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Cu(0)-mediated living radical polymerisation in dimethyl lactamide (DML); An unusual green solvent with limited environmental impact

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The synthesis of poly-acrylates, methacrylates and styrene derivatives by SET-LRP is reported in a user and environmentally friendly "green" solvent, dimethyl lactamide (DML). The occurrence of a SET-LRP mechanism in DML was demonstrated via UV-Vis spectroscopy measurements following the disproportionation of Cu(I) in the presence of *N*-containing ligands. The synthesis of hydrophobic and hydrophilic poly acrylate and methacrylate (methyl, n-butyl, lauryl, poly(ethylene glycol), 2-hydroxyethyl and 2-(dimethyamino)ethyl derivatives) and styrene was investigated. The controlled behaviour of the polymerisation was observed via kinetic experiments. Finally the possibility to produced well-defined polymers with functional chain-ends was demonstrated with the SET-LRP of poly(ethylene glycol) methyl ether acrylate.

Controlled/living radical polymerisation techniques (CRPs) have promoted the synthesis of many new functional materials allowing for the control of the molecular weight, dispersity, polymer architecture, composition and end group functionality.[1-5] Amongst the different CRP techniques, single electron transfer living radical polymerisation (SET-LRP) has attracted attention as it can retain extremely high chain-end functionality at very high conversion.[2-5] The versatility of this technique has been demonstrated in diverse polar solvents, including DMSO,[2,6] DMF,[7] alcohols,[8-10] water[7,8,11] and even in biological complex media[12] and is shown to be compatible with many functional vinyl monomers, including hydrophilic and hydrophobic acrylates, methacrylates and acrylamides.

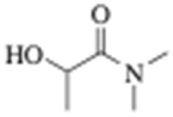

Figure 1: Dimethyl lactamide (DML)

A major drawback of polymerisation in organic solvents is the potential harmful effects of the solvent whereas dimethyl lactamide, Scheme 1, (DML) is considered to be relatively harmless with a similar solvating behaviour to DMSO, NMP and DMF.[13,14] Many environmental criteria need to be considered when developing new formulations. Solvents need to display excellent dissolving power and ideally can be made from plant or animal renewable resources and have low toxicity such as low skin irritation. DML has a high flashpoint and is able to dissolve a wide range of compounds including grease and wax.

Indeed, this solvent is increasingly used in the agrochemical industry and has been demonstrated to have limited ecological impact and no phytotoxic effects. Moreover, studies have shown that DML does not cause skin irritation.[13] All these factors make this solvent promising and user friendly for the wider chemical industry. DML is synthesised commercially via the reaction of lactide and dimethyl amine and is finding application in skin contact applications, agrochemistry and where reduced VOC emissions are desired.[15,16]

In this contribution we report the use of DML as a solvent for the synthesis of functional polymers by SET-LRP. The ability of the solvent to induce disproportionation of Cu(I)Br is investigated by UV-Vis spectroscopy. The synthesis of acrylic, methacrylic and styrenic homopolymers is reported in DML with the hydrophilic/hydrophobic nature of the monomer varied. Moreover, the synthesis of polymers bearing alcohol and amine functionality is demonstrated. Finally, the nature of the initiator is also varied for the synthesis of α-functional polymers.

Disproportionation of Cu(I) in DML

SET-LRP is proposed to involve the reversible activation/deactivation of an alkyl halide terminated polymer

by Cu(0)/Cu(II)X_2 species in the presence of *N*-containing donor ligands. A key requirement of SET-LRP is the instability of the Cu(I) complex towards disproportionation to Cu(II)X_2 and Cu(0). This is facilitated by the thermodynamic instability in polar solvent/coordinating solvents dominated mainly by the favourable crystal stabilisation energy of copper(II) species. The intrinsic instability of the copper(I) complex is determined by the nature of the Cu(I)/*N*-ligand complex in polar solvents and the extent of disproportionation depends heavily of the choice of both ligand and solvent. Thus ligands that stabilise Cu(I) by accepting electron density from, for example π* orbitals (ligand to metal charge transfer, LMCT) such as bipyridine and pyridine imines are usually unsuitable and aliphatic multidentate tertiary amines are usually the ligands of choice.[2]

