330 Macromolecules 2004, 37, 330−335

Copper-Mediated Living Radical Polymerization of 2-Vinyl-4,4-dimethyl-5-oxazolone

David Fournier, Sagrario Pascual, and Laurent Fontaine*

LCOM, Chimie des Polymères, UMR CNRS 6011, UCO2M, Université du Maine, Avenue O. Messiaen, 72089 Le Mans Cedex 9, France

Received July 16, 2003; Revised Manuscript Received November 25, 2003

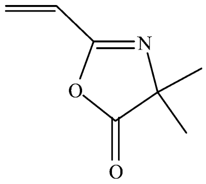
ABSTRACT: The copper-mediated living radical polymerization of 2-vinyl-4,4-dimethyl-5-oxazolone (VDM) was investigated. Ligand nature and concentration were varied in order to reach a controlled radical polymerization of VDM. When linear amines such as *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (PMDETA) in a 1 to 1 ratio relative to CuBr catalyst are used, very low conversions were obtained. This was attributed to an inactivation of catalyst by polymer complexation. An excess of PMDETA relative to CuBr catalyst yields to an increase of monomer conversion. The use of 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4Cyclam) as a cyclic amine ligand provided polymers in high yields in a short time but experimental molecular masses were higher than theoritical ones and polydispersities remained high. This is consistent with the presence of irreversible terminations. However, using Me_6-TREN as ligand led to a successful control of the polymerization: the polymers obtained have molecular mass values close to the theoritical ones and relatively narrow polydispersities. The controlled polymerization of VDM has been extended to statistical and block copolymerizations with styrene and methyl acrylate. Relatively low polydispersities (1.15−1.26) were obtained on statistical copolymers. Well-defined block copolymers were prepared by VDM polymerization from polystyrene and poly(methyl acrylate) starting blocks as well as by styrene and methyl acrylate polymerizations from polyVDM starting blocks.

Introduction

The electrophilic 4,4-dimethyl-5-oxazolone ring have attracted the attention of chemists because of its high reactivity toward nucleophiles such as amino end groups of primary amines, alcohols, thiols, and peptides.[1] The involved ring-opening reaction with a nucleophile connected to a functional molecule (a dye, a chromophore or a photosensitive group) through a suitable spacer allows the synthesis of functionalized side compounds. The main advantage of a such ring-opening addition is that it occurred without byproduct elimination.[2]

The free-radical polymerization of 2-vinyl-4,4-dimethyl-5-oxazolone (VDM−Scheme 1)[3] is of special interest because it is a key intermediate for a large range of novel polymers. Rasmussen et al.[4] have shown that highly cross-linked functional polymeric particles can be obtained by dispersion polymerization of VDM with appropriate comonomers and that the azlactone function can be used for the immobilization of protein A for affinity chromatography. Fréchet et al.[5] reported the preparation of grafted polyVDM macroporous monolithic disks; those disks have been used as scavengers of amines. Recently, we described the grafting of polyVDM onto electron-beam activated polypropylene films and fabrics.[6] Those materials were efficients for the immobilization of sericin, a natural protein issued from silk degumming. In all cases, the preparation of polymers is based entirely on a free-radical polymerization. As VDM is of special interest because of its potential applications, it appeared to be necessary to target VDM-based homo and block copolymers with low polydispersities and predetermined molecular masses. This synthesis will require the application of living radical polymerization techniques. Significant progress has been made in this area in recent years. Several new methologies to provide control over both molecular mass and molecular mass distribution are reported. Works have been published on nitroxide-mediated processes,[7] on reversible addition−fragmentation chain transfer polymerization (RAFT-MADIX)[8] and on transition-metal-mediated living radical polymerization.[9] Tully and coworkers[10] successfully performed a living radical polymerization of VDM and derivatives using nitroxide-mediated polymerization. In addition to narrow molecular mass distributions ($\overline{M}_w/\overline{M}_n < 1.10$), they were able to get accurate molecular masses.

Scheme 1. 2-Vinyl-4,4-dimethyl-5-oxazolone (VDM)



In this study, the copper-mediated living radical polymerization of 2-vinyl-4,4-dimethyl-5-oxazolone (VDM) was investigated. Catalytic systems based on copper halides and ligands such as linear amine, tripodal amine, and cyclic amine were attempted to address the controlled polymerization of VDM.

Experimental Section

Materials. Styrene (Sty, 99%) from Acros, methyl acrylate (MA, 99%) from Aldrich, and 2-vinyl-4,4-dimethyl-5-oxazolone (VDM, 99.4%) from SNPE were distilled under vacuum and were stored at −15 °C after purification. Ethyl 2-bromoisobutyrate (2-EBiB, 98%), methyl-2-bromopropionate (MBP, 97%), methyl-2-chloropropionate (MCP, 97%), copper powder (99%), and 2,2′-bipyridyl (bipy, 99+%) were used as received from

---

* Corresponding author. E-mail: laurent.fontaine@univ-lemans.fr.

