Preparation and Characterization of Homo- and Co-Polymers of Some Vinyl Monomers via ATRP by Using Imine Macrocycle as Ligand

A. Amin[a]; M. H. Ayoub[a]; M. Abd El-Ghaffar[a]; B. Rieger[b]

[a] Polymers and Pigments Department, National Research Center, Dokki, Cairo, Egypt [b] Department of Materials and Catalyses, University of Ulm, Ulm, Germany

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A. AMIN,[1] M. H. AYOUB,[1] M. ABD EL-GHAFFAR,[1] AND B. RIEGER[2]

[1]Polymers and Pigments Department, National Research Center, Dokki, Cairo, Egypt
[2]Department of Materials and Catalyses, University of Ulm, Ulm, Germany

Imine macrocyclic ligand M_1 was involved in homo- and co-polymerization of some vinyl monomers via atom transfer radical polymerization technique (ATRP). Hereby, vinyl acetate, styrene and methyl acrylate monomers were homopolymerized. On the other hand, they were involved in copolymerization with MMA. $M_1 : CuBr : initiator : monomer$ percentages were $1 : 2 : 4 : 400$. ^1HNMR confirmed the structures of the resulting polymers. The thermal behaviors of some selected polymers were studied.

Keywords imine macrocycles, homopolymers, copolymers, ATRP, thermal analyses

Introduction

Atom transfer radical polymerization (ATRP) is one of the most recent and important advances in polymer chemistry (1). ATRP allows chemists to produce progressive new materials whether with respect to their architecture or composition in a well-defined manner (2–4). Through ATRP, a large variety of monomers can undergo controlled living polymerization in a facile way. Employing new ligands in the ATRP processes is an important approach to develop that technique (5, 6). In Cu based ATRP, some ligands were used such as unsubstituted bipyridyls and substituted ones (7, 8). Also, phenanthrolines (9), pyridyl-methanimines (10–12), and multi-dentate aliphatic amine ligands were involved (13). During the last decades, macrocyclic ligands were used as good catalytic systems with more than one active metal center (14–16). In the literature, imine macrocycle M_1 was chosen as a novel ligand in ATRP. M_1 essentially formed $(2 + 2)$ macrocycles, which was confirmed by single crystal analysis as viewed in Figure 1 (17).
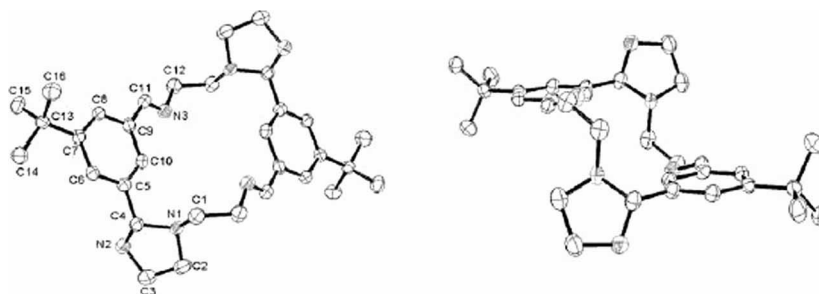
Figure 1. Isomers of M1 macrocycle- normal view and side view (hydrogens are omitted for clarity).

Experimental

Materials

All the monomers used such as methyl methacrylate (MMA), styrene (St), vinyl acetate (VA) and methyl acrylate (MA) were from Lancaster Synthesis Ltd., England. They were purified by filtration through an alumina column, collected in a Schlenk flask and stored under argon in the refrigerator. Benzhydrylbromide (BhBr), p-toluenesulfonylchloride (p-TsCl), ethyl-2-bromo propionate (Brpr), diethylbromomalonate (DEBrM) and diethyl-2-bromo-2-methylmalonate (DEBrMM) were received from Lancaster Synthesis Ltd., England. Toluene (T), o-xylene (X), acetonitrile and n-hexane were of pure grade from Merck Chemical Co., Germany. All the other chemicals (e.g., diethylene-triamine, copper (I) bromide were from Sigma-Aldrich Chemical Co., Germany and were used without further purification. Imine macrocycle M_1 was prepared as in the literature (17, 18).

Measurements

Molecular weights and polydispersities of the samples were determined by gel permeation chromatography (GPC) using a Waters Model 410 differential refractometer with $10^3 – 10^5$ Å ultrastyragel columns connected in series. THF was used as the eluent at a flow rate $1 \, ml \, min^{-1}$. A series of near monodisperse PMMA and PSt homopolymers were used as calibration standards. ^1H NMR spectra were recorded using 400 MHz Bruker AC-200 and AC-400 spectrometer, in CDCl$_3$. Thermal analyses were carried out on a PE-DSC differential scanning calorimeter using sample weights of 3–5 mg. The crystal data of M_1 were collected on a Rigaku AFC7S four-circle diffractometer using graphite monochromatized Mo-Kα radiation, $\lambda = 0.71073$ Å (17).

