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Three-Arm Star Homo- and Block Co-Polymers Via Atom Transfer Radical Polymerization

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Star homopolymers of some vinyl monomers such as methyl methacrylate, n-butyl methacrylate and styrene (MMA, nBMA, St.) were prepared by using a N,N,N'-tetramethylethylenediamine ligand/CuBr catalytic system via atom transfer radical polymerization (ATRP). A three armed benzene based core was successfully used as initiator. Low polydispersities and regular molecular weight values were obtained in most cases, especially at low conversions. MMA and BMA showed comparable behavior where controlled and true ATRP was observed even at high conversions. However, styrene monomer recorded irregular high polydispersities at high conversions in spite of the relatively low molecular weight values. Some block copolymers were obtained using MMA homopolymer as macroinitiator with the same strategy of ATRP. ¹H-NMR confirmed the structures of the resulting polymers. Transmission electron microscopy (TEM) proved the nano-structure of the star polymers. The thermal behavior of the MMA star homo and copolymers was studied. The effect of the star shape on thermal behavior was very clear with respect to the linear ones.

Keywords star polymers, MMA, n-BMA, styrene, thermal behavior, nano-structure

Introduction

Star polymers have become of great interest in recent years because of their unique rheological and physical properties and potential applications (1–4). The synthesis and characterization of star polymers continue to be vital areas of research in the pursuit of structure-property relationships (1). In 1948, preparation of star polymers was first documented by Schaeffgen and Flory (5). However, preparation of well-defined multi-armed polymers remained a challenge until the advent of living polymerization techniques. In 1956, Morton and co-workers were able to take advantage of the living anionic polymerization method to synthesize well-defined four-armed polystyrenes (6). Although, the product was a mixture of four- and three-arm stars, this work eventually led to further challenges. Regardless of the method of polymerization (ionic, group transfer, or radical), preparations of star polymers have been practiced using two different methodologies, via the so-called arm-first (7, 8) and core-first (9–11) methods. Recently, several living and controlled radical polymerization techniques were used in the synthesis of star polymers (9). Such methods are atom transfer radical polymerization

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(ATRP) (12), nitroxide-mediated polymerization (NMP) (13), iniferter techniques (9) and reversible addition-fragmentation chain transfer (RAFT) polymerization (14). The potential of ATRP as a powerful tool for the synthesis of new materials arises from the simplicity of the method, range of monomers that can be polymerized and the control over end group functionality. Here, the core-first method was involved. In that method, a multi-functional initiator (the core) was first synthesized followed by the extension of arms by monomer addition. In the core-first approach, it is easy to control the structure of the star polymers. Accordingly, Haddleton et al. (15) first prepared trifunctional phenolic ester-based initiators on the way to preparing three-arm star polymers via ATRP. However, no additional studies were carried out. Hence, in this publication, we extensively studied the polymerization, structural and thermal behavior of the three-arm star polymers of MMA, St and n-BMA and some prepared copolymers. Thus, N,N,N'-tetramethylethylenediamine ligand/CuBr catalytic system was involved in successful ATRP, using 1,3,5-(2-bromo-2'-methylpropionato) benzene as the initiator.

Experimental

Materials

Methyl methacrylate (MMA), n-butyl methacrylate (n-BMA), styrene (St.), vinyl acetate (VA) and methylacrylate (MA) monomers were purified by passing through an alumina column, collected and stored under argon. Copper (I) bromide and N,N,N'-tetramethylethylenediamine were from Fluka. All solvents were of pure grade supplied by Merck Chemical Company, Germany. All other chemicals were used as received. 1,3,5-(2-bromo-2'-methyl-propionato) benzene initiator was prepared as in the literature (15).

Measurements

$^1\text{H-NMR}$ spectra were recorded on a Varian Mercury-Oxford-300 MZ. TMS was used as internal standard and CDCl_3 as the major solvent. Molecular weights ($M_{n\text{GPC}}$) and polydispersities ($\bar{M}_w/\bar{M}_n = D$) of the samples were determined by gel permeation chromatography (GPC) using Agilent-1100 GPC-(Agilent Technologies, Germany). The refractive index detector was G-1362A with $100\text{-}10^4\text{-}10^5 \text{ \AA}^\circ$ Ultrastyrigel columns connected in series, (Germany). THF was used as the eluent with flow rate 1 ml min^{-1} . Commercially available (poly)methyl-methacrylate and polystyrene standards were used to calibrate the columns.

Thermal analyses were carried out on a Shimadzu-DSC differential scanning calorimeter using sample weights of 2 mg. Transmission electron microscopy (TEM) was used for the investigation of the morphology of some chosen polymer samples. Measurements were acquired with a Zeiss-electron spectroscopic microscope operated at 60KV. Samples were prepared by drop casting the suspension of the polymers onto carbon-coated copper grids, followed by evaporation of the solvent in air. Fine and Nano structure was expected for the prepared star polymers. Therefore, the suspended nanoparticles were stained by uranyl acetate for clarity of the images. Negatives were digitized at 600 dpi, and the corresponding images were analyzed and prepared for presentation by several software packages, including Adobe Photoshop.