10.1021/ma035012u CCC: $27.50

Table 1. Polymerization of VDM with Different Ligands

entry	catalytic system	temp (°C)	time (h)	convn[a] (%)	$\overline{M}_{n,th}$ (g/mol)	$\overline{M}_{n,SEC}$ (g/mol)[a]	$\overline{M}_w/\overline{M}_n$[b]
	2-EBiB:CuBr:bipy						
1	1:1:2	110	7	74.2	3713	*c*	-*c*
	2-EBiB:CuBr:PMDETA						
2	1:1:1	50	6	46.6	2331	2500	1.49
3	1:0.3:0.3	50	6	31.0	1551	1600	1.29
4	1:0.3:0.6	50	19	79.4	3973	5100	1.23
	2-EBiB:CuBr:CuBr$_2$:Me$_4$Cyclam						
5	1:1:0:1	25	0.5	68.9	3448	20 300	1.84
6	1:1:0.1:1	25	0.5	74.1	3707	17 700	1.76
	MCP:CuCl:Me$_6$TREN						
7	1:1:1	25	5	53.0	2760	5900	1.86
	2-EBiB:CuBr:Me$_6$TREN						
8	1:1:1	25	4	59.3	4329	3100	1.36

[a] Calculated by ^{1}H NMR. [b] Measured by SEC (calibrated with polystyrene standards). [c] Multimodal trace obtained by SEC.

Aldrich. 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me$_4$Cyclam, 98%), *N,N,N′,N′,N″*-pentamethylethylenetriamine (PMDETA, 99+%), anisole (99%), toluene (99%), *n*-hexane (95%), and silica gel (60−200 mesh) were purchased from Acros. The ligand Me$_6$Tren was prepared according to a reported procedure.[11] Copper(I) chloride (Acros, 99%) was used as received, and copper(I) bromide (Aldrich, 99.99%) was purified according to the published procedure.[12]

General (Co-) Polymerization Procedure. A Schlenk flask was charged with CuBr or CuCl. The flask was sealed with a rubber septum and was cycled three times between vacuum and nitrogen to remove oxygen. Then, monomer, solvent, and ligand previously degassed were added to the solid components through degassed syringe. The solution was further degassed by three freeze−pump−thaw cycles. The flask was then placed in an oil bath kept at the desired temperature. Once the reaction temperature was reached, the initiator was added under nitrogen ($t = 0$). After certain time intervals, samples were withdrawn from the reaction mixture using a degassed syringe. Samples were dissolved in dichloromethane and were passed through a silica gel column in order to remove copper complex and were precipitated in *n*-hexane. Similar procedure was used to synthesize block copolymers using ω-bromopolystyrene, ω-bromopoly(methyl acrylate), and ω-bromopolyVDM as macroinitiators.

Synthesis of ω-Bromopolystyrene Precursor. In a Schlenk tube, 1.21 mL (5.8 mmol) of PMDETA, 80 mL (0.69 mol) of styrene, and 0.85 mL (5.8 mmol) of ethyl 2-bromoisobutyrate previously degassed were added to another Schlenk tube containing 0.832 g (5.8 mmol) of CuBr through a degassed syringe. The reaction mixture was degassed by three freeze−pump−thaw cycles and back-filled with N$_2$. It was then placed in an oil bath thermostated at 100 °C. After 30 min polymerization time, the reaction mixture was cooled to room temperature, and the contents were dissolved in dichloromethane and passed through a silica gel column in order to remove copper salts. The polymer was precipitated in methanol, filtered and dried under vacuum overnight. Monomer conversion measured by gravimetry was 33.8%. SEC (THF): $\overline{M}_n = 4500$ g mol^{-1}, $\overline{M}_w/\overline{M}_n = 1.13$. Similar procedures were used for the synthesis of ω-bromopoly(methyl acrylate) macroinitiator using MBP as initiator and CuBr/PMDETA as catalytic system at 80 °C in 50 v/v% toluene and for the synthesis of ω-bromopolyVDM macroinitiator using 2-EBiB as initiator and CuBr/Me$_6$TREN as catalytic system at 25 °C in 50 v/v% toluene.

Typical Synthesis of PolyVDM Using CuBr/PMDETA. VDM was polymerized using CuBr as catalyst, PMDETA as ligand, and ethyl 2-bromoisobutyrate as initiator in toluene (50% v/v). Anisole (5% v/v) was used as the internal standard. Typically, previously deoxygenated distilled VDM (4.5 g, 32.4 mmol), deoxygenated PMDETA (190 μL, 0.9 mmol), deoxygenated 2-EBiB (132 μL, 0.9 mmol), and deoxygenated toluene (5 mL) were added through a degassed syringe to a Schlenk tube under nitrogen containing CuBr (129 mg, 0.9 mmol). The solution was degassed by three freeze−pump−thaw cycles before being heated to 50 °C. Samples were removed periodically via a degassed syringe for conversion and size exclusion chromatography analysis.

Measurements. Monomer conversion was determined by ^{1}H NMR. ^{1}H NMR spectra were measured in CDCl$_3$ on a Bruker AC 200 MHz spectrometer. Molecular masses and molecular mass distributions were measured using size exclusion chromatography (SEC) on a system equipped with a SpectraSYSTEM AS1000 autosampler, with a guard column (Polymer Laboratories, PL gel 5 μm Guard, 50 × 7.5 mm) followed by two columns (Polymer Laboratories, 2 PL gel 5 μm MIXED-D columns, 2 × 300 × 7.5 mm), with a SpectraSYSTEM RI-150 detector and a SpectraSYSTEM UV2000 detector. The eluent used was THF at a flow rate of 1 mL min^{-1} at 35 °C. Polystyrene standards [(580−483) × 10^3 g mol^{-1}] were used to calibrate the SEC.

