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# Employing Imine Macrocycle Ligand in the Atom Transfer Radical Polymerization of Methyl Methacrylate

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*Imine macrocycle $M_1$ was successfully used in conjunction with CuBr as a catalytic system in the atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA). The role of the reaction conditions was clearly observed. Such reaction conditions were found to be the molar ratios of the reactants, the chosen initiating systems, and some additional ambient conditions (e.g. temperature, solvent). MMA homopolymers were successively prepared via ATRP by using benzhydrylbromide, diethylmethylbromomalonate initiating systems under the appropriate reaction conditions. Definite well-known structures of the formed polymers were unambiguously identified with $^1H$ NMR.*

**Keywords** imine macrocycle, ATRP, MMA homopolymers, initiators

## Introduction

In the past few years, ATRP has recently gained increasing interest in the field of controlled\ living polymerization as a promising transition-metal living polymerization technique with respect to the majority of monomers in order to obtain novel, well-defined polymers (1, 2). Those polymers are with well-controlled molecular weights and low polydispersities, as well as various functionalities (3, 4). It is also a very useful approach for synthesizing novel polymer architectures such as star polymers (5, 6), polymer brushes (7), nanoparticle hybrids (8), and polymer monolayer (9).

Finding new ligands is a vital target in the current development of ATRP (10–13). Some main classes of nitrogen-based ligands were used as efficient ATRP catalysts when coordinated to Cu (e.g. 2,2′-bipyridines (1, 14, 15), 1,10-phenanthrolines (16), aryl/alkyl-2-pyridyl-methanimines (17, 18) and linear polyamines (19). The second half of the 1960's marked the beginning of current macrocyclic chemistry where it was realized that macrocyclic structures can produce particularly effective and selective complexing agents (20). The current approach was developed to construct macrocyclic ligands

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which are suitable for the complexation of two or more metal centers (21–23) Here, $M_1$ imine macrocycle (24) was chosen as a novel ligand in ATRP. It basically formed (2 + 2) macrocycles as a major product almost 99%. This fact was strongly confirmed by single crystal analysis, performed on a crystal obtained by diffusion of diethylether into a chloroform solution of the cycle. Its crystal structure manifested the presence of pure (2 + 2) macrocycles as shown in Figure 1.

## Experimental

### *Materials*

Methyl methacrylate monomer (MMA) was from Lancaster Synthesis Ltd., England. It was purified by filtration through an alumina column and then collected in a Schlenk flask, dried over molecular sieves, degassed by argon bubbling for 10 min, and then stored under argon in a refrigerator. 3-Bromopropionate (99%), 4-methyl benzyl bromide (98%), 1-bromo-ethyl benzene (97%), benzylbromide (99%), benzhydryl bromide (95%), ethyl-2-bromoisobutyrate (98%), 2-bromoethylbenzene (98%), P-toluenesulfonylchloride (99%), ethyl-2-bromo-propionate (97%), diethylbromomalonate (98%), diethyl-2-bromo-2-methylmalonate (98%), and 3-bromopropionitrile (99%). All these initiators were products of Lancaster Synthesis Ltd., England and were used as received. Solvents such as o-xylene, diphenyl ether, absolute methanol, toluene and n-hexane were of pure grade, Merck Chemical Co., Germany. Acetonitrile was of HPLC grade (99.93%), (Sigma-Aldrich Chemical Co., Germany). 5-Tert-butylbenzene-1,3-dicarbaldehyde was prepared as in the literature (24). Diethylenetriamine was received from Sigma-Aldrich Chemical Co., Germany. Copper (1) bromide (99.99%) was from Lancaster Chemical Co., England. Any other chemicals were from Sigma-Aldrich Chemical Co., Germany and were used without further purification.