General ATRP Polymerization Technique

The proper amounts of the ligand, CuBr and solvent (toluene or xylene) were added to a glass vial then it was purged with argon and immersed in a thermostated oil bath. The monomers and the initiators were successively added via syringes under argon. In the case of (BhBr) and (p-TsCl) initiators, the initiator amount was dissolved in a small

fraction of solvent and then slowly added to the reaction mixture to enhance the initiation efficiency. After a definite time period, the vial was opened and the formed polymer was dissolved in (THF) and precipitated in n-hexane. The conversion was gravimetrically determined. The exact molecular weights and polydispersities were verified via GPC. Accordingly, the polymer sample was redissolved in THF, passed through an alumina column and reprecipitated in n-hexane. The precipitated polymer was collected and dried under vacuum. The copolymerization processes were tried basically between (MA), (St.), (VA) and MMA, in 50/50 percent for each co-monomer relative to its molecular weight. The structures of the formed polymers were identified by ^{1}H NMR (Table 1).

Results and Discussion

According to a previous comparable study (18), the molar ratios of $M_1 : CuBr : Initiator : monomer$ were recommended to be $1 : 2 : 4 : 400$ in the case of using the macrocyclic ligand M_1. VA monomer failed to homopolymerize by using the ordinary ATRP initiators. That may be explained by its special nature as an electron rich monomer, which requires both a catalytic and highly active initiating system (19). With respect to (MA), two initiators were tried, such as (p-TsCl) and (Brpr). (Brpr) displayed a relatively good ATRP for MA in spite of some deviation whether with respect to the molecular weight values or the polydispersities. That was presumably explained by the influence of those bulky macrocycles. In styrene polymerization, the reactions were conducted at several temperatures and by using various initiating systems to choose the most convenient one. Thereby, (BhBr), (p-TsCl), (DEBrM) and (DEBrMM)) were used. It was clear that (p-TsCl) was an absolutely unsuitable initiator for ATRP polymerizations by using those macrocycles because of some steric and electronic factors (20). (DEBrM) showed successful ATRP for styrene monomer where the carbon centered radicals contain two ester groups of malonates, possess relatively low lying SOMOs, and react preferentially with electron rich olefins that contain high energy HOMOs (20). (BhBr) managed in copolymerizing MA, St and VA monomers with MMA. Copolymerization of MA with MMA was the fastest reaction with the highest conversion then that of VA and St, respectively with MMA. The polydispersity was relatively high and was attributed to the effect of the macrocycles. (DEBrMM) recorded low polydispersities where some kind of transfer reactions, (20) led to lower GPC molecular weight values. The structures of the obtained homo- and co-polymers were proved with the ^{1}H-NMR as in Figures 2–5. The ^{1}H-NMR in the case of st- homopolymer was difficult to obtain.

Thermal Analyses of Some Selected ATRP Polymers

The thermal behavior of the previously prepared MMA copolymers (C_1–C_5) was studied and compared with the MMA homopolymers in order to see the effect of copolymerization on that behavior. The studied MMA homopolymer probes were prepared via typical ATRP initiated with both (BhBr) and (DEBrMM) initiators (e.g., S_1–S_5 and S_6–S_{10}, respectively) (18). TGA and DSC were carried out. Firstly, for TGA, both homo-poly MMA categories (e.g., (BhBr-MMA) and (DEBrMM-MMA)) showed distinguished behavior other than that of the copolymers. The thermogravimetric degradation curves of both MMA homo- and copolymers were represented as in Figure 6. The homopolymers maintained their initial mass up to 200°C, then, lightly degraded gradually up to 330°C. Afterward,

