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Using of Novel Halides in the ATRP Polymerization. Estimation of Polymer Molecular Mass

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Summary: Two novel ATRP initiator (R-X): 2-bromo-2-methyl-*N*-(1-phenyl-ethyl) propanamide (**I**) and 2,2,2-trichloro-*N*-(1-phenylethyl)acetamide (**II**) were synthesized and characterized by ^{1}H-NMR, IR, EI. Also, crystal structures of (**I**) and (**II**) are reported. Compounds (**I**) and (**II**) were used in the ATRP reaction of methyl methacrylate (MMA) and acrylamide (AAD) at 48°C, using CuBr/Me_6TREN and ethanol/toluene (60:40) mixture as catalytic complex and solvent, respectively. End-group analysis by ^{1}H-NMR was used to determinate the molecular mass of the polymers synthesized via ATRP. The M_n values for poly(MMA) using (**II**) were 2333 and 3952 g/mol, which is higher in comparison with the M_n values obatined for (AAD)/(**II**) and (AAD)/(**I**) systems indicating that monomers containing ester moiety in their structure, such as acrylates and methacrylates, may be good candidates to polymerize with (**II**) and CuBr/Me_6TREN.

Keywords: atom transfer radical polymerization (ATRP); ATRP chiral initiators; polymer molecular mass; ^{1}H NMR end-group analysis

Introduction

Controlled/living radical polymerization (CRP) became one of the robust and powerful techniques for polymer synthesis during the past decade.[1] CRP can be achieved by maintaining a dynamic equilibrium between a dormant species and propagating radicals via a reversible deactivation procedure.[2] Several techniques have been developed to attain this equilibrium, including stable free-radical polymerization,[3,4] atom transfer radical polymerization (ATRP),[5,6] reversible addition-fragmentation chain transfer polymerization.[7] In particular, ATRP is one of the most efficient CRP methods, allowing the synthesis of novel (co)polymers with a predetermined degree of polymerization and narrow molecular weight distribution, the incorporation of a wide range of functional monomers, and the preparation of controllable macromolecular structures under mild reaction conditions. ATRP generally requires an alkyl halide (R-X) or pseudo-halide as an initiator and a transition metal complex as a catalyst. The effect of the ATRP initiators has been studied elsewhere.[8,9]

On the other hand, the physicochemical properties of polymers are intimately linked to molecular mass (MW).[10] The most common average MWs can be measured via a variety of different techniques such as gel permeation chromatography (GPC), osmometry, static light scattering, matrix-assisted laser desorption-ionization mass spectrometry, viscometry, field-flow fractionation, small-angle X-ray scattering, small-angle neutron scattering, ultracentrifugation, cryoscopy, ebulliometry and end-group analysis.[11–13] Ligth scattering (LS) and GPC are common ways to determine M_w. However, LS systems are not routinely available in most synthetic laboratories and

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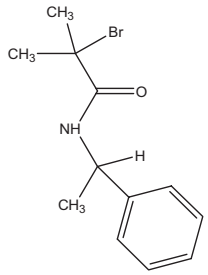
GPC analysis are often time-consuming (typically $\sim 15-60$ min per sample). GPC analysis consumes large amounts of organic solvent, requires regular calibration, columns and detectors are expensive and is incapable of yielding accurate Mw results at low Mw range (< 2000 g/mol). On the other hand, Nuclear Magnetic Resonance (NMR) has been the most powerful method for the characterization of synthetic macromolecules and to investigate their relationship between the structure and physical properties. In fact, 1-D and 2-D NMR techniques have been widely used to characterize number-average molecular mass (M_n), chemical composition and microstructures of polymers.[14–17] In fact, NMR is effective tool in measuring M_n via end-group analysis,[18,19] specially of polymers of relative low molecular weights and narrow molecular weight distributions, as occur in the case of polymers synthetized by controlled radical polymerization (CRP). In the CRP systems, it was possible to determinate the M_n of polymers via ^{1}H NMR end-group analysis when the proton signal assigned to the R fragment is not overlapped with the proton signal of the repeating unit. Thus, the molecular mass is calculated through the Equation 1, where MW_{eg} and MW_r are the molecular mass of the ends groups (R-X fragments) and the molecular mass of the repeating unit on the polymer backbone, *n* is the polymerization degree, which is calculated by the comparison of the integration corresponding to protons assigned to the R fragment signal with respect to the integration for the signals corresponding to the backbone chain (Equation 2).