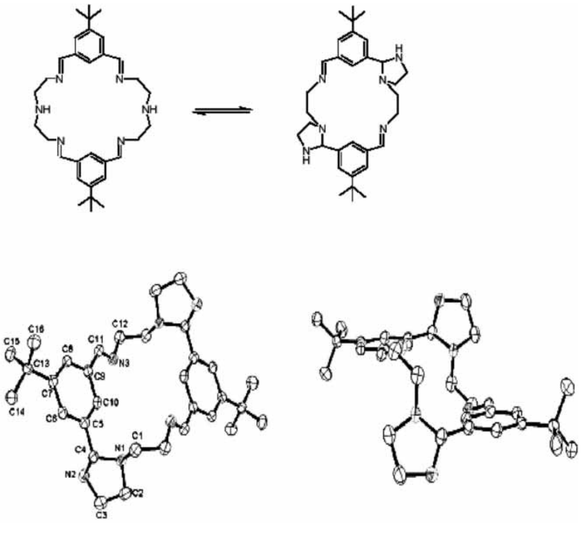


**Figure 1.** Isomers of $M_1$ macrocycle—normal view and side view (hydrogens are omitted for clarity).

### Measurements

Molecular weights and polydispersities of the samples were determined by gel permeation chromatography (GPC) using a Waters Model 510 pump, a Waters Model 410 differential refractometer and a Waters Model 730 Data module with 103–105 Å Ultrastyragel columns connected in series (Germany). THF was used as the eluent, commercially available poly(methylmethacrylate) standards were used to calibrate the columns. $^1$H NMR spectra were recorded on Bruker AC-200 and AC-400, (Germany) in $CDCl_3$ operated at 400 MHz using tetramethylsilane as an internal reference. Elemental analyses (EA) were performed with a Perkin-Elmer Series II 2400 CHNS analyzer, Bruker Reflex III (Bruker-Daltonik, Germany). A MALDI-TOF mass spectrometer was used for determining the molecular weight, as well as the different fragments in the case of macrocycles. The instrument was operated in a positive-ion linear mode with accelerating voltage of 25 kV. All samples were analyzed using 2,5-dihydroxybenzoic acid (DHB) as a general matrix from Sigma-Aldrich Chemical Co., Germany. Mass spectrometry-Chemical ionization (CI)-Finnigan MAT, SSQ 7000, and 70 ev was applied by using $CH_4$ as a reagent gas. In addition, mass spectrometry-fast atom bombardment (FAB)-Finnigan MAT, TSQ 7000, was applied by using m-NBA (meta—nitrobenzylalcohol). The crystal data of $M_1$ were collected on a Rigaku AFC7S four-circle diffractometer using graphite monochromatized Mo-K$\alpha$ radiation, $\lambda = 0.71073$ Å (24).

### General Procedure for the Preparation of the Expected Macrocycle (24)

A (3.75 mmol) solution of 5-tert-butylbenzene-1,3-dicarbaldehyde (24) in 80 ml of acetonitrile was added dropwise to a vigorously stirred solution (3.75 mmol) of the diethylenetriamine in 140 ml acetonitrile over 2 h at room temperature. The stirring of the reaction mixture continued for 24 h at room temperature in an inert gas atmosphere (argon) applying the standard Schlenk technique. The precipitated macrocycles were filtered off, washed intensively with acetonitrile, and dried under vacuum. The expected macrocycles produced a white precipitate in good yield. EA ($C_{32}H_{46}N_6$) M.wt 514: % Found (calculated): C: 74.58 (74.71), H: 8.98 (8.95), N: 16.27 (16.34). IR (KBr): $\nu$(C=N) at 1650 cm$^{-1}$, Mass-spectroscopy (CI, FAB) and MALDI-TOF MH$^+$: major band at 515 was referred to $(2 + 2)$ in about 99%.

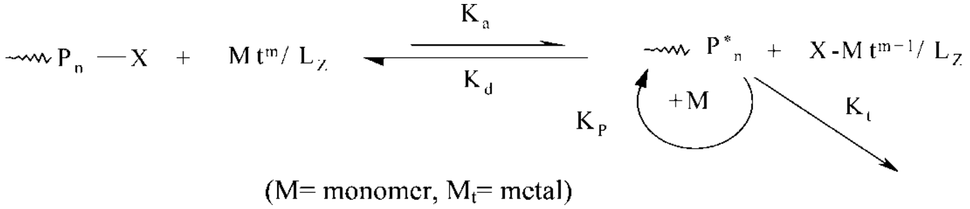
### General ATRP Polymerization Technique

The proper amounts of the ligand, CuBr and solvent were added to a glass vial. The vial was then sealed after purging the total reaction medium with argon for about 10 min. The vial was immersed in a thermostated oil bath adjusted for the desired temperature according to each case. The MMA monomer and the initiators were successively added via syringes previously washed with argon. In the case of benzhydrylbromide or p-toluenesulfonylchloride initiators, the desired initiator amount was dissolved in a small part of the solvent and then added to the reaction mixture slowly over 10 min to enhance the initiation efficiency. After a definite time interval according to each case, the vial was opened and the formed polymer was dissolved in tetrahydrofuran (THF) and precipitated whether in methanol in the case of diphenylether (DPE) mediated polymerization, or in n-hexane in the case of toluene (T), o-xylene (X) mediated polymerization. The conversion was determined gravimetrically by drying the resulting polymer and weighing it to determine the exact monomer conversion. For determination of the exact molecular weight and molecular weight distribution via GPC, the polymer sample was redissolved in THF, and then passed through an alumina column to remove the metal residuals. The resulting polymer solution was concentrated in *vacuo* and then reprecipitated in n-hexane. The precipitated polymer was collected and dried under vacuum. The structures of the formed polymers were identified by $^1$H NMR. The number of average molecular weights and the polydispersities was determined via GPC by using poly MMA standards.

## Results and Discussion

In order to display the results, the ATRP mechanism should be reviewed as shown in Scheme 1.

The molar ratio of the used reactants (i.e., ligand, CuBr, initiator, and monomer) was investigated as an expected principle factor to obtain true ATRP by using the macrocyclic ligands. In the case of $M_I$ imine macrocycle, two active centers are present, hence, the ligand: CuBr percentages would be 1 : 2. Accordingly, three main formulas were investigated (e.g. ligand, CuBr, initiator, and monomer = 1 : 2 : 1 : 100, 1 : 2 : 2 : 200 and 1 : 2 : 4 : 400) where the monomer percentage (MMA) would be 100 times relative to the initiator percentage in each case. It was found that different monomer percents did not have a great effect on polymerization itself, but may to some extent on the rate of polymerization. Benzhydrylbromide and p-toluenesulfonylchloride were used as common ATRP initiators for MMA (25). As shown in Table 1 and Figure 2, the best situation was observed in the case of the 1 : 2 : 4 : 400 formula. Some relative control was recorded over the polymerization processes where the equilibrium strongly shifted toward the dormant species formation. Therefore, a high concentration of dormant species relative to the active ones, was achieved and prevented the irreversible radical-radical termination (25). This could be represented whether in terms of the molecular weights or the polydispersities ($D = \bar{M}_w/\bar{M}_n$) which were still low enough. The relative agreement between the theoretical and the practical molecular weights ($\bar{M}_{nth}$ and $\bar{M}_{nGPC}$, respectively) was observed which especially increased at the higher conversions. The main drawback in the 1 : 2 : 4 : 400 formula was the dramatic decrease in conversion values in comparison with the other formulas at the same time intervals. That was ascribed to the expected lower number of active species. Moreover, the relative higher than predicted polydispersities and molecular weights could be explained somehow in terms of the steric and electronic effects of those macrocycles on the polymerization processes. Extra deactivation could happen due to the presence of the two copper atoms inside the macrocyclic moiety. The role of those two copper atoms needs more investigation beyond the scope of this publication and is in progress in our laboratory. Generally, p-toluenesulfonylchloride displayed strange behavior could be explained later. The effect of the solvent here was obvious. Con-