Polymerization Experiments

The required amounts of the CuBr, ligand, monomer and solvent were added subsequently to a glass vial then sealed and flushed with argon for 15 min before adding the initiator and starting the polymerization. Toluene was used as the major solvent at all temperatures (90°C, 100°C, and 110°C). The initiator was dissolved in part of the toluene and added slowly to the reaction vessel, which was placed in a thermostated oil bath for the desired time intervals. The reactants were added in molar ratio (ligand: CuBr: initiator: monomer = 6:3:1:100). The GPC measurements were carried out on polymer samples previously purified by passing their solutions in THF through alumina column then precipitated and dried. The copolymerization experiments were conducted at 90°C in toluene where MMA homopolymer was used as macroinitiator.

Results and Discussion

Due to the importance and vitality of the star polymers, our research group was interested in the preparation and characterization of those materials. The three-arm star polymers were prepared by using the 1,3,5-(2-Bromo-2'-methyl-propionato) benzene tri-functional initiator via ATRP with the core first methodology at different temperatures (i.e., 90, 100, 110°C) according to each monomer. Kinetic studies were carried out in the case of MMA, St and n-BMA as summarized in Tables 1, 2 and represented in Figures 1–3. In MMA, the polymerization was conducted at 90°C and 100°C in toluene. The MMA polymerization behavior was more regular than the others with respect to molecular weight values or the polydispersities as seen in Table 1 and Figure 1. Generally, fast and controlled polymerization reactions were found in the case of MMA up to 94% conversion with observed linear kinetic plots. Conversely, the polymerization rate of styrene was much slower

Table 1
ATRP of the three arm star MMA homopolymers

Entry	Temp.	Time	Conv. (%)	$M_{n,th.}$	$M_{n,GPC}$	D	M_o/M_t	Ln M_o/M_t
P1	90	0.25	30	3004	4504	1.1	1.43	0.36
P2	100	0.25	42	4205	9200	1.12	1.72	0.54
P3	90	0.5	63	6308	7658	1.2	2.70	0.99
P4	100	0.5	85	8610	13625	1.22	7.14	1.97
P5	90	1	79	7909	12313	1.24	4.76	1.56
P6	100	1	86	8660	15140	1.23	7.41	2
P7	90	1.5	83	8310	14896	1.29	5.88	1.77
P8	100	1.5	87	8710	14163	1.37	7.69	2.04
P9	90	2	85	8510	14452	1.33	6.67	1.90
P10	100	2	88	8771	9559	1.31	8	2.08
P11	90	2.5	86	8610	12215	1.32	7.14	1.97
P12	100	2.5	89	8811	11433	1.36	8.33	2.12
P13	90	3	88	8811	14306	1.48	8.33	2.12
P14	100	3	94	9411	14197	1.43	16.67	2.81

Table 2
ATRP of the St. and n-BMA three arm star homopolymers

Entry	Time h	Temp.	Conv. (%)	M_{nth}	M_{nGpc}	D	M_o/M_t	L_n M_o/M_t
S1	5	100	24	2496	2722	1.37	1.32	0.28
S2	5	110	40	4160	7703	1.2	1.67	0.51
S3	15.40	100	81	8424	12860	1.84	5.26	1.66
S4	17	110	86	8944	11125	1.72	7.14	1.97
S5	19.15	100	86	8944	9964	2	7.69	2.04
S6	18.55	110	90	9360	9542	2	10	2.30
S7	20	100	90	9360	10624	2	10	2.30
S8	20.20	110	92	9568	10346	2.2	12.5	2.53
S9	21	110	92	9568	10853	2.5	12.5	2.53
B1	1	90	69	9812	10105	1.3	3.23	1.17
B2	0.5	100	73	10381	10631	1.29	3.70	1.31
B3	2	90	73	10381	10674	1.4	3.70	1.31
B4	2.5	100	94	13367	13597	1.5	16.67	2.81
B5	3	90	94	13367	13617	1.59	16.67	2.81
B6	3	100	96	13651	13882	1.69	25	3.22
B7	4	90	96	13651	14550	1.67	25	3.22
B8	4	100	99	14078	14979	1.58	100	4.61

S and B refer to styrene and butyl methacrylate star homopolymers, respectively.