The stability of the Cu(I)/ligand complexes towards disproportionation in DML was investigated by UV-vis spectroscopy with both Me_6TREN and PMDETA ligands. CuBr and a deoxygenated solution of each ligand in DML (C_{CuBr} = 4.6 x 10^{-3} mol/L) were added to a quartz cuvette under an inert atmosphere. The UV-vis absorption spectrum of the solution was monitored over time (t = 0, 1, 10, 20, 30, 60 minutes). An increase in the absorbance arising from the d-d transition from d^{10} Cu(II) is observed as an evolution of the band at approximately λ = 900 nm for a solutions of CuBr/Me_6TREN and and λ = 680 nm for a solutions of CuBr/PMDETA in DML, Figure 1. In both cases the spectrum of the solution is identical to that from a solution of $CuBr_2$/ligand in DML (black curve in Figure 1a and b). Moreover, the appearance of Cu(0) powder is also observed (Figure S1). These two observations demonstrate the disproportionation of Cu(I)/ligand to into Cu(II)X_2 and Cu(0) in DML solution.

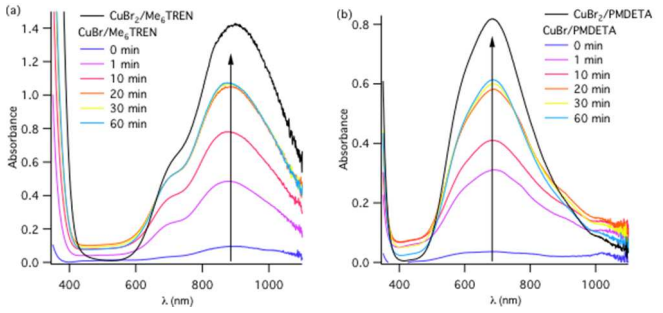

Figure 2: Evolution of the UV-Vis absorption spectra with time of a solution of CuBr/Ligand in DML (a) Me6TREN, (b) PMDETA.

It is noted that these experiments did not allow for the precise determination of the degree of disproportionation, due to the presence of the Cu(0) colloidal particles in the samples resulting in light scattering.[2] However, they do demonstrate that the steady state of the disproportionation equilibrium is reached within 20 min in both cases.

Polymer synthesis by SET-LRP in DML solution

The synthesis of acrylic, methacrylic and styrenic homopolymers was investigated using DML as solvent. In short this involved the pre-disproportionation of Cu(I)Br/Me_6TREN and Cu(I)Br/PMDETA complexes in DML followed by SET-LRP under standard SET LRP conditions, *i.e.* catalysed by a combination of copper(0) wire in the presence of $CuBr_2$ and an aliphatic multidentate ligand.

Polymerisation of acrylic monomers

Polymerisation of both hydrophilic and hydrophobic acrylic monomers was investigated. For hydrophobic monomers the alkyl chain length was varied between methyl and dodecyl/lauryl with three different monomers selected; methyl acrylate (MA), n-butyl acrylate (nBA) and lauryl acrylate (LauA). More hydrophilic monomers poly(ethylene glycol) methyl ether acrylate (PEGA, M_n = 480 g/mol), hydroxyethyl acrylate (HEA) and 2-(dimethylamino)ethyl acrylate (DMAEA) were also investigated. Polymerisations were carried out at 25°C using ethyl bromoisobutyrate (EBiB) as the initiator and a length of 5 cm of copper(0) wire, Table 1. Note: the length of the copper wire is given as this was used to ensure consistency between experiments. The molar ratios of [EBiB]/[$CuBr_2$]/[Ligand]/[Monomer] was fixed at 1/0.05/0.12/50 as previously reported for the polymerisation of MA and nBA in DMSO as solvent.[12,17,18]