**Scheme 1.** Atom transfer radical polymerization (ATRP).

**Table 1**
The effect of varying the reactants percentages on the polymerization processes

| Initiator | Sample | L : CuBr : I : MMA | Solvent | Conv. % | $\bar{M}_{nth.}$ | $\bar{M}_{nGPC}$ g/mol | D |
|---|---|---|---|---|---|---|---|
| Benzhydryl-bromide | $P_1$ | 1:2:1:100 | T | 88 | 8781 | 27630 | 1.24 |
| | $P_2$ | 1:2:2:200 | T | 88 | 8819 | 17310 | 1.31 |
| | $P_3$ | 1:2:4:400 | T | 40 | 4005 | 7600 | 1.39 |
| | $P_4$ | 1:2:1:100 | DPE | 35 | 3504 | 15630 | 1.14 |
| | $P_5$ | 1:2:2:200 | DPE | 36 | 3584 | 14650 | 1.23 |
| | $P_6$ | 1:2:4:400 | DPE | 26 | 2603 | 10060 | 1.23 |
| P-toluenesulfonyl-chloride | $P_7$ | 1:2:1:100 | T | 78 | 7836 | 34080 | 1.51 |
| | $P_8$ | 1:2:2:200 | T | 89 | 8913 | 29630 | 1.62 |
| | $P_9$ | 1:2:4:400 | T | 33 | 3250 | 9950 | 1.62 |
| | $P_{10}$ | 1:2:1:100 | DPE | 39 | 3904 | 39190 | 1.38 |
| | $P_{11}$ | 1:2:2:200 | DPE | 45 | 4506 | 22710 | 2.99 |
| | $P_{12}$ | 1:2:4:400 | DPE | 22 | 2224 | 11890 | 1.61 |

sequently, in DPE, relatively lower conversions and higher molecular weights were recorded. However, in toluene more controlled behavior was observed. In a successive comprehensive study, some initiators were involved in order to determine the suitable ones for successful ATRP of MMA by using those macrocycles as the proper ligands. That study was carried out by using the formula (ligand : CuBr : initiator : MMA = 1 : 2 : 4 : 400) at

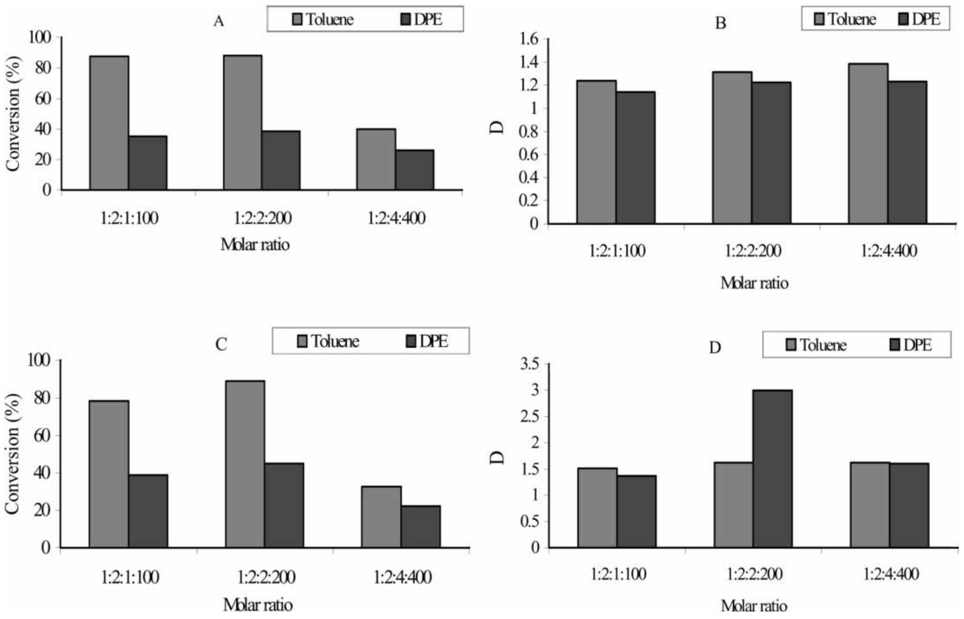


**Figure 2.** The effect of using variable molar ratios on ATRP of MMA in the case of using both (A, B) benzhydryl bromide, (C, D) p-toluene sulfonylchloride.