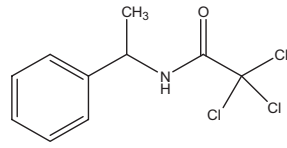
$$M_n = (MW_{eg}) + (MW_r)(n) \quad (1)$$

$$n = \frac{[\text{proton integrals/number of protons}]\ \text{corresponding to polymer backbone}}{[\text{proton inetgrals/number of protons}]\ \text{assigned to the R fragment}} \quad (2)$$

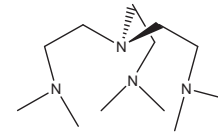
Previously, we have reported the synthesis of functional controlled polymers using ATRP and Reversible Addition Fragmentation Transfer (RAFT) Polymerization, focused in the study of the controlling agent (*i.e.* RAFT agent or ATRP initiator) on the living/controlled behaviour.[19,20,21] Also we calculated the M_n values via terminal end-group analysis of novel functional polymers. In this work are reported the synthesis, spectroscopic characterization and crystal structure of two novel ATRP initiators [R-X]: 2-bromo-2-methyl-*N*-(1-phenylethyl)propanamide (**I**) and 2,2,2-trichloro-*N*-(1-phenylethyl) acetamide (**II**), (Scheme 1) and their use in the ATRP polymerization of the monomers [M] methyl methacrylate (MMA) and acrylamide (AAD) with the catalytic system CuBr/M_e6TREN [M_t^n-Y]/[L]. Also, it is reported the molecular mass estimation by end-group analyses using ^{1}H NMR technique.



2-bromo-2-methyl-N-(1-phenyl-ethyl)propanamide
(**I**)



2,2,2-trichloro-N-(1-phenylethyl)acetamide
(**II**)



Me_6TREN

Scheme 1.
Initiators R-X and ligand used in this work.

Experimental Part

Materials and Instruments

Trichloroacetyl chloride, phenylethylamine, 2-bromo-2-methylpropionyl bromide, (*S*)-(−)-α-methylbenzylamine, CuBr, Methyl methacrylate (MMA) and acrylamide (AAD) were acquired from Aldrich Chemical Co. Tris[2-(dimethylamino)ethyl]amine (Me_6TREN) was synthesized according to a previously published method.[22] MMA was previously distilled before to use, AAD was crystallized from methanol and dried under vacuum. CuBr was purified by stirring with acetic acid overnight and after was filtrated. Afterwards it was washed with ethanol and then dried in a vacuum oven.

IR spectra were recorded on a Vertex 70 model Bruker FT-IR spectrophotometer by ATR. EI (Electron Impact) were recorded on a Jeol Mstation 700-D spectrometer. ^{1}H-NMR spectra were obtained on a Bruker 500 MHz NMR spectrometer. Melting points (mp) were measured using an SEV (0–300 °C) apparatus and they are uncorrected.

