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Unimolecular ligand–initiator dual functional systems (ULIS) for low copper ATRP of vinyl monomers including acrylic/methacrylic acids†

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A novel approach for ATRP has been developed which enables the polymerization of vinyl monomers including those bearing carboxylic acid groups such as acrylic/methacrylic acid in the free acid form with ppm amounts of copper. The quantity of copper used in the polymerization is comparable to those left in purified polymers obtained by a conventional ATRP process.

Atom transfer radical polymerization (ATRP)[1] is one of the most robust and powerful controlled polymerization techniques for the preparation of well defined polymeric materials of diverse architectures and functionality.[1] It is a promising technological development which initially suffered from drawbacks like high amounts of metal residue, inability to polymerize polar vinyl monomers bearing free carboxylic acids and non-conjugated vinyl monomers, *etc.* The residual metal content has been dramatically brought down by developments like initiators for continuous activator regeneration (ICAR)[2] and activators generated by electron transfer (ARGET).[3] However, direct homo- or copolymerization of polar vinyl monomers like acrylic or methacrylic acid is not yet possible by ATRP with the exception of sodium methacrylate.[4a] Poisoning of catalyst by acidic vinyl monomers has been proposed as a possible cause of this inability.[4b] However, this proposition has recently been disputed.[5]

In order to address these issues, we recently designed and developed unimolecular ligand–initiator systems (ULIS) whereby the ligand used for complexing the metal and the initiator employed for initiating polymerization are part of the same species (Fig. 1).[6] Through this modification, we visualized that the polymerization may proceed more homogeneously and the active–dormant cycles of the ATRP process may become intramolecular in nature. Also, the energy barrier for the cleavage of the C–X bond leading to the formation of radicals as well as that of the red–ox process involving Cu^I/Cu^{II} transformation can be expected to be different in the case of ULIS as compared to the conventional ATRP process due to its intramolecular nature.

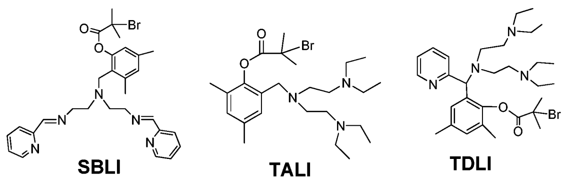

Fig. 1 Different unimolecular ligand–initiator systems (ULIS) synthesized for this study.

Even though, at first look, it appeared that this process could retain all the metal salt employed in the polymerization since the ligand will be preserved as the ω-chain end of the polymer, the possibility of polymerization proceeding homogeneously actually allows the use of metal salt in lower quantities.

(Scheme S1 in ESI† compares the polymerization by conventional ATRP with ULIS promoted ATRP). Unlike the case of ATRP where the metal catalyst remains isolated during active–dormant cycles, in ULIS promoted ATRP, the catalyst is part of the polymer chain during the active–dormant cycles. Even though the complexing agent (*i.e.* ligand) and the initiating moiety have been part of the same species before,[8] it has only been used as an initiator with additional catalyst systems. We have observed that ULIS are capable of polymerizing vinyl monomers using CuBr in quantities which are comparable to the residual metal impurities in purified polymers. The metal impurities in purified polymers obtained by ATRP have been reported to vary from hundreds to thousands of ppm.[9] Also, it is possible to directly homo- and copolymerize free carboxylic acid bearing vinyl monomers using ULIS as reported here. For this work we have synthesized many unimolecular ligand–initiator systems (ULIS),[6] three of which are presented here in Fig. 1, namely, SBLI, TALI and TDLI, with different ligand components by employing various synthetic protocols (see the experimental section in ESI†).

At first, when SBLI was used as the dual functional ligand–initiator for the polymerization of styrene (St) in toluene at 110 °C at a ratio of St : SBLI : CuBr = 250 : 1 : 1 ([CuBr] = 4000 ppm) without any further use of an external ligand, the polymerization (**P1** in Table 1) proceeded *via* normal ATRP with good control and yielded a polymer with narrow polydispersity index (PDI). Surprisingly the use of much lesser amount of CuBr (**P2** in Table 1) where [SBLI] : [CuBr] = 50 : 1 did not disturb the living nature of the polymerization significantly as seen in the kinetics study (see Fig. S1 in ESI†). The molecular weight ($M_{n,GPC}$) of the resultant polymer (characterized by GPC without any purification or precipitation) increased linearly with the conversion of monomers. However, the use of lesser

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Table 1 Polymerization of St and MMA using SBLI and ppm amounts of CuBr