Polymerisation of methyl acrylate in DML was carried out giving full monomer conversion to polymer with M_n = 2,250 g/mol and $Đ$ = 1.11 (Entry 1, Table 1). Polymerisation of nBA was held for 8h to give 82% monomer conversion (Entry 2). It is noted that the formation of a biphasic reaction mixture was observed at the end of this reaction, with an upper rich polymer phase and a lower rich DML phase, which contained the catalyst as a green (copper(II)) solution. This behaviour has already been observed for the polymerisation of nBA in DMSO with the polymer layer separating from the solvent leaving the catalyst resides in the solvent (DMSO) with monomer observed in both phases but no detectable polymer in the solvent phase.[17,18] The polymer had a narrow molecular weight distribution ($Đ$= 1.05, M_n = 8,900 g/mol). When the hydrophobicity of the monomer is increased (LauA), a conventional free radical polymerization is observed as in this case the monomer is insoluble and monomer exchange between the two phases is required for controlled polymerisation to take place. Polymerisation of LauA with both Me_6TREN and PMDETA resulted in poorly defined polymers, with dispersity = 5.47 and 3.69 respectively (Entries 3 and 4). This is due to low solubility of the very hydrophobic monomer.[2,8,17]

Table1: SET-LRP of acrylate in DML

Monomer[a]	Ligand	t (h)	conv[b] (%)	M_n[c] (g/mol)	$Đ$[c]
MA	Me_6TREN	16	>99	2,250	1.11
nBA[d]	Me_6TREN	8	81.6	8,900	1.05
LauA[e]	Me_6TREN	4	55.5	6,670	5.47
LauA	PMDETA	5	41.4	61,550	3.69
$PEGA_{480}$[e]	Me_6TREN	4	83.6	7,850	1.17
HEA[f]	Me_6TREN	15	63.2	11,430	1.24
HEA[f]	Me_6TREN	2.25	77.4	4,650	1.29
DMAEA	Me_6TREN	15	79.2	5,900	1.16

[a]Reaction conditions: EBiB/$CuBr_2$/L/M=1/0.05/0.12/50 molar ratio; Cu(0) wire = 5 cm; DML 40 wt%; T = 25°C; [b]Determined by ^{1}H NMR in $CDCl_3$.[c]Molar mass (M_n) and dispersity ($Đ$) was determined by GPC in THF with PMMA standard.[d]Realised with EBiB/nBA=1/90 molar ratio; [e]Realised with EBiB/PEGA=1/25 molar ratio; [f]GPC in DMF with PMMA standard.

Polymerisation of $PEGA_{480}$ was carried out with EBiB/$CuBr_2$/Me_6Tren/PEGA= 1/0.05/0.12/25 molar ratio at 25°C in DML (40 wt%) for 4h. Well-defined PPEGA with M_n = 7,850 g/mol and $Đ$ = 1.17 was achieved at 83.6 % conversion (Entry 5). Polymerisation of HEA was carried out with an EBiB/$CuBr_2$/Me_6Tren/HEA = 1/0.05/0.12/50 molar ratio. Two polymerisations were carried out and the polymerisation time was varied from 15h to 2.25h giving reasonable dispersity with results similar than the SET-LRP of HEA in alcohols and DMSO.[19] The conversion of HEA to polymer stopped at approximately 60-70% and formation of a PHEA gel was observed on the surface of the Cu(0) wire.[19] DMAEA was polymerised with an EBiB/$CuBr_2$/Me_6Tren/DMAEA= 1/0.05/0.12/50 molar ratio at 25°C for 15h giving 79.2% conversion and M_n = 5,900 g/mol ($Đ$ = 1.16).

Kinetic experiments for the polymerisation of nBA in DML were carried out under positive N_2 atmosphere with sampling *via* a cannula so as to minimise quenching of the polymerisation by oxygen, Figure 2(a). With EBiB/$CuBr_2$/Me_6Tren/nBA = 1/0.05/0.12/100 a linear first order behaviour is observed indicating a constant concentration of active species throughout the polymerisation. The molecular weight of the polymer increased linearly with the conversion and the molecular weight distribution became narrower with an increase of the conversion to reach PDI = 1.06 at 78% conversion. The kinetics of the PEGA polymerisation was also investigated giving a linear variation of the ln([M_0]/[M]) with time (Figure 2 (b)).; the molecular weight increased linearly with conversion and the $Đ$ decreases.