X-Ray Crystallography

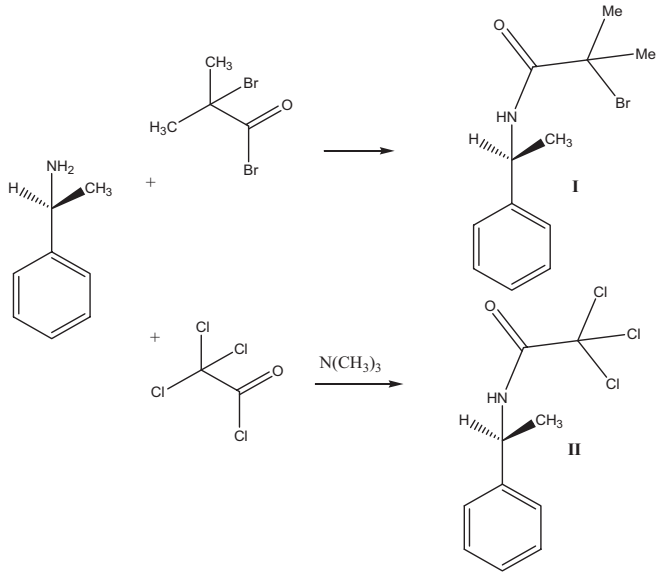
All reflection intensities were measured at 110(2) K or 100(2) K using a KM4/Xcalibur (detector: Sapphire3) with enhance graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and under Cu Kα radiation (λ = 1.54178 Å) for **I** and **II** respectively. The program CrysAlisPro (Version 1.171.36.20, Agilent Technologies, 2012) was used to refine the cell dimensions and data reduction. The structure was solved with the program SHELXS-97 (Sheldrick, 2008) and was refined on F^2 with SHELXL-97 (Sheldrick, 2008).[23] Analytical numeric absorption corrections based on a multiface crystal model were applied using CrysAlisPro (Version 1.171.36.20, Agilent Technologies, 2012). The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms (unless when specified) were placed at calculated positions using the instructions AFIX 13, AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 times Ueq of the attached C atoms.

Synthesis and Crystallization of 2-Bromo-2-methyl-*N*-(1-phenylethyl)propanamide (I) and (2,2,2-Trichloro-*N*-(1-phenylethyl) acetamide (II)

The compound (**I**) was synthesized from (*S*)-(−)-α-methylbenzylamine and 2-bromo-2-methylpropionyl bromide (Scheme 2). The molar relation used was 1:1. (*S*)-(−)-α-methylbenzilamine (0.055 mol) was added to 2-bromo-2-methylpropionyl bromide (0.055 mol) in a round-bottomed flask fitted in ice bath. The reaction mixture was stirred about 24 h at room temperature. The mixture was treated with water until the solid beige formation, which was purified by recrystallization with hexane. The yield was of 15.2%. The compound (**I**) in single crystals form was obtained dissolved it in 100 ml of hexane heated and after 12 h white crystals were obtained with a melting point of 78 °C.

IR (KBr), ν(cm^{-1}): 3320 (s, νNH), 1646 (s, amide I, νC = O), 1533 (s, amide II, δNH). ^{1}H NMR (CD_3Cl) δ (ppm): 1.53 (d, 3H, -CH_3); 1.95 (d, 3H, -CH_3); 5.04 (m, 1H, -CH-); 6.95 (broad, 1H, -NH-); 7.26–7.38 (m, 5H, Ar). Mass calculated 270, mass estimated 269 for the molecular peak $[C_{12}H_{15}NOBr]^+$, EI: m/z (%) 190(100), 120(15), 105(75), 77(11), 41(9).

The compound (**II**) was synthesized also using the (*S*)-(−)-α-methylbenzilamine, with trichloroacetyl chloride and triethylamine (Scheme 2). The molar relation was of 1:1:1. (*S*)-(−)-α-methylbenzylamine (0.072 mol) was dissolved in 15 mL of THF at room temperature in a round-bottomed flask fitted with water-cooled condenser. To the solution was added trichloroacetyl chloride (0.08 mol) and triethylamine (0.08 mol) as catalyst. The solution presented lightly color changes from yellow-light to yellow-dark until the formation of a solid. Then, it was added 5mL of THF solvent and the reaction was continued at reflux until it was not observe any change about 4 h. The white precipitate was filtrated at vacuum and purified with ethanol:ethyl acetate:hexane (1:1:1) mixture, forming the compound in single crystals form. The yield was 43.5%, mp 83–85 °C.