Table 1
Polymerization experiments

| Sample	M.	Initi.	Solv.	Temp. (°C)	Time (h)	Conv. (%)	$\bar{M}_{nth}$	$\bar{M}_{nGPC}$	$\bar{M}_w/\bar{M}_n$
H_1	MA	pTsCl	T	90	4	64.9	5,587	33,308	1.755
H_2	MA	Brpr.	T	90	2.30	60	5,165	11,339	1.422
H_3	St.	BhBr.	T	100	10.30	18.73	1,948	23,120	2.622
H_4	St.	BhBr.	T	100	9.15	22	2,288	8,960	1.934
H_5	St.	BhBr.	X	120	12.30	35	3,640	33,559	1.931
H_6	St.	pTsCl	T	100	9.20	30	3,120	13,886	1.999
H_7	St.	DEBrMM	T	90	15	6.041	628	20,925	1.739
H_8	St.	DEBrM	T	90	15.15	47.5	4,940	7,083	1.365
C_1	MMA/MA	BhBr	T	90	24	41.58	7,743	6,349	1.596
C_2	MMA/St.	BhBr	T	90	24	24	4,899	7,392	1.76
C_3	MMA/VA.	BhBr	T	90	48	34.13	6,355	7,878	1.645
C_4	MMA/VA.	DEBrMM	T	90	48	60	11,359	5,862	1.538
C_5	MMA/St.	DEBrMM	T	90	48	58	11,839	5,727	1.624
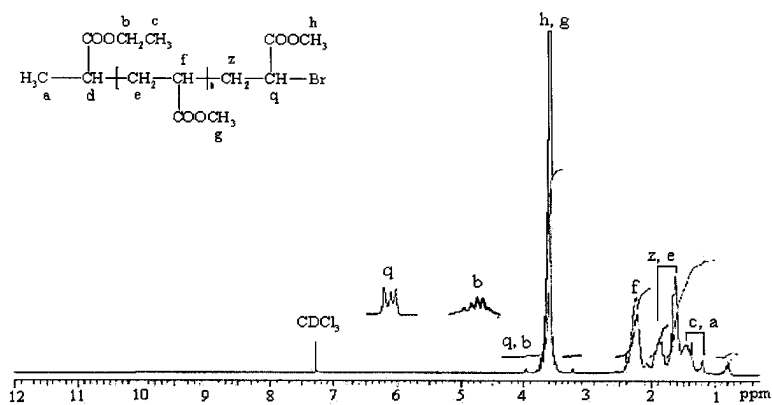
Figure 2. ^{1}H-NMR spectra of poly MA initiated with ethyl-2-bromopropionate.
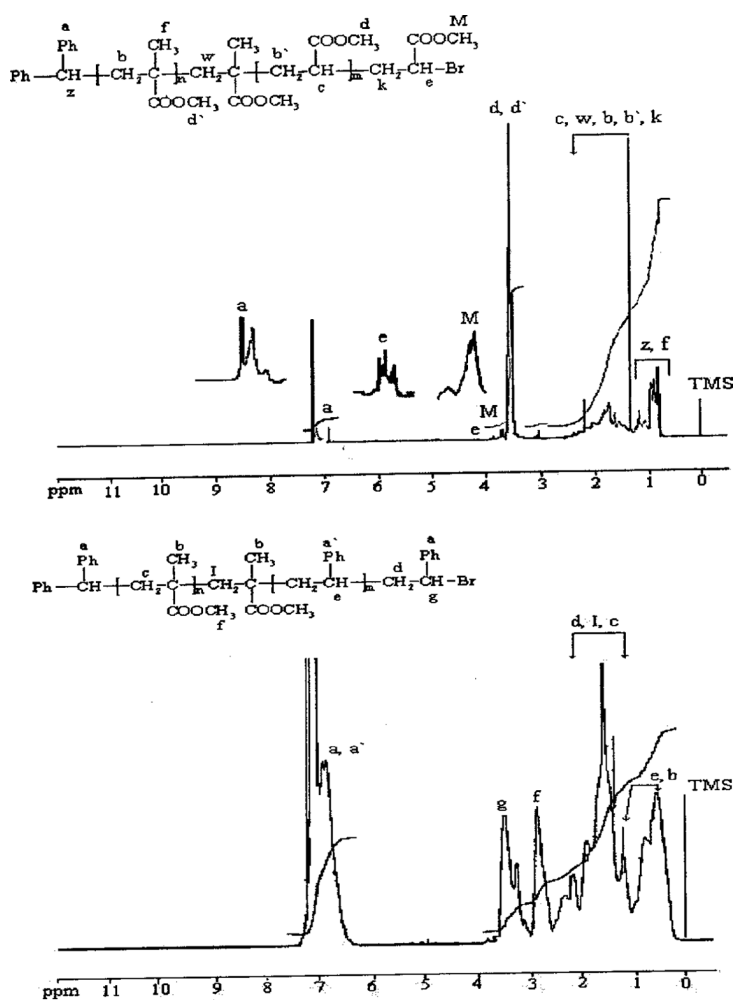