90, 100°C in toluene. Several initiators were involved representing different initiators categories (25). 2Br-propionate, ethylbromoisobutyrate, p-toluenesulfonylchloride, 1Br-ethylbenzene, benzhydryl- bromide and diethyl-2-bromo-2-methylmalonate were utilized. Generally, the true ATRP initiating system should fulfill some conditions (26) as the fast initiation, in comparison with propagation to ensure efficient generation of the polymer chains. Therefore, may be avoided. On the other hand, the initiating system should minimize the probability of side reactions. 1Br-ethylbenzene displayed no controlled higher molecular weight values and polydispersities polymerization where it showed normal free radical polymerization with very high molecular weights and polydispersities

**Table 2**

The effect of using various initiators on the polymerization processes

| Initiator | Sample | Temp. °C | Time min. | Conv. % | $\bar{M}_{nth.}$ | $\bar{M}_{nGPC}$ g/mol | D |
|---|---|---|---|---|---|---|---|
| Ethyl-2-bromo-isobutyrate (IB) | $P_1$ | 90 | 40 | 11 | 1101 | 35140 | 1.38 |
| | $P_2$ | 90 | 59 | 15 | 1502 | 43080 | 1.38 |
| | $P_3$ | 90 | 90 | 24 | 2403 | 44000 | 1.39 |
| | $P_4$ | 100 | 32 | 15 | 1665 | 34570 | 1.39 |
| | $P_5$ | 100 | 57 | 29 | 2850 | 35090 | 1.49 |
| | $P_6$ | 100 | 90 | 44 | 4405 | 41000 | 1.49 |
| Ethyl-2-bromo-propionate (BrPr) | $P_7$ | 90 | 64 | 10 | 1001 | 11290 | 1.66 |
| | $P_8$ | 90 | 115 | 18 | 1808 | 12900 | 1.67 |
| | $P_9$ | 90 | 150 | 28 | 2803 | 20000 | 1.69 |
| | $P_{10}$ | 100 | 62 | 12 | 1201 | 89270 | 1.62 |
| | $P_{11}$ | 100 | 115 | 24 | 2403 | 90000 | 1.62 |
| | $P_{12}$ | 100 | 150 | 30 | 3004 | 92200 | 1.62 |
| P-toluenesulphonyl-chloride (pTsCl) | $P_{13}$ | 90 | 105 | 23 | 2273 | 11690 | 1.59 |
| | $P_{14}$ | 90 | 188 | 26 | 2603 | 11050 | 2.24 |
| | $P_{15}$ | 90 | 307 | 37 | 3704 | 11510 | 1.59 |
| | $P_{16}$ | 100 | 108 | 22 | 2187 | 8791 | 1.74 |
| | $P_{17}$ | 100 | 180 | 28 | 2839 | 5933 | 2.56 |
| | $P_{18}$ | 100 | 240 | 33 | 3250 | 11760 | 1.62 |
| Benzhydryl-bromide (BhBr) | $P_{19}$ | 90 | 370 | 25 | 2493 | 7176 | 1.37 |
| | $P_{20}$ | 90 | 485 | 34 | 3404 | 6849 | 1.35 |
| | $P_{21}$ | 90 | 780 | 48 | 4806 | 11180 | 1.33 |
| | $P_{22}$ | 100 | 360 | 44 | 4395 | 8524 | 1.39 |
| | $P_{23}$ | 100 | 490 | 58 | 5787 | 11400 | 1.42 |
| | $P_{24}$ | 100 | 780 | 85 | 8510 | 12200 | 1.31 |
| Diethyl-2-bromo-2-methyl-malonate (DEBrMM) | $P_{25}$ | 90 | 70 | 52 | 5206 | 11247 | 1.25 |
| | $P_{26}$ | 90 | 161 | 80 | 8010 | 12667 | 1.24 |
| | $P_{27}$ | 90 | 240 | 87 | 8679 | 9594 | 1.34 |
| | $P_{28}$ | 100 | 66 | 59 | 5907 | 10337 | 1.29 |
| | $P_{29}$ | 100 | 120 | 74 | 7399 | 9628 | 1.31 |
| | $P_{30}$ | 100 | 240 | 90 | 8991 | 9745 | 1.32 |

than the predicted ones, i.e., polydispersities up to 2 and $\bar{M}_{nth.}/\bar{M}_{n,GPC}$ 5006/90790 at 100°C in almost all solvents. Also, benzyl bromide behaved in a similar way where traditional free radical polymerization was observed. It gave poor molecular weight control during the polymerization and very high polydispersities. On the other hand, no distinguished polymerization was observed by using 2-bromoethylbenzene, 3-bromo-propionitrile and 4-methylbenzylbromide. That was attributed to the inefficient initiation. Therefore, high molecular weight polymers continually formed throughout the experiment. The results of the other initiators were represented as shown in Table 2 and Figure 3. Ethyl-2-bromoisobutyrate showed uncontrolled polymerization, and that appeared in the complete disagreement between the $\bar{M}_{nth}$ and $\bar{M}_{nGPC}$ in spite of relatively lower polydispersity. The deviation was presumably due to an unidentified transfer process and the slow initiation. The slow