Scheme 2.
Synthesis of R-X initiators (**I**) and (**II**).

IR (KBr), $\nu(cm^{-1})$: 3374 (s, νNH,), 1691 (s, amide I, $\nu C=O$), 1512 (s, amide II, δNH). ^1H NMR (CD_3Cl) δ (ppm): 1.61 (d, 3H, $-CH_3$); 5.08 (m, 1H, -CH-); 6.84 (broad, 1H, NH); 7.30–7.41 (m, 5H, Ar). Mass calculated 266, mass estimated 265 for the molecular peak $[C_{10}H_9ONCl_3]^+$, EI: m/z (%), 250(12), 230(88), 196(14), 105(100), 77(16).

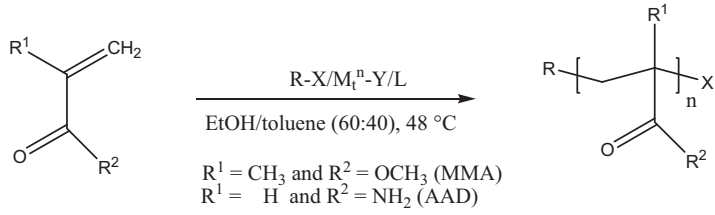
ATRP Polymerization of Acrylamide and Methyl methacrylate

The solutions were prepared with 0.5 M of monomer (MMA or AAD), using ethanol: toluene mixture (60:40) as solvent, the molar ratio of the monomer ranged from 100–400 whereas the $[R\text{-}X]_0/[M_t^n\text{-}Y]_0/[L]_0$ relation was kept constant at a ratio of 15:15:15, where $[R\text{-}X]_0$ was (**I**) or (**II**), $[M_t^n\text{-}Y]_0$ was CuBr and $[L]_0$ was Me_6TREN (Scheme 3). The oxygen was removed by bubbling high purity argon gas for 30 min. After that, the ampoule containing reaction mixture was sealed and dipped in a water bath kept at constant temperature of 48 °C. Polymers were precipitated in ethanol (poly(MMA)) and hexane (poly-(AAD)). All polymers were dried at vacuum.

Results

Crystal Structure of 2-Bromo-2-methyl-*N*-(1-phenylethyl)propanamide (I) and 2,2,2-Trichloro-*N*-(1-phenylethyl)acetamide (II)

The crystals data, together with the details on the data collection and structure refinement, are given in Table 1. The molecular



Scheme 3.
ATRP Polymerization of the MMA and AAD using R-X initiators (**I** or **II**), L = Me_6TREN and M_t^n-Y = CuBr.

Table 1.
Crystallography Data for (**I**) and (**II**) compounds.

	(I)	(II)
Empirical formula	$C_{12}H_{16}BrNO$	$C_{10}H_{10}Cl_3NO$
Crystal system	monoclinic	Monoclinic
Color, Habit	colorless, plate	colorless, plate
Formula weight	270.17	266.54
Space group	P 21	C 2
T(K)	110(2)	100(2)
a(Å)	8.54892(16)	26.1526(5)
b (Å)	16.1145(2)	5.54679(13)
c (Å)	9.44788(18)	7.99912(17)
α(°)	90.00	90.00
γ (°)	108.941(2)	97.677(2)
β (°)	90.00	90.00
V (Å^3)	1231.08(4)	1149.98(4)
Z	4	4
Dc(g cm^{-3})	1.458	1.540
F (000)	552	544
μ (mm^{-1})	3.314	6.992
λ (Å)	0.71073	1.54178
Crystal size (mm^3)	0.40 × 0.35 × 0.25	0.37 × 0.17 × 0.05
2θmax(°)	71.95	71.84
N	12060	6610
N° (I>2.0 σ(I))	4714	2073
R_1	2.45	2.86
wR_2	6.26	7.67
goodness-of-fit	1.055	1.040
Largest diff peak and hole (e Å^{-3})	1.04 and −0.84	0.48 and −0.5

structure and atom numbering of (**I**) and (**II**) are shown in Figure 1. For the compound (**I**) the H atoms attached to the N1A/N1B atoms, as well as, for compound (**II**) the H atom attached to N1 were found from Fourier difference maps and their atomic coordinates were refined freely. The structure (**I**) is ordered,