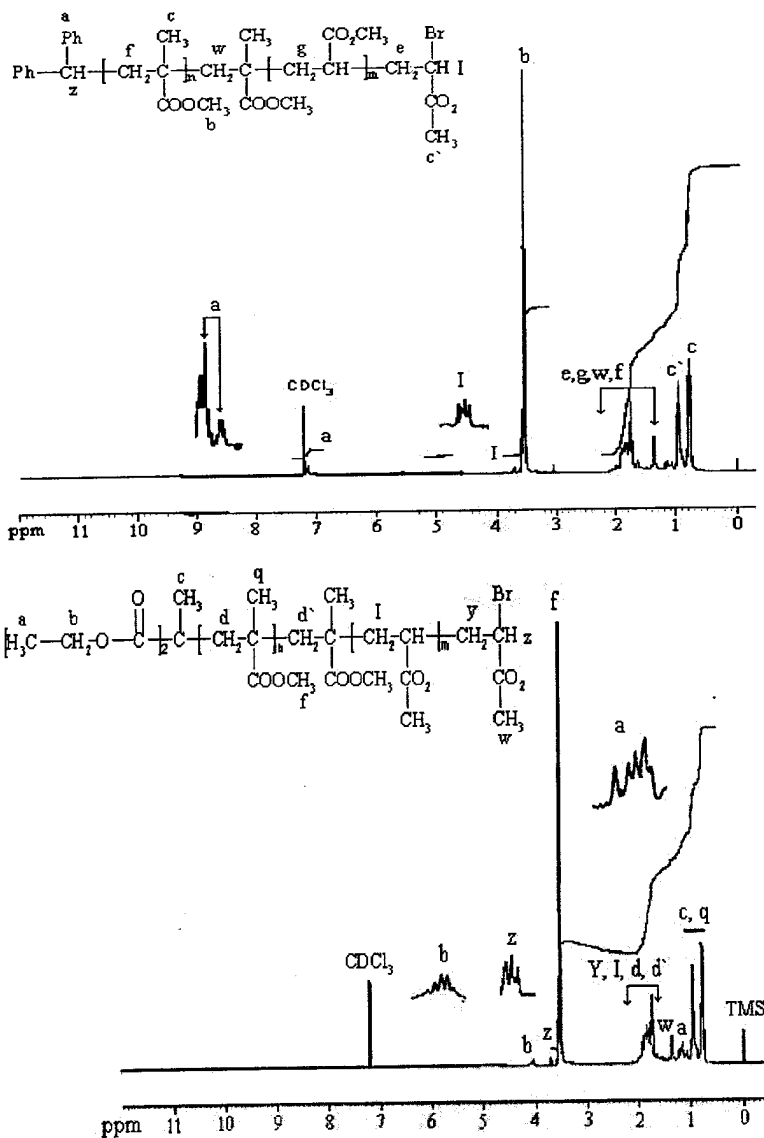**Figure 3.** ^{1}H-NMR of C_1, C_2, respectively.

Figure 4. ^{1}H-NMR of C3, C4, respectively.