Results and Discussion

Copper-mediated living radical polymerization of VDM as monomer has never been investigated. To successfully understand VDM behavior in such polymerization, the effects of ligand structure and catalyst concentration were studied. Ethyl 2-bromoisobutyrate (2-EBiB) was used as the initiator and CuBr/ligand as the complex of the copper-mediated living radical polymerization of VDM. A preliminary experiment was performed using 2,2′-bipyridine as ligand at 110 °C in toluene. After 7 h polymerization, the conversion of VDM reached 74.2% (entry 1, Table 1) but the polymerization was uncontrolled as a multimodal trace was obtained by SEC. However when PMDETA or Me$_6$TREN was used as the ligand, better control of the polymerization of VDM was observed. This point led us to investigate more deeply those catalytic systems.

Polymerization of VDM Using PMDETA as a Ligand. The linear amine PMDETA is a ligand commonly used in conjunction with CuBr or CuCl to afford relatively good control of acrylates and styrene polymerizations.[13] Linear amines are not expensive, and the copper complexes generated are less colored than those generated with bipyridines or *N*-(*n*-alkyl)-2-pyridylmethanimines. Then, first kinetic studies were performed using PMDETA as ligand. Experiments were carried out in toluene at 50 °C using monomer/initiator ratio of 36/1 and different complex/initiator ratios (entries 2−4, Table 1).

Figure 1 shows that although reactions were initially fast, the monomer conversion was incomplete (31.0% and 46.6%). The limited conversion depends on the complex/initiator ratio. When the ratio equal to 1/1, a conversion of 46.6% is obtained after 6 h polymerization (entry 2, Table 1); the decrease of complex/initiator ratio

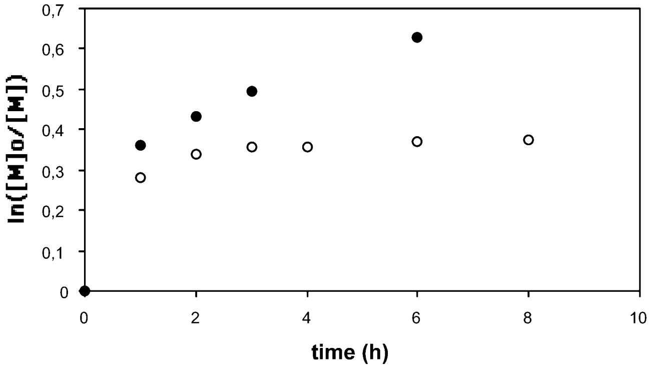


Figure 1. Kinetic plots for the solution polymerization of VDM at 50 °C using PMDETA as ligand and different complex/initiator ratios: (○) $[VDM]_0/[2\text{-}EBiB]_0/[CuBr]_0/[PMDETA]_0 = 36/1/0.3/0.3$ in 50% v/v toluene; (●) $[VDM]_0/[2\text{-}EBiB]_0/[CuBr]_0/[PMDETA]_0 = 36/1/1/1$ in 50% v/v toluene.

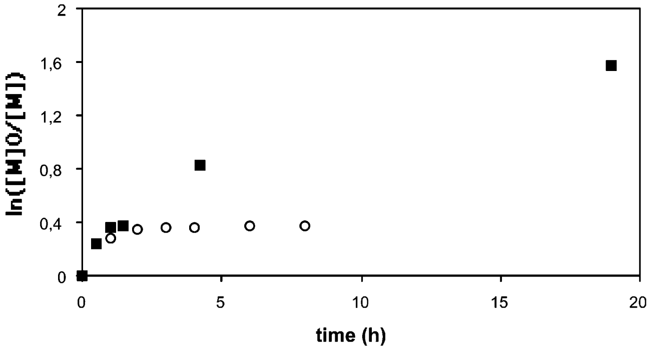


Figure 2. Kinetic plots for the solution polymerization of VDM at 50 °C using PMDETA and different ligand/CuBr ratios: (○) $[VDM]_0/[2\text{-}EBiB]_0/[CuBr]_0/[PMDETA]_0 = 36/1/0.3/0.3$ in 50% v/v toluene; (■) $[VDM]_0/[2\text{-}EBiB]_0/[CuBr]_0/[PMDETA]_0 = 36/1/0.3/0.6$ in 50% v/v toluene.

to 0.3/1 undergoes a decrease of VDM conversion to 31.0% (entry 3, Table 1). Moreover the first-order kinetic plot showed a curvature which indicates the presence of irreversible terminations. This phenomenum could be confirmed by the relatively broad polydispersities ($\overline{M}_w/\overline{M}_n = 1.29-1.49$).

However, the limited conversions cannot be explained by a total deactivation of the growing species as it would have led to much higher experimental molecular masses than calculated ones. Therefore, the curvature of the first-order kinetic plot could be due to an inactivation of terminal end groups of dormant species or to a progressive reduction of the concentration of the available catalyst. This can be explain by an inactivation of catalyst by polymer complexation as is presumably the case with (meth)acrylamides.[14,15] To investigate this point, we carried out two complementary experiments: the first one increasing ligand concentration relative to CuBr concentration (Figure 2) and the second one adding 10 wt % of polyVDM in the copper-mediated radical polymerization of methyl acrylate (MA) (Figure 3).