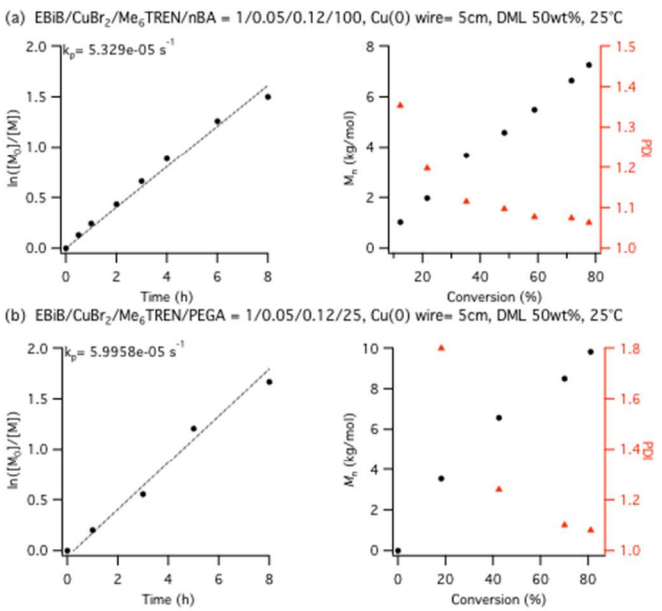

Figure 3: kinetic study of the SET-LRP of nBA (a) and PEGA (b) in DML: ln ([M_0]/[M]) *vs.* time kinetic plot and experimental M_n and PDI *vs* conversion.

Polymerisation of Methacrylic Monomers

Polymerisation of the hydrophobic monomers methyl methacrylate (MMA), n-butyl methacrylate (nBMA) and lauryl methacrylate (LauMA) and hydrophilic monomers poly(ethylene glycol)methyl ether methacrylate (PEGA, M_n = 300 g/mol), hydroxyethyl methacrylate (HEMA) and 2-(dimethylamino)ethyl methacrylate (DMAEMA) was investigated.

Polymerisation of MMA with EBiB/$CuBr_2$/Me_6TREN/MMA = 1/0.05/0.12/50 at 25°C in DML (40 wt%) over 5h resulted in PMMA with M_n = 6,640 g/mol ($Đ$ = 1.22) at 76% conversion (Table 2). The GPC chromatogram revealed a tailing at low molecular weight but with a relatively narrow dispersity (Figure S3). In order to avoid the observed tailing, two factors were investigated: the nature of the ligand and the molar ratio of $CuBr_2$ to alter the activation/deactivation equilibrium towards deactivation in an attempt to decrease the probability of termination and transfer reactions. The effect of the ligand was investigated by replacing Me_6TREN by PMDETA.[20] The polymerisation was carried out with EBiB/$CuBr_2$/PMDETA/MMA = 1/0.05/0.12/50 at 25°C in DML (40 wt%) for 4h to give PMMA with a narrower dispersity, however, changing the ligand had little effect on the product (Table 2, M_n = 7550 g/mol, $Đ$ = 1.20). The amount of $CuBr_2$ was increased from [EBiB]/[$CuBr_2$] = 1/0.05 to 1/0.1 (Table 2) to EBiB/$CuBr_2$/PMDETA/MMA = 1/0.1/0.15/50 leading to a more well defined PMMA with M_n = 7,980 g/mol with narrow distribution ($Đ$ = 1.14). Although a decrease of the $Đ$ is observed with a more deactivating ligand and also when the

Table 2: SET-LRP of methacrylates in DML

Entry[a]	Monomer	EBiB/$CuBr_2$/L/M (molar ratio)	Ligand	t (h)	conv[b] (%)	M_n[c] (g/mol)	$Đ$ [c]
1	MMA	1 / 0.05 / 0.12 / 50	Me_6TREN	5	76	6,920	1.22
2	MMA	1 / 0.05 / 0.12 / 50	PMDETA	4	69	7,550	1.20
3	MMA	1 / 0.1 / 0.15 / 50	PMDETA	4.75	84	7,980	1.14
4	nBMA	1 / 0.05 / 0.12 / 50	Me_6TREN	20	65	8,750	1.15
5	LauMA	1 / 0.1 / 0.15 / 50	PMDETA	5	33	122,000	2.39
6	$PEGMA_{300}$	1 / 0.05 / 0.12 / 25	Me_6TREN	6	74	13,400	1.41
7	$PEGMA_{300}$	1 / 0.1 / 0.15 / 25	Me_6TREN	6	83	11,800	1.35
8	$PEGMA_{300}$	1 / 0.05 / 0.12 / 25	PMDETA	6	87	20,800	1.90
9	$PEGMA_{300}$	1 / 0.1 / 0.15 / 25	PMDETA	6	92	14,000	1.46
10d	HEMA	1 / 0.05 / 0.12 / 50	Me_6TREN	7.5	71	12,800	1.25
11	DMAEMA	1 / 0.05 / 0.12 / 50	Me_6TREN	6	81	9,950	1.24
12	DMAEMA	1 / 0.1 / 0.15 / 50	PMDETA	4.75	87	11,100	1.25