a complete and abrupt degradation of the polymer was observed losing its mass. The situation in the copolymers was slightly different depending on the shared co-monomer in each case. DSC results were compiled as in Table 2. The relevance between the polymerization conditions (e.g., temperature, initiator, etc.) and the attained molecular weights was very obvious. Accordingly, the glass transition temperature (T_g) was strongly affected by the variation in the molecular weight values. With respect to the copolymers, the effect of temperature and the solvent were stable where 90°C and toluene were used as general copolymerization conditions. Another factor was observed relating to the nature of the comonomers. Generally, the benzhydryl copolymers with the higher
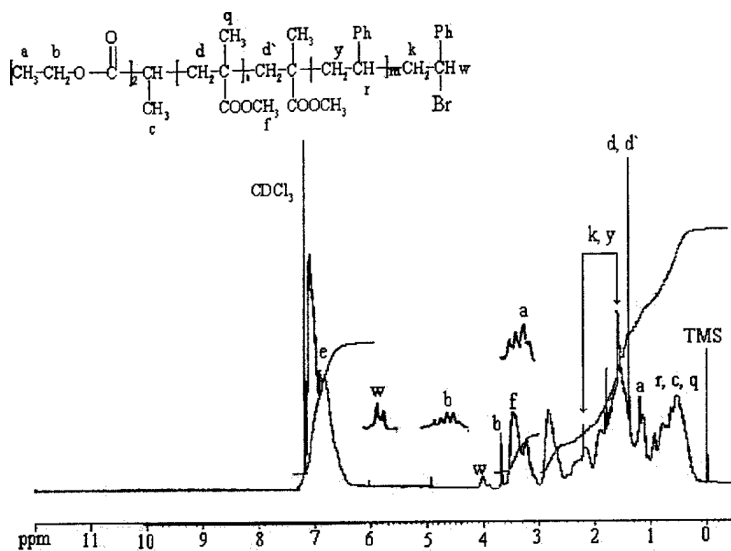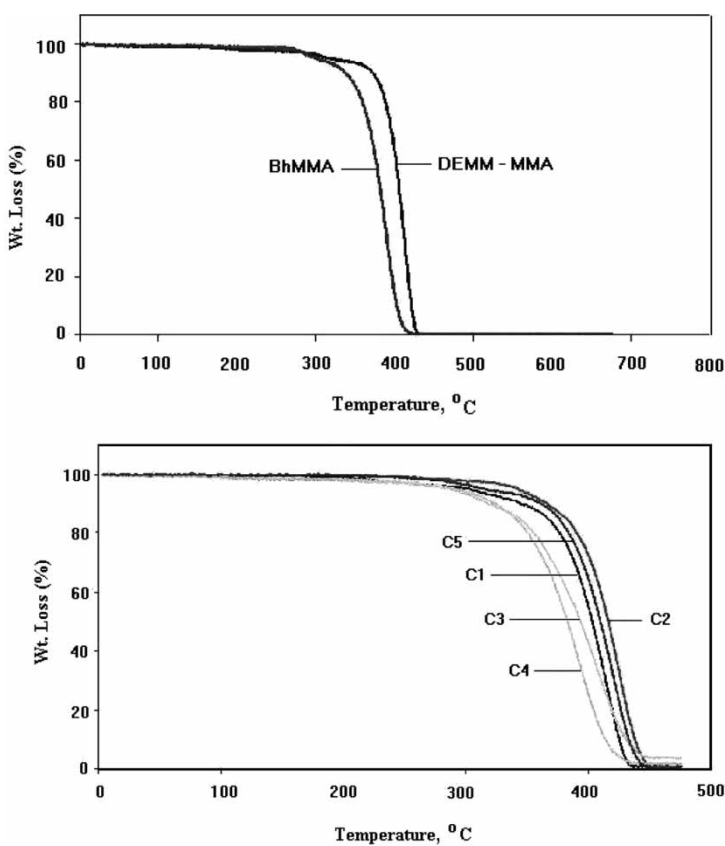
Figure 5. ^{1}H-NMR of C5.

Figure 6. TGA analyses for both MMA homo- and copolymers, respectively.

Table 2
DSC data for MMA homo- and copolymers

Sample	Temp. ($^\circ$C)	Solvent	Conv. (%)	M.wt (g/mol)	$\bar{M}_w/\bar{M}_n$	T_g ($^\circ$C)	ΔC_p (J/g$^\circ$C)
S_1	90	T	34.03	6,849	1.346	103.54	0.374
S_2	90	X	43.1	8,200	1.610	103.54	0.338
S_3	100	T	57.77	11,400	1.418	112.86	0.472
S_4	100	X	59.9	10,450	1.448	110.98	0.437
S_5	110	X	69.13	11,740	1.449	109.26	0.375
S_6	90	T	86.69	9,594	1.339	110.12	0.52
S_7	90	X	89	11,623	1.342	112.11	0.322
S_8	100	T	89.82	9,745	1.315	111.94	0.462
S_9	100	X	90.63	11,573	1.263	110.28	0.331
S_{10}	110	X	91.5	11,080	1.177	105.98	0.317
C_1	90	T	41.58	6,349	1.596	54.66	0.387
C_2	90	T	24	7,392	1.76	94.32	0.439
C_3	90	T	34.13	7,878	1.645	97.75	0.557
C_4	90	T	61	5,862	1.538	89.59	0.529
C_5	90	T	58	5,727	1.624	83.94	0.503

molecular weights recorded higher glass transition temperatures than those of the lower molecular weights in malonates.

Conclusions

Styrene and methylacrylate monomers managed to homopolymerize by using diethyl-2-bromomalonate and ethyl-2-bromopropionate initiators, respectively in the presence of macrocyclic ligand M_1 via true ATRP. Consequently, successful copolymerizations were carried out by using different comonomers (e.g., MMA/VA, MMA/MA and MMA/St) and various initiating systems. ^{1}H-NMR spectra proved that true ATRP successfully happened to attain well defined structures. The thermal behaviors of the homopolymers were completely different than that in copolymers. T_g values were strongly affected by the different comonomers. Generally, ATRP processes by using imine macrocycle M_1 are quite possible with some precautions to avoid its steric and electronic factors where suitable reaction conditions facilitate ATRP for several vinyl monomers.

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