When a PMDETA/CuBr ratio of 2 to 1 was used, the first-order kinetic plot was linear at the beginning indicating that the concentration of active species is constant for the first step of the polymerization. When the polymerization time increased until 19 h, 79.4% of monomer conversion was reached. The polydispersity index in this case decreased to 1.23 and number-average molecular mass obtained was slightly higher than theoretical one (entry 4, Table 1) but this could be attributed to relative values of $\overline{M}_n$ because calibration was performed with polystyrene standards. This experiment clearly shows that an increase of PMDETA to catalyst CuBr ratio allows a better control of the polymerization.

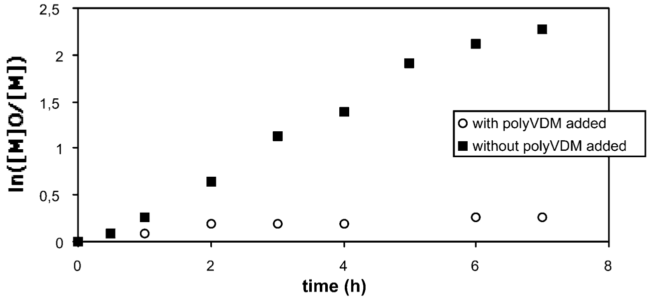


Figure 3. Kinetic plots for the solution polymerization of methyl acrylate (MA) at 80 °C using MBP as initiator and CuBr/PMDETA as catalyst with and without polyVDM added in the system: (■) $[MA]_0/[MBP]_0/[CuBr]_0/[PMDETA]_0 = 200/1/1/1$ in 50% v/v toluene without polyVDM added; (○) $[MA]_0/[MBP]_0/[CuBr]_0/[PMDETA]_0 = 200/1/1/1$ in 50% v/v toluene with 10 wt % polyVDM added.

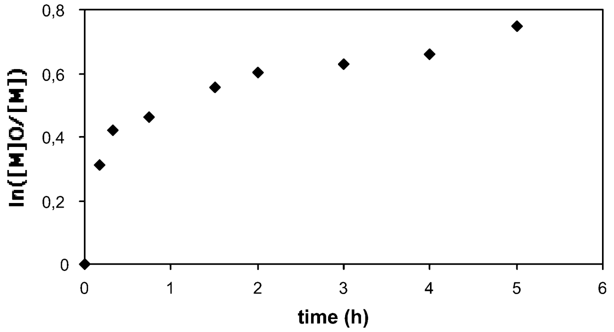


Figure 4. Kinetic plot of copper-mediated living radical polymerization of VDM using $[VDM]_0/[MCP]_0/[CuCl]_0/[Me_6TREN]_0 = 36/1/1/1$ in 50% v/v toluene at 25 °C.

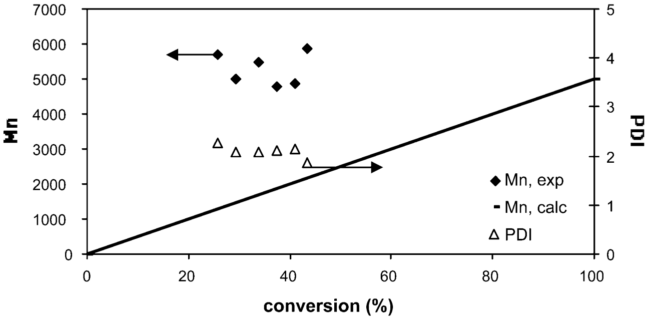


Figure 5. Dependence of $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ (PDI) on monomer conversion for the solution polymerization of VDM using $[VDM]_0/[MCP]_0/[CuCl]_0/[Me_6TREN]_0 = 36/1/1/1$ in 50% v/v toluene at 25 °C.

When 10 wt % of polyVDM ($\overline{M}_n = 20\,600$ g/mol, $\overline{M}_w/\overline{M}_n = 3.11$) prepared by conventional radical polymerization was added to the polymerization mixture of MA using methyl-2-bromopropionate as initiator and 1 equiv of CuBr/PMDETA relative to initiator at 80 °C, a decrease of the polymerization rate (7.7-fold) was observed: 23% conversion were reached after 7 h in the presence of polyVDM instead of 90% conversion without polyVDM (Figure 3). The large local concentration of complexing groups in the polymer limits the conversion of methyl acrylate. It can then be concluded that during polymerization of VDM, the catalyst is deactivated by complexation to the growing polymer, limiting the monomer conversion.

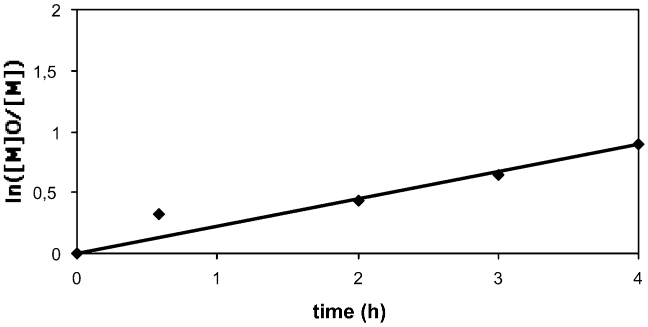


Figure 6. Kinetic plot of copper-mediated living radical polymerization of VDM using $[VDM]_0/[2\text{-EBiB}]_0/[CuBr]_0/[Me_6TREN]_0 = 36/1/1/1$ in 50% v/v toluene at 25 °C (solid line: fit of the data points to a first-order plot).