[a]Reaction conditions: Cu(0) wire = 5 cm; DML 40 wt%; T = 25°C.[b]Determined by ^{1}H NMR in $CDCl_3$ or MeOD.[c]Molar mass (M_n) and dispersity ($Đ$) was determined by GPC in THF with PMMA standards.[d]GPC in DMF with PMMA standards.

[$CuBr_2$]/[EBiB] molar ratio is increased, the tailing at low molar masses is still observed in the GPC (Figure S3, MMA).

Polymerisation of nBMA in DML (40 wt%) at 25°C with EBiB/$CuBr_2$/Me_6TREN/nBA = 1/0.05/0.12/50 for 20 h gave PnBMA with M_n = 8,750 g/mol and $Đ$ = 1.15 (conversion = 65 %, Entry 4). Polymerisation of lauryl methacrylate using optimised conditions for MMA: EBiB/$CuBr_2$/PMDETA/MMA = 1/0.1/0.15/50 at 25°C for 5h (Entry 5, Table 2) resulted in a high molecular weight and broad dispersity indicating an uncontrolled polymerisation. It is to be noted that the lauryl methacrylate is insoluble in DML (Figure S4).[17] However, the SET-LRP of PEGMA in DML shows less control with PDIs ranging from 1.35 to 1.90 observed. A possible cause of this is the reduced rate of monomer diffusion which would have the result of reducing the rate of propagation relative to termination which is accentuated with methacrylate relative to acrylate due to the inherent slower rate of chain growth Polymerisation of HEMA with EBiB/$CuBr_2$/Me_6TREN/HEMA = 1/0.05/0.12/50 at 25°C for 7h 30 (Entry 10, Table 2) gave polymer with M_n = 12,800 g/mol and $Đ$ = 1.25.[23] Polymerisation of DMAEMA with EBiB/$CuBr_2$/Me_6TREN/DMAEMA = 1/0.05/0.12/50 and EBiB/$CuBr_2$/PMDETA/DMAEMA = 1/0.1/0.15/50 gave PDMAEMA with reasonable PDIs at high conversion (conv > 80%).

The kinetic experiment for the polymerisation of nBMA in DML at 25°C with EBiB/$CuBr_2$/Me_6TREN/nBA = 1/0.05/0.12/100 in DML (50 wt%) gave a linear increase indicating a control behaviour of the polymerisation (Figure 3). However, an induction period is observed for this polymerisation ($t_{induction}$ = 39 min). The plot of the evolution of the M_n increased linearly with conversion and the dispersity decreased to reach a $Đ$ value = 1.19 at 89% conversion.

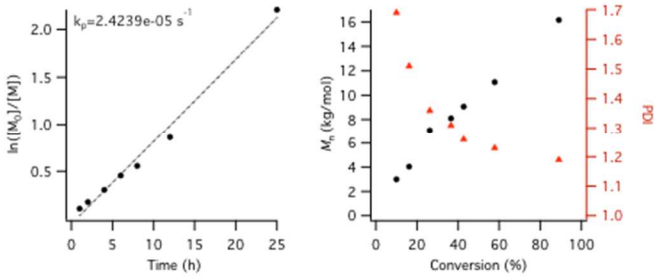

Figure 4: kinetic study of the SET-LRP of nBMA in DML: ln ([M_0]/[M]) *vs.* time kinetic plot and experimental M_n and PDI *vs* conversion.