								GPC results[d]	
Polymer code	ULIS system	Monomer[a]	Target DP	[CuBr], ppm	Time/h	Conv.[b] (%)	$M_{n,Theo}$[c]	$M_{n,GPC}$	PDI
P1	SBLI	St	250	4000	2	19.8	5200	8800	1.25
					7	38.3	10 600	16 000	1.28
P2	SBLI	St	250	80	2	17.6	5100	10 500	1.86
					7	34.2	9500	15 900	1.76
					30	82.3	21 400	33 400	1.59
P3	SBLI	St	250	40	2	25.9	7300	16 200	2.02
					7	49.2	13 400	25 400	2.09
					24	88.3	23 600	45 800	1.76
P4	SBLI	MMA	250	0	19	—	—	No polymer	—
P5	SBLI	MMA	250	200	1	41.5	10 900	12 900	1.32
					4	65.2	22 800	27 400	1.30
					6	95.2	24 400	30 400	1.31
P6	SBLI	MMA	250	100	1	27.5	7400	18 300	1.43
					6	81.3	20 900	29 500	1.47
P7	SBLI + EBIB (1 : 4)	MMA	250	100	6	19.8	5500	16 400	1.43
					26	45.4	11 900	18 200	1.54
P8	TALI	MMA	250	100	6	36.9	9700	19 100	1.89
					24	90.3	23 000	30 500	1.83
P9	TDLI	MMA	250	100	2	52.0	13 600	32 800	1.83
					6	90.1	23 100	39 000	1.66
P10[e]	SBLI	MMA	250	75	6	86.5	17 900	34 200	1.49
		St	375	50[f]	24	42.8	34 600	65 300	1.59
P11[g]	TDLI	St + MMA (3 : 1)	187/63	100	2	3.8/14.2	2200	14 900	1.93
					22	57.7/84.7	17 200	21 400	2.03

[a] St was polymerized in a 11 : 42 monomer to toluene ratio at 110 °C and MMA was polymerized in a 11 : 41 monomer to toluene ratio at 100 °C without any external ligand; target DP is equal to monomer to initiator ratio. [b] Calculated from ^{1}H NMR spectra. [c] Including ULIS as the end group. [d] As obtained from the polymerization and without further purification except for polymer **P1** where the polymer was purified by passing through an alumina column. [e] Sequential polymerization of MMA and St to synthesize PMMA-*b*-PS. [f] With respect to total amount of MMA and St. [g] Random copolymerization of St and MMA using monomer mixture.

amount of CuBr under similar polymerization conditions (**P3** in Table 1), although showed living nature and increase in $M_{n,GPC}$ with the conversion, produced polymers of broader PDI.

Indeed we have applied the same methodology for the polymerization of methyl methacrylate (MMA) in toluene at 100 °C (**P4–P6** in Table 1). However, no significant polymerization was observed using SBLI without the use of CuBr, which rules out the possibility of self-dissociation of the ligand–initiator, SBLI (**P4** in Table 1). Use of 200 ppm of CuBr (**P5**) in MMA polymerization showed good control and use of 100 ppm of CuBr (**P6**) yielded reasonably well controlled PMMA with respect to both $M_{n,GPC}$ and PDI. Interestingly, use of SBLI together with the traditional ATRP initiator ethyl α-bromoisobutyrate (EBiB) showed moderate control in the polymerization of MMA (**P7**). Polymerization of MMA using 100 ppm of CuBr in the presence of TALI and TDLI (**P8** and **P9** respectively, in Table 1) produced polymers with relatively higher PDI values. The living nature of the polymerization of vinyl monomers using SBLI and ppm amounts of copper was further confirmed by the synthesis of a diblock copolymer by chain extension reaction (**P10** in Table 1 and Fig. S3 in ESI†).

Most interestingly these unimolecular ligand–initiator systems (ULIS) were able to polymerize acid monomers with <100 ppm of copper. Polymerization of methacrylic acid (MAA) using TALI in toluene yielded polymers *via* dispersion polymerization (**P12** and **P13** in Table 2) reaction. The polymers produced were completely white and were analysed by THF GPC after methylation reaction using (trimethylsilyl)diazomethane (TMSDM)[10] solution in CH_3OH–THF mixture. Polymerization in these cases was uncontrolled and yielded polymers with much higher $M_{n,GPC}$ than expected although the PDI values were moderately low. Solution polymerization of MAA in D_2O (**P14** in Table 2) using TALI showed time dependent increase in $M_{n,GPC}$ with conversion like typical living radical polymerization. However the $M_{n,GPC}$ obtained were much higher than the theoretical values. Polymerization of MAA using TDLI (**P17**) produced a polymer with very high conversion with reasonable control with respect to both molecular weight and PDI value. Methylation of **P17** produced completely white PMMA (**P17m**). Polymerization of acrylic acid (AA) in the presence of TDLI (**P18**) produced a very high molecular weight polymer with a reasonable PDI. Random copolymerization of St and MAA at a 3 : 1 molar ratio in toluene using TDLI was completely homogeneous throughout polymerization and the St-*r*-MAA copolymer produced was collected by precipitating from methanol. Methylation of this copolymer by TMSDM[10] yielded St-*r*-MMA with a St/MMA molar ratio of 1.71 : 1 (obtained from the ^{1}H NMR spectrum of the polymer) which is different from the copolymerization of St and MMA under similar conditions (**P11** in Table 1 where the St/MMA molar ratio in the polymer was 2.67 : 1).