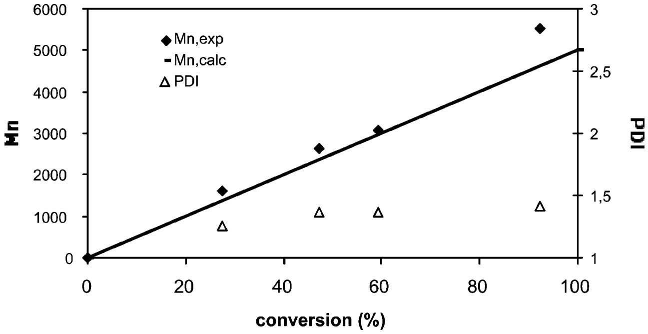


Figure 7. Dependence of $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ (PDI) on monomer conversion for the solution polymerization of VDM using $[VDM]_0/[2\text{-EBiB}]_0/[CuBr]_0/[Me_6TREN]_0 = 36/1/1/1$ in 50% v/v toluene at 25 °C.

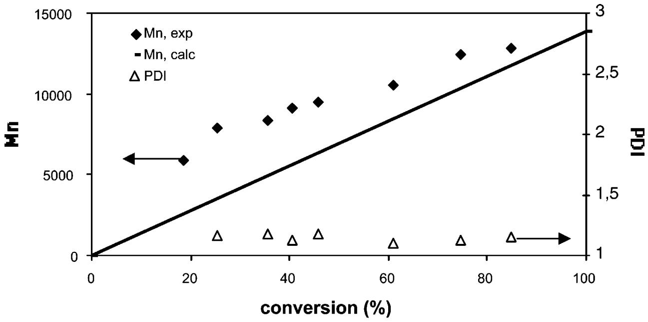


Figure 8. Dependence of $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ (PDI) on monomer conversion for the solution polymerization of VDM using $[VDM]_0/[2\text{-EBiB}]_0/[CuBr]_0/[Me_6TREN]_0 = 100/1/1/1$ in 50% v/v toluene at 25 °C.

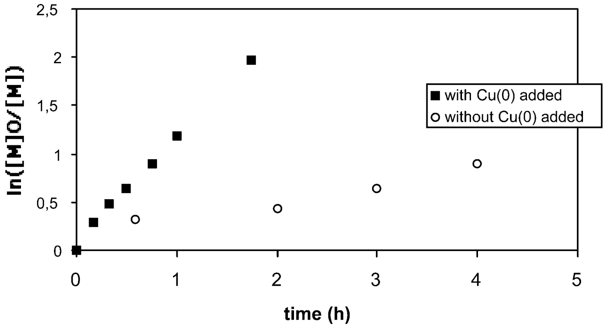


Figure 9. Kinetic plots for the solution polymerization of VDM at 25 °C with and without Cu(0) added. (○) $[VDM]_0/[2\text{-EBiB}]_0/[CuBr]_0/[Me_6TREN]_0 = 36/1/1/1$ in 50% v/v toluene. (■) $[VDM]_0/[2\text{-EBiB}]_0/[CuBr]_0/[Me_6TREN]_0/[Cu(0)]_0 = 36/1/1/1/0.1$ in 50% v/v toluene.

Polymerization of VDM Using Me_4Cyclam as a Ligand. Me_4Cyclam, because of its cyclic structure, has a complexation constant for transition metals higher than those of the open chain ligands,[16] and therefore, the copper complex may not interact as easily with the functional polymer. When polymerization of VDM was carried out using 2-EBiB as the initiator and 1 equiv of CuBr/Me_4Cyclam relative to initiator at 25 °C, the conversion of VDM reached 68.9% within 30 min (entry 5, Table 1). Of course, this fast reaction time is undesirable for living radical polymerization as a low radical concentration toward $Cu^{II}Br_2$ and a fast dynamic equilibrium between active and dormant species have to be maintain in order to minimize spontaneous irreversible terminations. In our case, it appeared that the system reaches a highly active species concentration, molecular mass increases rapidly and significant terminations occur. This is consistent with a slow deactivation of the polyVDM growing species which cannot compete effectively with monomer addition. This phenomenum is confirmed by a broad polydispersity ($\overline{M}_w/\overline{M}_n = 1.84$; entry 5, Table 1) and higher experimental molecular masses than theoretical ones. Using Me_4Cyclam as ligand seems to minimize the complexation of copper with azlactone ring; however, it leads to important irreversible terminations due to a slow deactivation of active species. To improve the control of molecular masses and polydispersities in such polymerizations, addition of a small amount of deactivating agent $CuBr_2$ was used in previous work.[17] In the case of VDM polymerization with Me_4Cyclam-based catalytic system, the addition of 10 mol % $CuBr_2$ with respect to CuBr did not improve the polymerization control. After 30 min of polymerization time, there is still a poor agreement between experimental and theoretical molecular masses and the polydispersity was still high ($\overline{M}_w/\overline{M}_n = 1.76$) for a controlled polymerization (entry 6, Table 1). The catalytic system is not sufficiently dynamic to enable efficient exchange reactions. So far, VDM behavior in copper-mediated living radical polymerization seems similar to acrylamides behavior.[14]

Polymerization of VDM Using Me_6TREN[18] as a Ligand. As well-controlled *N*,*N*-dimethylacrylamide polymerization has been achieved using alkyl chlorides as initiators and copper chloride/Me_6TREN as catalyst,[14] first polymerization on VDM was carried out using the MCP/CuCl/Me_6TREN system in 1/1/1 ratio at room temperature in toluene (entry 7, Table 1). The kinetic plot showed that the conversion increased rapidly at the beginning of the polymerization but leveled off at about 53% after 5 h (Figure 4).