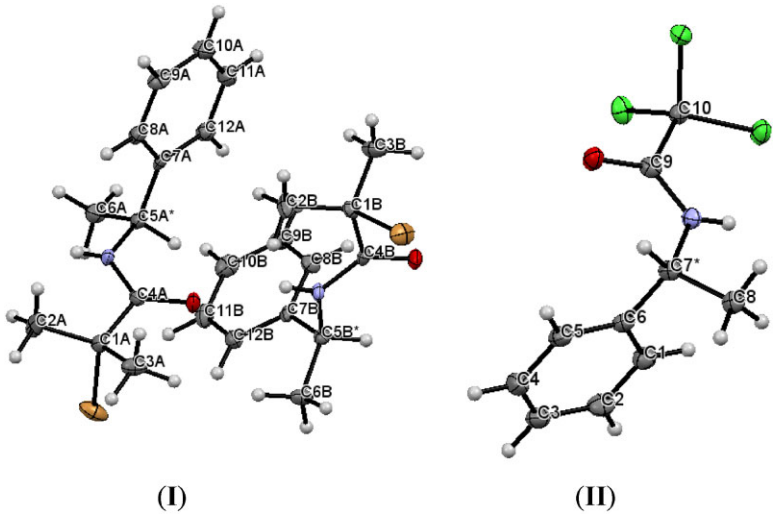


Figure 1.
Molecular structures of (**I**) and (**II**). Displacement ellipsoids are drawn at 30% probability level and H atoms are shown as small spheres of arbitrary radii.

and the asymmetric unit contains two formula units. The absolute configuration was established by anomalous-dispersion effects in diffraction measurements on the crystal. The Flack parameter refines to -0.011(6). For compound (**II**) the structure is also ordered and the absolute configuration was established by the structure determination of a compound containing a chiral reference molecule of known absolute configuration (C7 R) and was confirmed by anomalous-dispersion effects in diffraction measurements on the crystal. The Flack and Hooft parameters refine to -0.027(14) and -0.017(7). The selected bond lengths (Å), bond and torsion angles (°) are listed in Table 2.

X-ray studies of (**I**) and (**II**) single crystals were made to evaluate the R-X bond, which is involving homolytic cleavage by a transition metal complex in ATRP. In the molecules of the structure (**I**) the bond length Br-C(1A) was of 1.996(3) Å slightly longer than Br-Csp^3 of 1.910 Å.[24] The skeleton part C(2A)-C(1A)-C(4A)-N(1) showed a torsion angle of -24.1(4)° and fragment Br(1)-C(1A)-C(4A)-O(1A) = -83.5(2)° indicating that the Br is not coplanar with the fragment C(2A)-C(1A)-C(4A)-N(1). The molecule of the structure (**II**), the molecule skeleton part N(1)-C(9)-C(10)-Cl(1) is found almost coplanar with a torsion angles of 123.1(2)° due to the presence of amide group, the bond angle C(9)-N(1)-C(10) and O(1)-C(9)-N(1) were 117.7(2)° and 126.0(2)°, respectively. The linkage of C(10)-Cl is between of 1.773(3) Å, 1.761(3) Å and 1.771(3) Å, which is slightly shorter than for Csp^3-Cl reported of 1.790 Å (see Table 2).[24]

ATRP Plymerization of AAD and MMA Using (I) and (II)

In ATRP, alkyl halides (R-X) are typically used as the initiator and the rate of the polymerization is first order with respect to the concentration of R-X. Thus far, when X is either bromine or chlorine, the molecular mass control is the best. It has been indicated that one of the approaches to

Table 2.
Selected bond lengths (Å), and angles (°) in crystal structure of compounds (**I**) and (**II**).