Polymerisation of Styrene

Styrene has been less studied by SET-LRP.[24,25] The polymerisation of styrene with Fe wire was investigated by Wang et al in DMF.[26] copolymer of styrene and acrylamide was also synthesised with Fe/TMEDA in DML.[27] As styrene has a low activity polymerisation of styrene in DML was investigated with EBiB/$CuBr_2$/Me_6TREN = 1/0.05/0.25 molar ratio. Polymerisations were carried out at 40 and 60°C so as to increase the polymerisation rate. Polymerisation was conducted with [styrene]/ [EBiB] = 200 at 40°C in DML (40 wt%) giving 42% conversion after 41 h with of the M_n = 12,900 g/mol and narrow dispersity ($Đ$ = 1.10; Table 3). Polymerisation at 60°C with [EBiB]/[Sty] = 1/40 for 48 h gave polymer with $Đ$ = 1.13.

Table 3: SET-LRP of styrene in DML

Entry	Sty eq.	T (°C)	t (h)	Conv[b] (%)	M_n[c] (g/mol)	$Đ$[c]
1	200	40	41	42.6	12,900	1.10
2	40	60	48	71.8	3,250	1.13

[a]Reaction conditions: EBiB/$CuBr_2$/Me_6TREN=1/0.05/0.25 molar ratio; Cu(0) wire = 5 cm; DML 40 wt%; [b]Determined by ^{1}H NMR in $CDCl_3$;[c]Molar mass (M_n) and dispersity ($Đ$) was determined by GPC in THF with PS standard.

A kinetic experiment for the polymerisation of styrene with EBiB/$CuBr_2$/Me_6Tren/Sty= 1/0.05/0.25/100 molar ratio in DML (50wt%) at 60°C gave a linear increase of conversion *vs.* time with an apparent rate of polymerisation = 1.59 x 10^{-5} s^{-1}

(Figure 4 (right)). The M_n increased linearly with the conversion and dispersity varying from 1.10 to 1.24 were observed. Inspection of the GPC chromatograms (Figure S7) revealed the appearance of a population at high molar mass when the conversion is > 35% ascribed to termination by radical coupling. The appearance of the high molar mass population is first observed after 6h of polymerisation (36% of conversion). This second population explains the increase of dispersity monitored in figure 4.

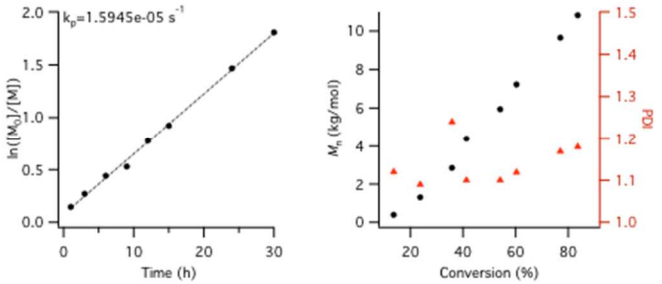

Figure 5 kinetic study of the SET-LRP of styrene in DML: ln ([M_0]/[M]) *vs.* time kinetic plot and experimental M_n and PDI *vs* conversion.

Effect of the Initiator

In addition to the control over molecular weight and molecular weight distribution, CRPs gave access to the control of the chain-end functionality allowing, for example, for the coupling between polymer-polymer[28-30] and polymer-protein[31,32]. Several bromoisobutyrate derivatives were selected to demonstrate that a wide range of functional group can be inserted at the polymer chain-end (Figure S8): ethyl-2-bromoisobutyrate (EBiB), cholesteryl-2-bromoisobutyrate (Chol-BiB), pyrenyl-2-bromisiobutyrate (Py-BiB), *N*-succinimidyl-2-bromoisobutyrate (Succ-BiB), 2-bromo-2-methyl propionic acid 2-(3,5-dioxo-10-oxa-4-azatricyclo[5.2.1.02,6]dec-8-en-4-yl) ethyl ester (Mal-BiB), adamantyl-2-bromoisobutyrate (Adam-BiB) and dihydroxypropyl-2-bromoisobutyrate (diOH-BiB). Polymerisation to PEGA using these initiators with I/$CuBr_2$/Me_6Tren/PEGA= 1/0.05/0.12/25 at 25°C in DML (50 wt%) were carried out (Table 4). Polymerisation times were altered so as to obtain conversion between 60 and 85%. In all cases, PPEGA with narrow molecular weight were obtained ($1.08 < Đ < 1.19$) and the GPC traces showed a shoulder at high molecular weight (Fig S9). Moreover, the coupling reaction seems to be more pronounced when high conversion is attained since the conversion at the end of the polymerisation is respectively 84 and 82 % for the EBIB and Mal-BiB initiators.