It appears that the molecular mass remained constant when monomer conversion increased, being higher than calculated values (Figure 5). Those points may indicate a too fast initiation accompanied by a partial deactivation of primary radicals by irreversible terminations. This is confirmed by high values of polydispersity indexes. As well, it seems that C−X bond at the chain end of covalent species cannot be easily activated by the catalyst which led to a high concentration of dormant species in the medium.

To improve the activation of dormant species, alkyl bromides and copper bromide rather than chlorides should be used. The $\ln([M]_0/[M])$ vs time plot (Figure 6) of the polymerization of VDM catalyzed with CuBr/Me_6TREN using 2-EBiB as an initiator is linear, indicating a constant concentration in active species.

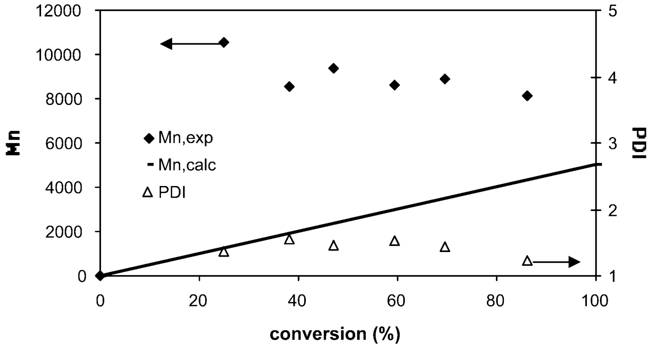


Figure 10. Dependence of $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ (PDI) on monomer conversion for the solution polymerization of VDM at 25 °C in the presence of Cu(0) added. $[VDM]_0/[2\text{-}EBiB]_0/[CuBr]_0/[Me_6TREN]_0/[Cu(0)]_0 = 36/1/1/1/0.1$ in 50% v/v toluene.

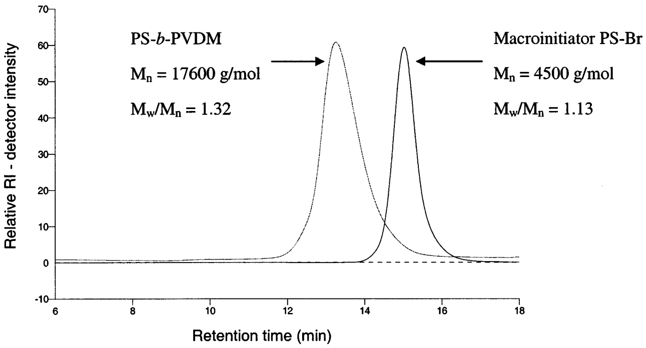


Figure 11. SEC traces of block copolymer PS-*b*-PVDM and macroinitiator PS−Br. $[VDM]_0/[PS{-}Br]_0/[CuBr]_0/[PMDETA]_0 = 144/1/1/1$ in 75% v/v toluene at 90 °C.

Table 2. Synthesis of Statistical Copolymer Poly(VDM-*stat*-styrene) at 25 °C[a]

entry	time (h)	VDM/styrene molar composition[b]	$\overline{M}_{n,SEC}$ (g/mol)[c]	$\overline{M}_w/\overline{M}_n$[c]
1	4	5.98/11.28	8100	1.15
2	25	11.68/21.76	13 100	1.26

[a] Polymerization conditions: $[styrene]_0/[VDM]_0/[2\text{-}EBiB]_0/[CuBr]_0/[Me_6TREN]_0 = 80/20/1/1/1$ in 50% v/v toluene. [b] Calculated by ^1H NMR. [c] Measured by SEC (calibrated with polystyrene standards).

Figure 7 shows that the molecular masses of the resulting polyVDM increased linearly with conversion and the overall polydispersities remained low throughout the polymerization (entry 8, Table 1). These results indicate that the rate of equilibration between the active species and dormant species is fast and that termination and other side reactions are insignificant. When higher molecular masses are targeted and therefore VDM/initiator ratio increased from 36/1 to 100/1, good control over molecular masses is obtained as illustrated by both a linear relationship between theoretical and experimental molecular masses and polydispersities consistently under 1.20 (Figure 8).

Previous reports have shown that the addition of a small amont of Cu(0) to copper-mediated living radical polymerization systems lead to significant rate enhancements,[19] and this was also observed in the case of VDM polymerization investigated here. When a small amount of copper powder was added to the polymerization of VDM using CuBr/Me_6TREN as the catalytic system, an increase of the polymerization rate was observed (Figure 9). The zerovalent copper reacts with copper(II) in order to regenerate copper(I) in the system. Decreasing the amount of copper(II) enhanced the polymerization rate, as this one is inversely proportional to Cu(II) concentration.[17] However in our system, experimental number-average molecular masses were higher than theoretical ones (Figure 10). This may be due to a low concentration of deactivator at the beginning of the reaction, necessary for the control of the polymerization.

VDM-Based Statistical Copolymers. VDM was copolymerized with styrene using CuBr/Me_6TREN (1/1 molar ratio) as catalytic system at 25 °C. After 4 h polymerization time, a copolymer poly(VDM-*stat*-styrene) was obtained with a narrow polydispersity ($\overline{M}_w/\overline{M}_n = 1.15$). Molecular masses increased with conversion and monomodal peaks are obtained by SEC (Table 2).