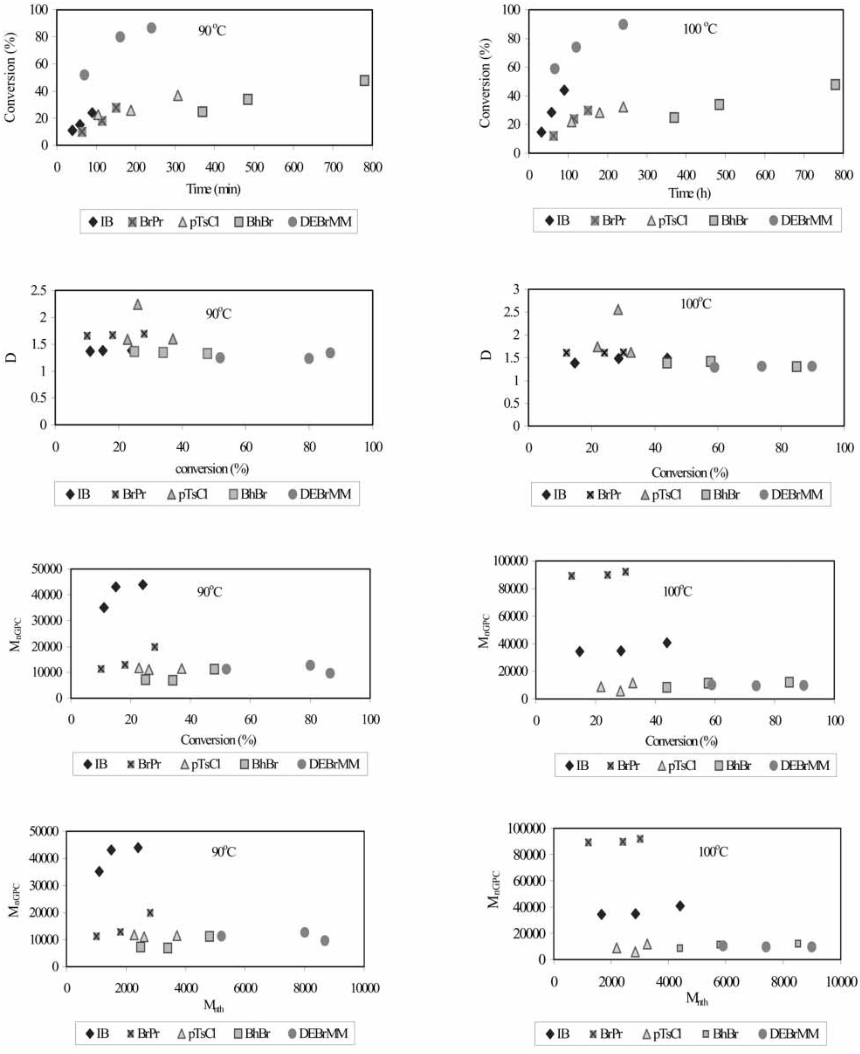
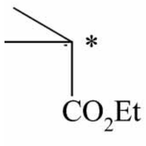


**Figure 3.** Plots of ATRP of MMA by using $M_1$ imine macrocycle/CuBr catalytic system with respect to various initiating systems at 90, 100°C, respectively.

initiation could be explained in terms of the transformation of the radical resulting from the reaction between CuBr/Br-IB to the propagating radical 2 on its quick addition to MMA. Because of the back strain effect, the reactivity of the propagating radical 2 toward MMA should be lower than that of 1 (25).



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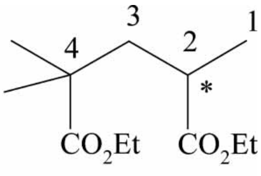

2

Accordingly, ethyl-2-bromopropionate initiating system showed severe deviation and obvious disagreement between the $\bar{M}_{nth.}/\bar{M}_{nGPC}$ values accompanied by noticeable high polydispersities especially at higher temperatures. The peculiarity was ascribed to the much slower initiation, which led, to some degree of side reactions and the behavior was nearly the same as in the conventional free radical polymerization.

**Table 3**

ATRP of MMA initiated with diethylmethylbromomalonate

| Sample | Solvent | Temp. °C | Time min. | Conv. % | $\bar{M}_{nth}$ | $\bar{M}_{nGPC}$ | D | Ln $M_0/M_t$ |
|---|---|---|---|---|---|---|---|---|
| $D_1$ | T | 90 | 40 | 29 | 2904 | 7700 | 1.25 | 0.342 |
| $D_2$ | T | 90 | 70 | 52 | 5208 | 11247 | 1.25 | 0.734 |
| $D_3$ | T | 90 | 188 | 80 | 8010 | 12667 | 1.24 | 1.609 |
| $D_4$ | T | 90 | 240 | 87 | 8679 | 9594 | 1.34 | 2.017 |
| $D_5$ | T | 90 | 270 | 91 | 9111 | 9500 | 1.34 | 2.408 |
| $D_6$ | X | 90 | 40 | 36 | 3604 | 7800 | 1.34 | 0.446 |
| $D_7$ | X | 90 | 65 | 65 | 6536 | 10588 | 1.34 | 1.058 |
| $D_8$ | X | 90 | 132 | 67 | 6731 | 11072 | 1.34 | 1.116 |
| $D_9$ | X | 90 | 180 | 76 | 7609 | 11109 | 1.34 | 1.427 |
| $D_{10}$ | X | 90 | 240 | 89 | 8911 | 11623 | 1.34 | 4.976 |
| $D_{11}$ | T | 100 | 40 | 42 | 4205 | 8500 | 1.29 | 0.545 |
| $D_{12}$ | T | 100 | 66 | 59 | 5904 | 10337 | 1.29 | 0.8909 |
| $D_{13}$ | T | 100 | 120 | 74 | 7394 | 9628 | 1.31 | 1.341 |
| $D_{14}$ | T | 100 | 240 | 90 | 8993 | 9745 | 1.32 | 2.2847 |
| $D_{15}$ | X | 100 | 40 | 43 | 4345 | 8600 | 1.32 | 0.5692 |
| $D_{16}$ | X | 100 | 65 | 71 | 7057 | 10888 | 1.33 | 1.220 |
| $D_{17}$ | X | 100 | 120 | 88 | 8774 | 9628 | 1.41 | 2.0899 |
| $D_{18}$ | X | 100 | 240 | 91 | 9074 | 11573 | 1.26 | 2.368 |
| $D_{19}$ | X | 110 | 40 | 44 | 4405 | 9000 | 1.21 | 0.5802 |
| $D_{20}$ | X | 110 | 70 | 72 | 7212 | 12224 | 1.21 | 1.274 |
| $D_{21}$ | X | 110 | 130 | 87 | 8704 | 10847 | 1.25 | 2.036 |
| $D_{22}$ | X | 110 | 240 | 92 | 9161 | 11080 | 1.18 | 2.465 |