Bond Length(Å)			
Br(1)-C(1A)	1.996(3)	C(10)-Cl(1)	1.773(3)
C(1A)-C(2A)	1.506(3)	C(10)-Cl(2)	1.761(3)
C(1A)-C(3A)	1.511(4)	C(10)-Cl(3)	1.771(3)
C(1A)-C(4A)	1.536(3)	C(9)-C(10)	1.565(3)
C(4A)-O(1A)	1.232(3)	C(9)-O(1)	1.221(4)
C(4A)-N(1A)	1.332(3)	C(9)-N(1)	1.327(4)
C(5A)-N(1A)	1.459(3)	C(7)-N(1)	1.476(3)
Bond Angle(°)			
C(2A)-C(1A)-C(3A)	112.0(2)	Cl(2)-C(10)-Cl(3)	108.65(13)
C(2A)-C(1A)-C(4A)	116.0(2)	Cl(2)-C(10)-Cl(1)	108.98(14)
C(3A)-C(1A)-C(4A)	110.8(2)	Cl(3)-C(10)-Cl(1)	109.96(15)
C(2A)-C(1A)-Br(1)	108.2(2)	C(9)-C(10)-Cl(2)	114.4(2)
C(3A)-C(1A)-Br(1)	107.41(17)	C(9)-C(10)-Cl(3)	107.38(17)
C(4A)-C(1A)-Br(1)	101.60(16)	C(9)-C(10)-Cl(1)	107.46(17)
O(1A)-C(4A)-N(1A)	122.7(2)	O(1)-C(9)-N(1)	126.0(2)
O(1A)-C(4A)-C(1A)	119.3(2)	O(1)-C(9)-C(10)	117.7(2)
N(1A)-C(4A)-C(1A)	117.9(2)	N(1)-C(9)-C(10)	116.3(2)
C(4A)-N(1A)-C(5A)	122.1(2)	C(9)-N(1)-C(7)	120.4(3)
Torsion Angle (°)			
C(2A)-C(1A)-C(4A)-O(1A)	159.5(3)	O(1)-C(9)-C(10)-Cl(1)	−57.1(3)
Br(1)-C(1A)-C(4A)-O(1A)	−83.5(2)	O(1)-C(9)-C(10)-Cl(2)	−178.3(2)
C(3A)-C(1A)-C(4A)-O(1A)	30.3(3)	O(1)-C(9)-C(10)-Cl(3)	61.1(3)
Br(1)-C(1A)-C(4A)-N(1A)	92.9(2)	N(1)-C(9)-C(10)-Cl(1)	123.1(2)
C(2A)-C(1A)-C(4A)-N(1A)	−24.1(4)	N(1)-C(9)-C(10)-Cl(2)	2.0(3)
C(3A)-C(1A)-C(4A)-N(1A)	−153.2(2)	N(1)-C(9)-C(10)-Cl(3)	−118.6(2)
O(1A)-C(4A)-N(1A)-C(5A)	10.1(4)	O(1)-C(9)-N(1)-C(7)	−1.6(4)

improve the efficiency of initiation is the exchange of ligands.[25] This is due to the fact that alkyl bromides are easier to activate than alkyl chlorides at the initiation stage whereas at the propagation stage predominantly alkyl chlorides are formed. To determine the effect of initiator, AAD was polymerized using (**I**) and (**II**) using the catalyst system CuBr/Me_6TREN, in ethanol:toluene (60:40) at 48°C, during 7 h and to determine the effect of monomer it was polymerized MMA with (**II**) at the same reaction conditions. Figure 2 shows the ^{1}H NMR spectra of ATRP initiators (**I**) and (**II**) and Figure 3 shows ^{1}H NMR spectra of poly(AAD) (**i**) and poly(MMA) (**ii**) synthesized in presence of (**II**), In Figure 3, it can be noted the disappearance of the signals at at 6.32 and 5.81 ppm corresponding to the vinyl protons for AAD and 6.09 and 5.55 ppm for MMA, respectively, provided evidence for the formation of