Table 4: Variation of initiator for the SET-LRP of PEGA in DML

Initiator[a]	t (h)	conv[b] (%)	M_n[c] (g/mol)	$Đ$[c]
EBiB[d]	4	84	7,850	1.17
Chol-BiB	6	61	8,500	1.17
Py-BiB	18.25	68	8,000	1.08
Succ-BiB	6	73	8,300	1.07
Mal-BiB	7	82	10,400	1.19
Adam-BiB	7	80	9,150	1.09
diOH-BiB	7	73	9,380	1.09

[a]Reaction conditions: Initiator/$CuBr_2$/Me_6TREN/$PEGA_{480}$=1/0.05/0.12/25 molar ratio; Cu(0) wire = 5 cm; DML 50 wt%; T = 25°C; [b]Determined by ^{1}H NMR in $CDCl_3$; [c]Molar mass (M_n) and dispersity ($Đ$) was determined by GPC in THF with PMMA standard. [d] realised with DML (40wt%)

An interesting feature observed for SET-LRP in DML is the possibility to obtain well-defined polymer when the solubility of the initiator in the solvent is limited. Indeed, it was observed that with cholesteryl-2-bromoisobutyrate and adamantyl-2-bromoisobutyrate which are only slightly soluble in DML, a dispersion of the initiator is observed prior to the addition of the Cu(0) wire (Fig S10). This feature is easily macroscopically observed since a transition from a turbid solution to a crystal clear occurs after 10 min of polymerisation in the case of the Chol-BiB initiator and effective polymerisation (Figure S10).

Conclusions

In this contribution, the synthesis of polymer by Cu(0) mediated polymerisation in a new environmentally friendly solvent, dimethyl lactamide, has been investigated. UV-Vis spectroscopy confirms that Cu(I)Br disproportionates in this solvent in presence of either PMDETA or Me_6TREN. The polymerisation of hydrophilic and hydrophobic acrylates and methacrylates was studied and kinetic experiments demonstrated that the SET-LRP in DML leads to well-defined polymers. The polymerisation of methacrylates in DML showed similar to better results than the SET-LRP in DMSO and DMF. Moreover, the synthesis of well-defined polystyrene, with dispersity < 1.3. Finally, it was demonstrated with the SET-LRP of PEGA that various functional initiator may be used for the synthesis of well-defined polymer with functional chain-end. DML is a relatively new solvent with green credentials which has some excellent characteristics making this solvent an excellent alternative where hydrophilic aprotic solvents are required.

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Notes and references

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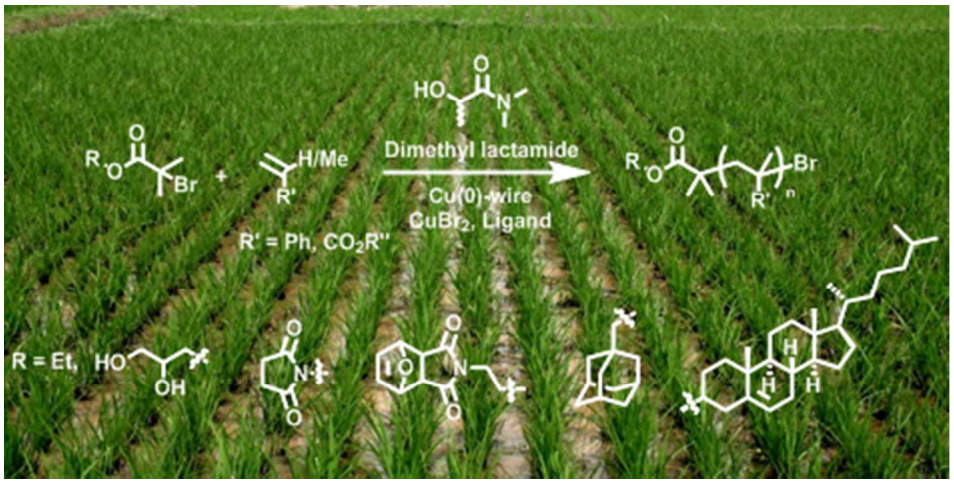

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