P-toluenesulphonylchloride displayed different uncontrolled behavior other than that in the literature as a good MMA initiating system (27, 28). As indicated in Table 2, that behavior could be explained in terms of slow initiation and deactivation where some steric effects released from the macrocyclic moiety itself. Additionally, the difficulty in bond cleavage of C–Cl more than that of C-Br bond led to a slower exchange reaction and relatively uncontrolled polymerization. With respect to the benzhydrylbromide initiating system, generally slower polymerization reactions were observed with respect to the other initiating systems. Higher conversions were accomplished at elevated temperatures with relatively low polydispersities. The molecular weights increased linearly with the monomer consumption and the conversion in each case indicating the constant number of the active species. The difference between the $\bar{M}_{nth.}/\bar{M}_{nGPC}$ values could be attributed to significant side reactions (i.e., chain coupling). Generally, benzhydryl bromide (BhBr) performed true ATRP polymerization reaction. The diethyl-2-bromo-2-methylmalonate (dEBMM) system produced polymers with low polydispersities. The deviation in the experimental molecular weight values was attributed to transfer reactions previously described. The presence of a methyl group in dEBMM changed the radical to a less electron deficient one, which added to MMA efficiently and successfully initiated the polymerization. Generally, dEBMM initiating system demonstrates true ATRP system

**Table 4**
ATRP of MMA initiated with benzhydrylbromide

| Sample | Solv. | Temp. °C | Time (h) | Conv. (%) | $\bar{M}_{nth.}$ | $\bar{M}_{nGPC}$ | D | Ln $M_o/M_t$ |
|---|---|---|---|---|---|---|---|---|
| $R_1$ | T | 90 | 3 | 15 | 1525 | 11460 | 2.16 | 0.1652 |
| $R_2$ | T | 90 | 6 | 25 | 2491 | 7176 | 1.37 | 0.2862 |
| $R_3$ | T | 90 | 8 | 34 | 3407 | 6849 | 1.34 | 0.4160 |
| $R_4$ | T | 90 | 13 | 48 | 4819 | 11180 | 1.33 | 0.6564 |
| $R_5$ | X | 90 | 3 | 21 | 2062 | 7086 | 1.33 | 0.2305 |
| $R_6$ | X | 90 | 6 | 35 | 3526 | 8269 | 1.42 | 0.4341 |
| $R_7$ | X | 90 | 8 | 43 | 4314 | 8200 | 1.61 | 0.5637 |
| $R_8$ | X | 90 | 13 | 51 | 5097 | 8271 | 1.35 | 0.7117 |
| $R_9$ | T | 100 | 1 | 15 | 1502 | 7574 | 1.28 | 0.1632 |
| $R_{10}$ | T | 100 | 3 | 39 | 3897 | 7597 | 1.39 | 0.4937 |
| $R_{11}$ | T | 100 | 6 | 44 | 4391 | 8524 | 1.39 | 0.5782 |
| $R_{12}$ | T | 100 | 8 | 58 | 5784 | 11400 | 1.42 | 0.8631 |
| $R_{13}$ | T | 100 | 13 | 85 | 8510 | 12200 | 1.31 | 1.893 |
| $R_{14}$ | X | 100 | 1 | 23 | 2313 | 7918 | 1.53 | 0.2627 |
| $R_{15}$ | X | 100 | 3 | 31 | 3073 | 8104 | 1.39 | 0.3666 |
| $R_{16}$ | X | 100 | 6 | 50 | 5048 | 9420 | 1.38 | 0.7024 |
| $R_{17}$ | X | 100 | 8 | 60 | 5997 | 10450 | 1.45 | 0.9134 |
| $R_{18}$ | X | 100 | 13 | 87 | 8710 | 12680 | 1.38 | 2.0402 |
| $R_{19}$ | X | 110 | 1 | 28 | 2803 | 6400 | 1.38 | 0.3285 |
| $R_{20}$ | X | 110 | 3 | 51 | 5117 | 9844 | 1.39 | 0.7164 |
| $R_{21}$ | X | 110 | 6 | 61 | 6125 | 11560 | 1.41 | 0.9454 |
| $R_{22}$ | X | 110 | 8 | 69 | 6921 | 11740 | 1.45 | 1.174 |
| $R_{23}$ | X | 110 | 13 | 90 | 9011 | 12200 | 1.45 | 2.837 |

and produces well-controlled polymerization with relatively low polydispersities (25). The initiator efficiency increased by elevating the polymerization temperatures. The effect of the macrocyclic structure could not be denied especially on increasing the initiator percentage. Presumably, in that case, steric hindrance should increase to some extent. Therefore, the high molecular weight and the polydispersity values were recorded under the influence of those macrocycles.

Some successive kinetic studies were carried out in the case of diethyl-2-bromo-2-methylmalonate and benzhydrylbromide initiators using the formula 1 : 2 : 4 : 400 $M_1$: CuBr: I: MMA as indicated in Table 3, Table 4, Figures 4 and 5, respectively.

