA]_0 = 0.20$ M; $[MMA]_0 = 1.8$ M; $[R\text{–}X]_0 =$ 20 mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(Oi\text{-}Pr)_3]_0 = 40$ mM. R–X: (○, △) $CHCl_2COPh$; (●, ▲) CCl_3Br.

The ^1H NMR spectrum (Fig. 4C) of the products obtained from the equimolar mixture is different from a simple sum of those of homopolymers (Fig. 4A and 4B). The signals (d) of the methyl ester protons of MMA units in Fig. 4C are not single, unlike that of the homopoly(MMA) (Fig. 4B), and the methyl protons of DMAA units (signal a) were broadened in comparison with the homoply(DMAA) (Fig. 4A). Similar changes were also observed for other absorptions. These show that the products are not mixtures of the homopolymers but statistical or random copolymers. This is also the case for the products from the 1/9-mixture of DMAA and MMA (Fig. 4D). The number-average degrees of polymerization (DP_n) of each monomer, calculated from the peak intensity ratios of the main-chain units to the phenyl groups originated from $CHCl_2COPh$, were slightly higher than the calculated values based on the feed ratio and the gas-chromatographic conversions. However, the unit ratios were close to the calculated values.

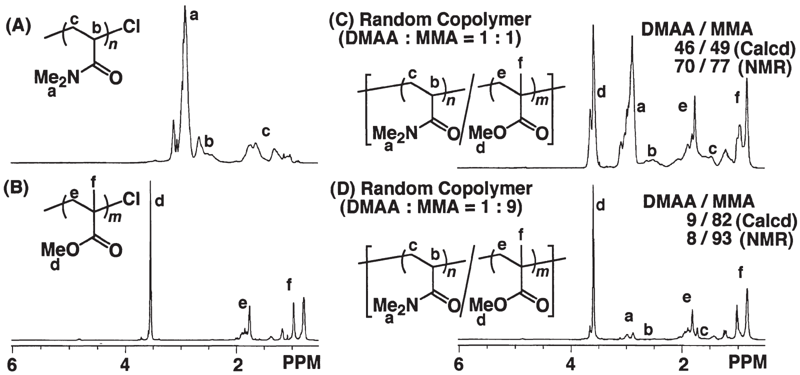


Fig. 4: ^{1}H NMR spectra of poly(DMAA) (A), poly(MMA) (B), copolymers of DMAA and MMA at 1/1 (C) and 1/9 (D) feed ratio obtained with $CHCl_2COPh/RuCl_2(PPh_3)_3/Al(O\textit{i}\text{-}Pr)_3$ in toluene at 80°C.

These results indicate that the $R\text{–}X/RuCl_2(PPh_3)_3/Al(O\textit{i}\text{-}Pr)_3$ initiating system induced living random copolymerization of DMAA and MMA.

Acceleration of Polymerization by DMAA

As described above, the consumption of MMA was much faster than that in the homopolymerization. This indicates a fast cross propagation between the two monomers or due to some interaction of DMAA with the Ru(II)-catalyst, which increases the catalytic activity.

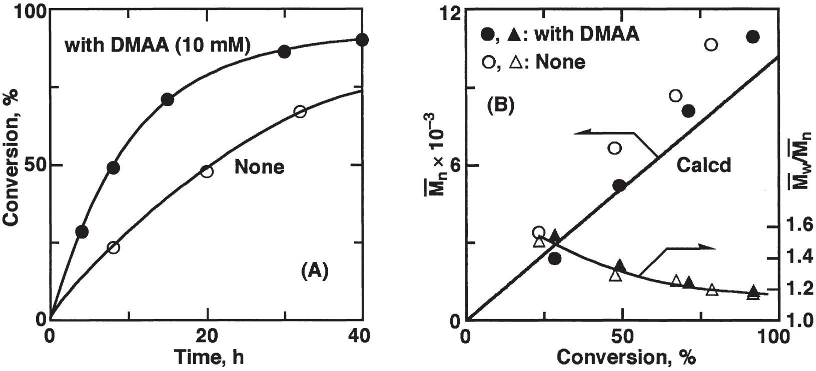


Fig. 5: Polymerization of MMA with $CHCl_2COPh/RuCl_2(PPh_3)_3/Al(O\textit{i}\text{-}Pr)_3$ in toluene at 80°C in the presence (●) and the absence (○) of DMAA: $[MMA]_0 = 2.0$ M; $[CHCl_2COPh]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(O\textit{i}\text{-}Pr)_3]_0 = 40$ mM; $[DMAA]_0 = 10$ mM.

To investigate this, homopolymerization of MMA was carried out in the presence of small amount (10 mM) of DMAA, equimolar to $RuCl_2(PPh_3)_3$ or only 0.5 mol% of MMA. As shown in Fig. 5A, a small amount of DMAA accelerated the MMA polymerization almost 2.5 times. Such a large increase in rate by a small amount of added DMAA indicates that it is mainly due to some interaction between DMAA or the repeat unit in the polymer chain and the Ru(II) complex. Interestingly, a similar acceleration also occurs on addition of nitrogen compounds like butyl amines9). The M_n increased in direct proportion to monomer conversion and agreed well with the calculated, as with that obtained without DMAA (Fig. 5B).