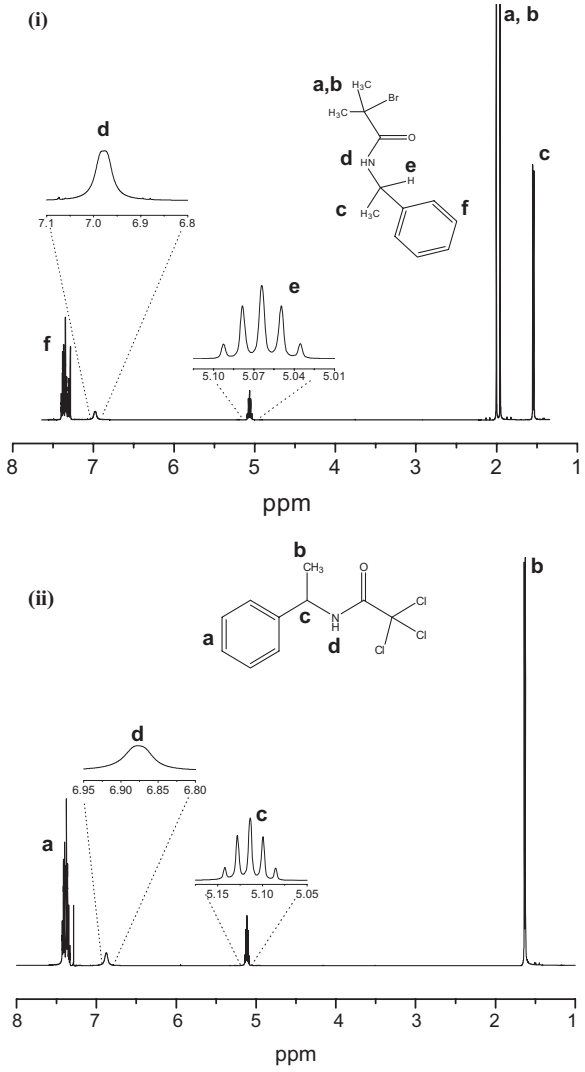


Figure 2.
^{1}H NMR spectra of compounds 2-bromo-2-methyl-*N*-(1-phenyl-ethyl)propanamide (**I**) **(i)** and 2,2,2-trichloro-*N*-(1-phenylethyl) acetamide (**II**) **(ii)** recorded in $CDCl_3$.