Generally, fast polymerization reactions were recorded in the case of DEBrMM system than in BhBr initiating system where the polymerization in the case of

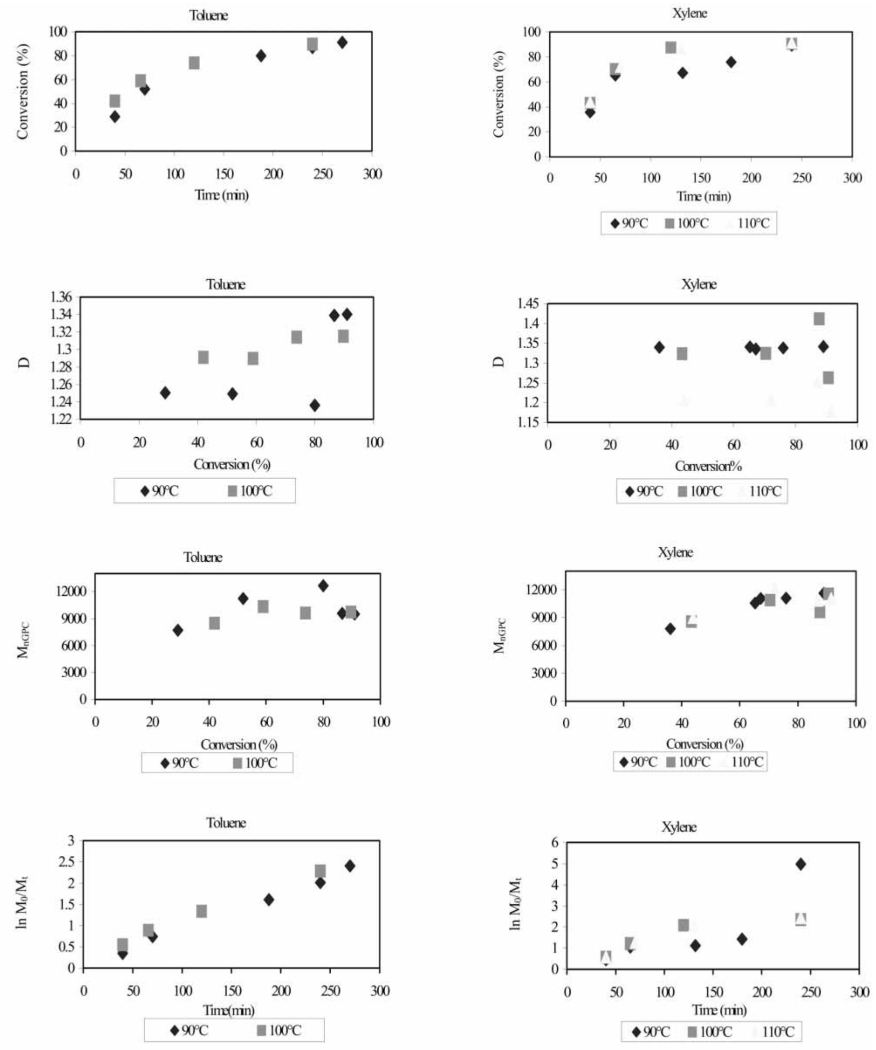

**Figure 4.** Kinetic plots for ATRP of MMA by using $M_1$ imine macrocycle/CuBr catalytic system in case of diethylmethylbromomalonate.

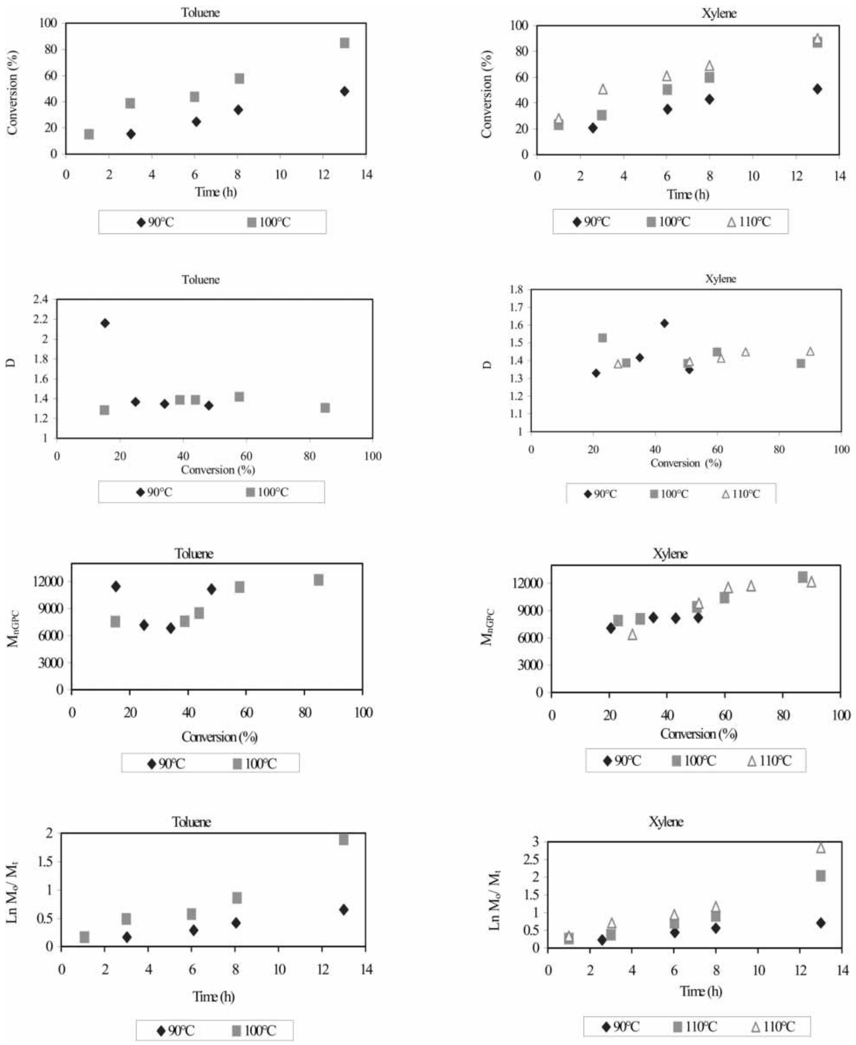

**Figure 5.** Kinetic studies plots for ATRP of MMA by using $M_1$ imine macrocycle/CuBr catalytic system in case of benzhydryl bromide.