VDM-Based Block Copolymers. Block copolymers were synthesized by different procedures. In the first one, a well-defined ω-bromopolystyrene was preliminary synthesized. 2-EBiB was used as the initiator for the polymerization of styrene which was performed in bulk at 100 °C with the CuBr/PMDETA (1/1) system. The calculated number-average molecular mass obtained after 33.8% of conversion ($\overline{M}_{n,th} = 4200$ g mol^{-1}) and experimental number-average molecular mass ($\overline{M}_{n,SEC} = 4500$ g mol^{-1}) are in good agreement, and the polydispersity index ($\overline{M}_w/\overline{M}_n = 1.13$) is narrow. This ω-bromopolystyrene was purified and used as the macroinitiator for the polymerization of VDM with CuBr/Me_6TREN (1/1) system at 25 °C. The resulting block copolymer poly(styrene-*b*-VDM) was obtained with 38.9% conversion of VDM after 2 h. The experimental number-average molecular mass ($\overline{M}_{n,SEC} = 17\,600$ g mol^{-1}) is slightly higher than theoretical ones ($\overline{M}_{n,th} = 12\,300$ g mol^{-1}). The SEC trace shows a monomodal curve with no detectable quantities of unreacted macroinitiator indicating that the polymerization of the second block was initiated quantitatively (Figure 11). The polydispersity index of the final block copolymer increased, indicating a slightly broad distribution of the polyVDM block.

In the second procedure, a well-defined ω-bromopoly(methyl acrylate) was preliminary synthesized, purified and used as macroinitiator for the polymerization of VDM using CuBr/Me_6TREN (1/1) as catalytic system at 25 °C in 66 v/v% toluene. For the synthesis of the ω-bromopoly(methyl acrylate) precursor, MBP was used as initiator and CuBr/PMDETA (1/1) as catalytic system at 80 °C. The calculated number-average molecular mass obtained after 14.5% of conversion ($\overline{M}_{n,th} = 2520$ g mol^{-1}) and experimental number-average molecular mass ($\overline{M}_{n,SEC} = 2700$ g mol^{-1}) are in good agreement and the polydispersity index ($\overline{M}_w/\overline{M}_n = 1.19$) is narrow. After polymerization, the resulting block copolymer poly(MA-*b*-VDM) was obtained with 65.4% conversion of VDM after 14 h (entry 3, Table 3). The experimental number-average molecular mass ($\overline{M}_{n,SEC} = 29\,000$ g mol^{-1}) is higher than theoretical ones ($\overline{M}_{n,th} = 19\,932$ g mol^{-1}). The polydispersity index of the final block copolymer increased ($\overline{M}_w/\overline{M}_n = 1.54$) indicating a slightly broad distribution of the polyVDM block as obtained with poly(styrene-*b*-VDM) block copolymer.

The last procedure used to prepare block copolymers consists of chain extension from PVDM-Br with styrene and methyl acrylate. A block copolymer poly(VDM-*b*-styrene) was obtained using CuBr/Me_6TREN = 1/1

Table 3. Synthesis of PolyVDM-Based Block Copolymers

entry	$[M]_0/[MI]_0/[CuBr]_0/$ $[Me_6TREN]_0$	temp (°C)	time (h)	convn (%)	$\overline{M}_{n,SEC}$[a] (g/mol)	$\overline{M}_w/\overline{M}_n$[a]
1[b]	240/1/1/1	100	16	45	29 800	1.59
2[c]	276/1/1/1	80	18	55.6	19 100	1.51
3[d]	200/1/1/1	25	14	65.4	29 000	1.54

[a] SEC calibrated with polystyrene standards. [b] M = styrene; MI = PVDM-Br with $\overline{M}_{n,SEC}$ = 2900 g mol^{-1}, $\overline{M}_w/\overline{M}_n$ = 1.23 [c] M = methyl acrylate; MI = PVDM-Br with $\overline{M}_{n,SEC}$ = 2900 g mol^{-1}, $\overline{M}_w/\overline{M}_n$ = 1.23 [d] M = VDM; MI = PMA-Br with $\overline{M}_{n,SEC}$= 2700 g mol^{-1}, $\overline{M}_w/\overline{M}_n$ = 1.19

molar ratio as catalytic system and PVDM-Br ($\overline{M}_{n,SEC}$ = 2900 g mol^{-1}, $\overline{M}_w/\overline{M}_n$ = 1.23) as macroinitiator for the polymerization of styrene at 100 °C. The resulting copolymer showed a monomodal molecular mass distribution ($\overline{M}_{n,th}$ = 12 555 g mol^{-1}, $\overline{M}_{n,SEC}$ = 29 800 g mol^{-1}), and polydispersity was equal to 1.59 (entry 1, Table 3). When the same macroinitiator was used for the polymerization of MA using CuBr/Me$_6$TREN at 80 °C, a well-defined diblock copolymer was obtained (entry 2, Table 3). Experimental molecular mass ($\overline{M}_{n,SEC}$ = 19 100 g mol^{-1}) of the resulting poly(VDM-*b*-MA) block copolymer was close to the theoretical one ($\overline{M}_{n,th}$ = 14 800 g mol^{-1}) and the polydispersity value was 1.51. As Tully et al.[10] did not succeed in the preparation of such block copolymers poly(VDM-*b*-MA) using nitroxide-mediated living radical polymerization, it is obvious that copper-mediated radical polymerization provides a highly efficient method for the synthesis of well-defined poly(vinyl oxazolones)-based copolymer architectures. The preparation of new (co)polymers obtained by nucleophilic ring-opening of the pendant oxazolone rings with amines is under investigation and will be reported in due course.