Block Copolymers of MMA and DMAA

We also investigated the synthesis of AB-type block copolymers of MMA and DMAA with the Ru(II)-based initiating system. MMA was thus polymerized with a monofunctional chloride initiator, H–(MMA)$_2$–Cl10), coupled with $RuCl_2(PPh_3)_3$ and Al(O*i*-Pr)$_3$ to give living homopoly(MMA) with M_n = 11000 and M_w/M_n = 1.32, into which was added an equimolar amount of DMAA (Fig. 6). Added DMAA was smoothly polymerized to increase the molecular weights with keeping monomodal MWDs (M_n = 23900, M_w/M_n = 1.80). This shows the formation of block copolymers of MMA and DMAA.

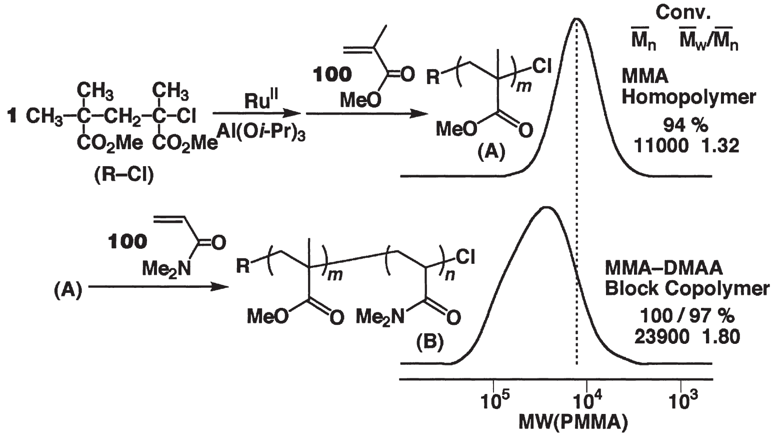


Fig. 6: SEC curves of poly(MMA) (A) and MMA–DMAA block copolymers (B) obtained with **1**/$RuCl_2(PPh_3)_3$/Al(O*i*-Pr)$_3$ in toluene at 80°C: $[MMA]_0$ = 2.0 M; $[\mathbf{1}]_0$ = 20 mM; $[RuCl_2(PPh_3)_3]_0$ = 10 mM; [Al(O*i*-Pr)$_3$]$_0$ = 40 mM; DMAA/MMA = 1/1.

Fig. 7 also supports the formation of block copolymers. As shown in Fig. 7B, the spectrum showed absorptions (d–f) due to DMMA repeat units in addition to those of MMA units. The absorptions of MMA units remain sharp, unlike the spectra of the random copolymers (cf. Fig. 4C). The methyl ester protons adjacent to the PMMA ω-end chloride (a') completely disappeared in Fig. 4D, which suggests that the polymerization of DMAA was initiated from the living PMMA to form AB-type block copolymers. The unit ratio of MMA to DMAA measured by their peak intensity ratios was 0.90 close to that from the calculated value (1.02). The copolymer was soluble in methanol whereas the prepolymer of MMA was insoluble. These results indicate that the R–Cl/$RuCl_2(PPh_3)_3$/Al(O*i*-Pr)$_3$ initiating system is effective in the synthesis of block copolymers of DMAA and MMA.

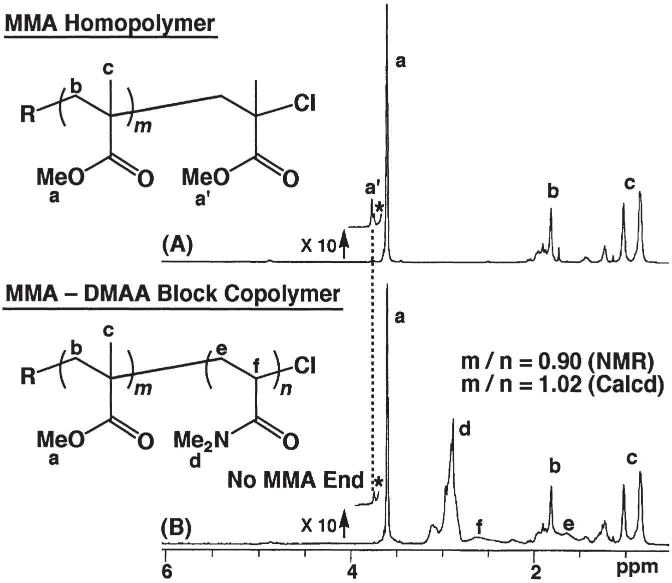


Fig. 7: ^{1}H NMR spectra of poly(MMA) (A) and MMA–DMAA block copolymers (B) obtained with **1**/$RuCl_2(PPh_3)_3$/Al(O*i*-Pr)$_3$ in toluene at 80°C. The lines marked by * are ascribed to satellite lines.

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