DEBrMM system proceeded smoothly up to 90% conversion within 4 h at 100°C. In both cases, conversions continuously increased with the monomer consumption. Also, an almost linear plot of ln $[M_0]/[M_t]$ vs. time was clear especially at higher temperatures. This mostly indicated a constant concentration of the active species in addition to a certain amount of termination (i.e., $k_p$ $[p^*] = \text{constant}$) (10a, 29). A shorter induction period was observed in the case of the DEBrMM system in comparison with that in (BhBr) initiating system, especially at lower temperatures. The DEBrMM system showed lower polydispersities with relative agreement between the theoretical and GPC molecular weights. The deviations were presumably due to unidentified transfer process as previously indicated with respect to ethylbromoisobutyrate (25). In the case of benzhydrylbromide, relative higher polydispersities may be attributed to the expected side

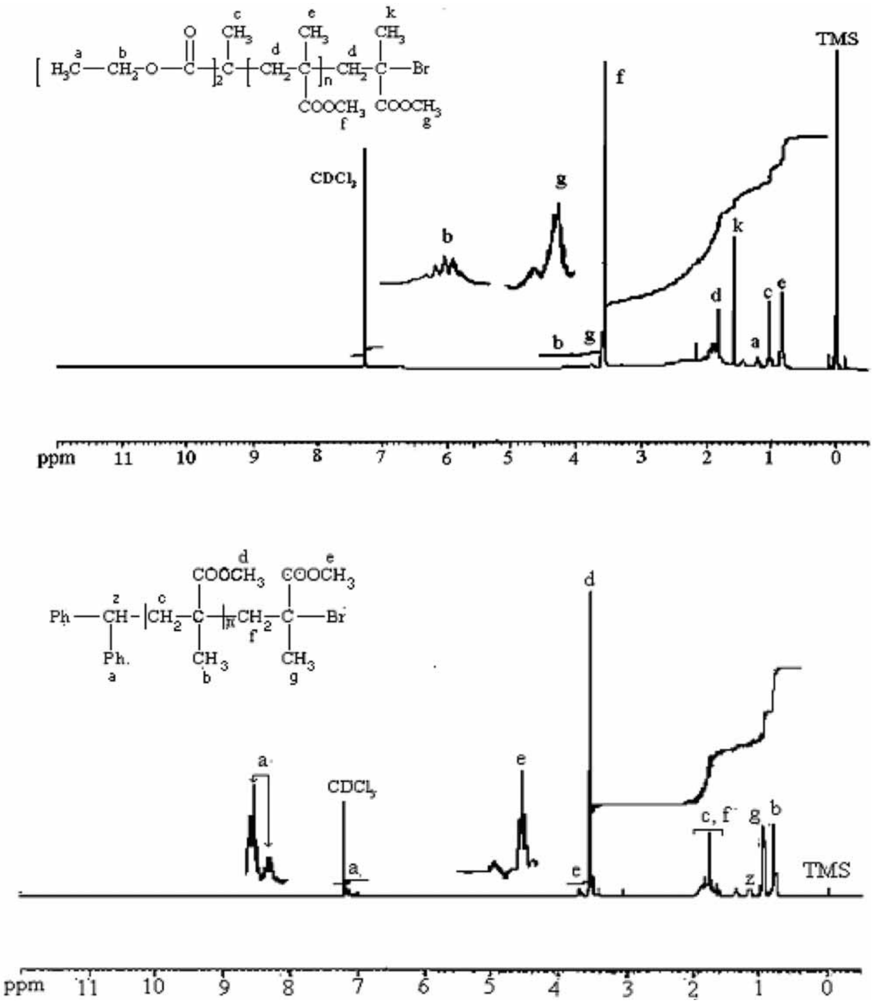

**Figure 6.** $^1$HNMR spectra of poly MMA initiated with diethylmethylbromomalonate and Benzhydrylbromide initiators, respectively.

reactions (i.e., chain coupling) in addition to some steric effects from the macrocyclic structure itself. Therefore, relatively slow initiation took place especially in lower temperatures. The situation was accompanied with a certain amount of termination increased at higher conversions, where the rate of propagation decreased with the monomer consumption (29). At higher temperatures, the molecular weights increased linearly with conversions and regular behavior was observed. Generally, in both cases, higher reaction rates and polydispersities with relative regular behavior were observed with respect to xylene more than in toluene. $^1$H NMR spectra indicated the well-known structures of the formed polymers by using DEBrMM and BhBr initiators in the ATRP polymerization reactions of MMA. That fact also confirmed that the diethylmethylbromomalonate and the benzhydrylbromide initiators displayed true polymerization reactions of MMA (see Figure 6).

## Conclusion

Finally, in light of the previous facts, those macrocycles may be used successfully to some extent as good catalytic systems in the ATRP of MMA and may be extended in the future to other monomers but with some restrictions. Those restrictions are related to the special reaction conditions that must be taken in consideration to attain successful ATRP. Obvious higher molecular weights are obtained due to the steric effects of those macrocycles that can slow down polymerization reactions. Therefore, the correct choice of the initiating system is one of the critical points with respect to the ATRP mediated with those macrocycles where the highly active and the functionalized ones are recommended.

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