Conclusions

In conclusion, copper-mediated living radical polymerization of VDM has been successfully carried out at ambient temperature using CuBr/Me$_6$TREN as the catalyst. The polymers obtained have molecular mass values close to the theoretical ones and relatively narrow polydispersities are obtained. When a linear amine such as PMDETA is used as ligand, inactivation of the catalyst by polymer complexation leads to limited conversions. When a cyclic amine such as Me$_4$Cyclam is used, a high level of irreversible terminations occurs, limiting the dynamic equilibrium (necessary for the control of the polymerization) between active and dormant species. Furthermore, the synthesis of well-defined VDM-based statistical and block copolymers can be readily achieved using copper-mediated living radical polymerization. This work put forward a novel synthetic approach for oxazolone-based polymers and copolymers.

Acknowledgment. The authors would like to thank G. Sennyey and J. P. Senet (ISOCHEM−SNPE) for a generous gift of 2-vinyl-4,4-dimethyl-5-oxazolone.

References and Notes

(1) (a) Taylor, L. D.; Platt, T. E. *J. Polym. Sci., Polym. Lett. Ed.* **1969**, *7*, 597. (b) Rasmussen, J. K.; Heilmann, S. M.; Palensky, F. J.; Smith, H. K.; Melancon K. C. *Makromol. Chem. Rapid Commun.* **1984**, *5*, 67−76.

(2) (a) Taylor, L. D.; Kolesinski, H. S.; Metha, A. C.; Locatell, L.; PLarson, P. S. *Makromol. Chem. Rapid Commun.* **1982**, *3*, 779. (b) Rasmussen, J. K.; Heilmann, S. M.; Krepski, L. R. *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N., Overberger, C. G., Menges, G., Eds.; Wiley-Interscience: New York, 1988, Vol. 11, p 558. (c) Rasmussen, J. K.; Heilmann, S. M.; Krepski, L. R.; Jensen, K. M.; Mickelson, J.; Johnson, K. Z.; Coleman, P. L.; Milbrath, D. S.; Walker, M. M. *React. Polym.* **1991/92**, *16*, 199.

(3) Guichard, B.; Noël, C.; Reyx, D.; Thomas, M.; Chevalier, S.; Senet, J.-P. *Macromol. Chem. Phys.* **1998**, *199*, 1657−1674.

(4) Drtina, G. J.; Heilmann, S. M.; Moren, D. M.; Rasmussen, J. K.; Krepski, L. R.; Smith, H. K., II; Pranis, R. A.; Turek, T. C. *Macromolecules* **1996**, *29*, 4486-4489.

(5) Tripp, J.-A.; Stein, J. A.; Svec, F.; Fréchet, J. M. J. *Org. Lett.* **2000**, *2*, 195−198.

(6) Fontaine, L.; Lemêle, T.; Brosse, J.-C.; Sennyey, G.; Senet, J.-P.; Wattiez, D. *Macromol. Chem. Phys.* **2002**, *203*, 1377−1384.

(7) (a) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Trends Polym. Sci.* **1994**, *2*, 66. (b) Hart, E. *Chem. Rev.* **2001**, *101*, 3661−3688.

(8) (a) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559−5562. (b) Destarac, M.; Bzducha, W.; Taton, D.; Gauthier-Gillaizeau, I.; Zard, S. Z. *Macromol. Rapid Commun.* **2002**, *23*, 1049−1054.

(9) (a) Matyjaszewski, K. *Controlled Radical Polymerization*; ACS Symposium Series 685; American Chemical Society: Washington, DC, 1998; pp 258−360. (b) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921−2990. (c) Coessens, V.; Pintauer, T.; Matyjaszewski, K. *Prog. Polym. Sci.* **2001**, *26*, 337−377.

(10) Tully, D. C.; Roberts, M. J.; Geierstanger, B. H.; Grubbs, R. B. *Macromolecules* **2003**, *36*, 4302−4308.

(11) Ciampolini, M.; Nardi, N. *Inorg. Chem.* **1966**, *5*, 41−44.

(12) Keller, R. N.; Wycoff, H. D. *Inorg. Synth.* **1946**, *2*, 1−4.

(13) Xia, J.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 7697−7700.

(14) Teodorescu, M.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 4826−4831.

(15) Since the polymerization reactions were conducted under anhydrous conditions, the presence of acid/amid side-chain resulting from a partial hydrolysis, and acting as bidentate ligand, was ruled off.

(16) Constable, E. C. In *Metals and Ligand Reactivity*; Ellis Harwood Ltd.: Chichester, U.K., 1990; p 150.

(17) Patten, T. E.; Matyjaszewski, K. *Adv. Mater.* **1998**, *10*, 901−915.

(18) Queffelec, J.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* **2000**, *33*, 8629−8639.

(19) Matyjaszewski, K.; Coca, S.; Gaynor, S. G.; Wei, M.; Woodworth, B. E. *Macromolecules* **1997**, *30*, 7348−7350.

MA035012U