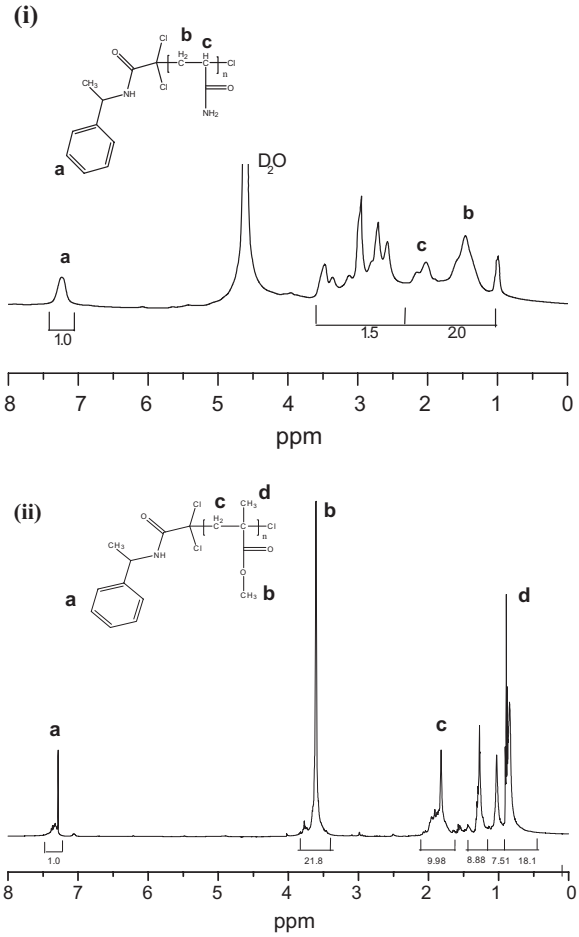


Figure 3.
^{1}H NMR spectra of poly(AAD)/(**II**) in D_2O (**i**) and poly(MMA)/(**II**) in $CDCl_3$ (**ii**).

polymers. The broad signal around of 7.3 ppm was assigned to aromatic protons corresponding to the R group from the ATRP initiator, which is not overlapped with any other signal. These results allow us determinate the number-average molecular mass (M_n) of the polymer using Equation 1. For comparison purpose the signal integration of the aromatic group corresponding to the R group with the backbone polymer peak at 1.2–2.4 ppm for the case of poly(AAD) and 3.45 ppm for the case of poly(MMA) were used.

M_n values of the polymers synthesized at the different reaction conditions are presented in Table 3. It can be seen in the case of AAD, is not clear a trend in the molecular mass with respect to the increase of the monomer concentration $[M]_0$, this behavior could be due to the inactivation of the catalyst by complexation of copper,[26,27] considering the structural resemblance of the initiator with the monomer, *i.e.* the α-bromopropionates are good initiators for the ATRP.[25] However, (**I**) can experiment non homolytic reaction due to that the bond length in C-Br in (**I**) is higher than C-Cl bond length in (**II**) as was determined by X-ray. Also, (**II**) has three chlorine atoms that facilities the catalytic cyclic in comparison with (**I**) that has one C-Br bond. With respect to the monomer,

Table 3.
Summary of molecular mass data.

Entry	Polymer	Molar ratio $[M]_o/[CuBr]_o/[Me_6TREN]_o/[I]_o$	Solubility	Mn (g/mol)
1	polyAAD/	100:15:15:15	Water	725
2	(**I**)	200:15:15:15		623
3		300:15:15:15		2229
4		400:15:15:15		1784
5	polyAAD/	100:15:15:15	Water	1804
6	(**II**)	200:15:15:15		1544
7		300:15:15:15		1201
8		400:15:15:15		2988
9	polyMMA/	100:15:15:15	THF, CH_3Cl, toluene	2333
10	(**II**)	200:15:15:15		3952

Table 3 shows that the experiments 5 and 6 provide lesser M_n values in comparison with the experiments carried out in experiments 9 and 10 indicating that the system MMA/(**II**) present a better controlled/living behavior than AAD/(**II**).

Conclusion

In the present work is reported the synthesis, spectroscopic characterization and crystal structure of two novel ATRP initiators (R-X): 2-bromo-2-methyl-*N*-(1-phenyl-ethyl) propanamide (**I**) and 2,2,2-trichloro-*N*-(1-phenylethyl)acetamide (**II**). (**I**) and (**II**) were used in the ATRP reaction of MMA and AAD. The novel initiators were designed in order to perform the end-group analysis by ^{1}H-NMR, which is an easy and fast tool in the polymer characterization. Thus, in terms of the monomer structure, MMA/(**II**) system provides polymers with high molecular mass in comparison with the ADD/(**II**) system, while in terms of the initiator structure, (**II**) gives polymers with higher molecular mass than (**I**). Currently, our group is conducting a study about to correlation the initiator and monomer structure with respect to the living/controlled behavior using electrochemical methods, in order to improve and understand the ATRP mechanism of functional monomers and measure their corresponding M_n values by ^{1}H NMR and SEC-MALS techniques.

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Supplementary Data

Crystallographic data (excluding structure factors) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 988062 and 988063. Copies of available material can be obtained, free of charge, on application to the CCDC, 12 Union Road. Cambridge CB2 IEZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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