The successful homo- and copolymerization of vinyl monomers bearing a free carboxylic acid group by ULIS is most likely due to their unique structure which results in the formation of stable inner-sphere complexes. From the results presented here, it is clear that catalyst poisoning does not occur. Copper(I) and copper(II) complexes exist in different geometries, namely, four-coordinate tetrahedral and distorted octahedra respectively.[7] Thus during the red–ox transitions of the active–dormant cycles, the ligand cage has to undergo such structural transformation as well. This structural change may be more difficult in the polymerization of

Table 2 Polymerization of methacrylic acid (MAA) and acrylic acid (AA) using TALI or TDLI and ppm amounts of CuBr

								GPC results[d]	
Polymer code	Monomer, ULIS system	Solvent[a,b] (status)	Target DP	Temp./°C	Time/h	Conv.[c] (%)	$M_{n,Theo}$[c]	$M_{n,GPC}$	PDI
P12	MAA, TALI	Toluene (precipitate)	50	110	17	62.0	3600	71 600	1.81
P13	MAA, TALI	Toluene (precipitate)	600	110	17	27.8	17 200	94 200	1.60
P14	MAA, TALI	D_2O (solution)	250	100	1	30.4	8100	37 400	2.42
					2	44.6	11 700	42 800	2.18
					5	72.7	18 700	59 900	3.41
P15	MAA, TDLI	Toluene (solution)	250	70	24	3.7	NA	NA	NA
P16	MAA, TDLI	Methanol (solution)	200	80	30	18.6	NA	NA	NA
P17	MAA, TDLI	D_2O (solution)	250	95	2	84.4	21 700	32 700	1.59
P18	AA, TDLI	D_2O (solution)	250	95	2	60.2	15 600	75 400	1.73
P19[e]	St + MAA (3 : 1), TDLI	Toluene (solution)	187/63	100	2	19.1/38.3	6700	21 400	1.70
					22	67.1/96.2	19 700	29 700	1.95

[a] (M)AA was polymerized in a 1 : 1 monomer to solvent ratio of mentioned solvent except **P15** where a 1 : 1.6 monomer to solvent ratio was used; target DP is equal to monomer to initiator ratio. [b] [CuBr] used were 80–90 ppm (mol mol^{-1}). [c] Calculated from ^{1}H NMR spectra. [d] Of corresponding methylated polymer (*i.e.* P(M)MA). [e] Random copolymerization of St and MAA using monomer mixture.

(M)AA thereby resulting in more of Cu^I species which could shift the equilibrium more towards the active state. This may be the reason for why the polymerization is very fast and not well controlled nevertheless living. It has been reported that polydispersity for a living polymerization exceeds 1.5 when the rate of exchange between the active and dormant species is slow.[11] The contribution of viscosity of the medium too could be one of the reasons for the high PDI observed. The large deviation from theoretical molecular weight could also be due to poor efficiency of ULIS. It is worthwhile to note that the amount of CuBr used is far lower than that of the initiator. This leads to the formation of complexed and uncomplexed initiators which would exhibit different reactivity and hence varying efficiency to initiate polymerization. It has been confirmed by employing ^{14}C-radiolabelled initiators that in a conventional ATRP process continued initiation of new chains occur throughout polymerization and some unreacted initiators are left at the end of the polymerization even after achieving very high conversion of monomers.[12] The end group fidelity of TDLI promoted synthesis of PMAA (**P17**) and its methylated derivatives *i.e.* PMMA (**P17m**) was further confirmed by the presence of aromatic protons corresponding to the ligand portion of TDLI in their ^{1}H NMR spectra (see Fig. S7 in ESI†).

In summary, we have reported a novel approach using unimolecular ligand–initiator systems (ULIS) for the ATRP process which broadens the scope of the existing process by way of homo- and copolymerizing vinyl monomers including acidic monomers like (meth)acrylic acid. The polymerizations were performed using ppm amounts of copper salt. The control on polymerization was dependent on the structure of ULIS and also the solvent used for polymerization. As the polymerization works well in water as well,[6] we believe that this system is highly adaptable for emulsion polymerization in the conventional manner. The ability to make super absorbent polymers is another attractive feature of this modified process.[6]

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