than that in MMA, reaching only 40% after 5 h at 110°C. In general, the rate of polymerization seems to be reduced when steric hindrance is increased on either the ligand or the monomer (16). However, the ligand here has no such effect, but actually the styrene monomer is bulkier than MMA. That effect was evidenced by not only a decrease in rate, but also an associated increase in the polydispersity values. Accordingly, the styrene polymerization recorded higher polydispersities at higher conversions as shown in Table 2. On the other hand, the polymerization rate in the case of n-BMA was relatively close to that of MMA, especially at higher temperatures. However, higher polydispersities were observed at higher conversions as indicated in Table 2, (e.g., $D = 1.5$ at 94% conversion). This may be explained by the decrease in number of free radicals at higher conversions, where the possibility of termination would be strongly present (17). Successive copolymerization experiments were carried out involving MMA three-arm star homopolymer as macroinitiator (mI) with different molecular weights for further polymerization with St., MA and VA monomers (e.g., MMA-St, MMA-MA, and MMA-VA), as indicated in Table 3. Regardless of the generally higher polydispersity and molecular weight values than the predicted ones for normal ATRP, controlled polymerization was expected and evidenced by the well-defined structures of the formed homo- and copolymers obtained by the 1H -NMR as indicated in Figures 4–6. TEM was actively used to confirm the specific nano structure of the star polymers. Consequently, as an example, TEM was applied on the MMA star homo- and co-polymers with St., MA and VA monomers, as shown in Figure 7. Generally, fine particles were observed and required staining with uranyl acetate. The MMA-MA copolymer showed relatively

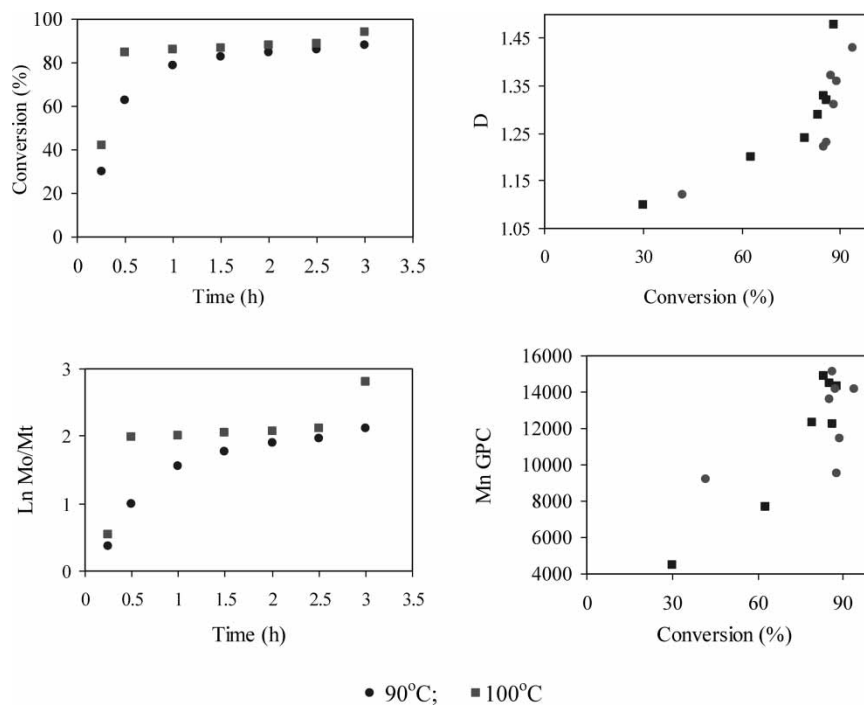


Figure 1. Kinetic plots for the MMA three-arm star homopolymers prepared via ATRP.

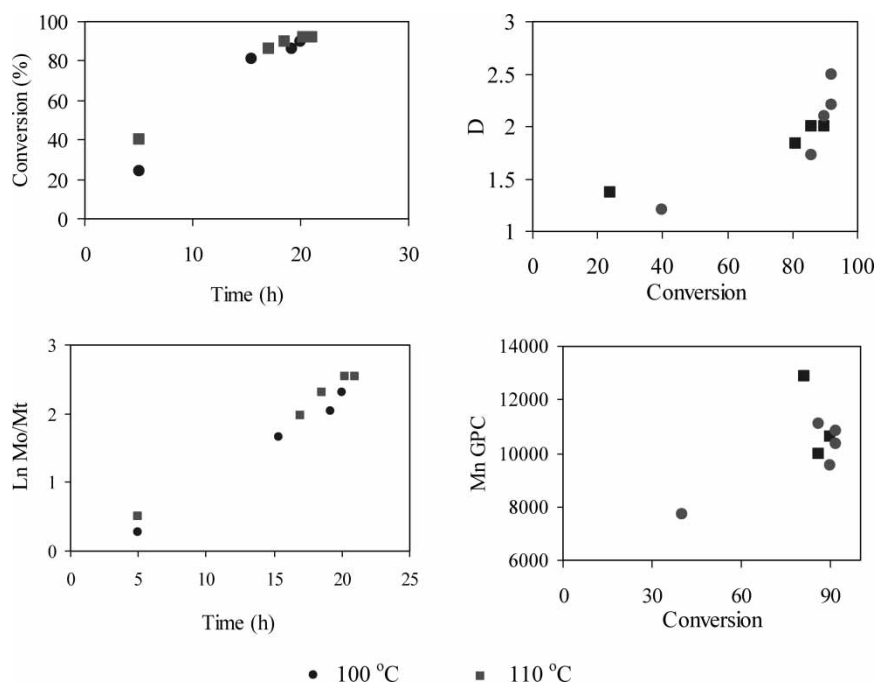


Figure 2. Kinetic plots for the St. three-arm star homopolymers prepared via ATRP.

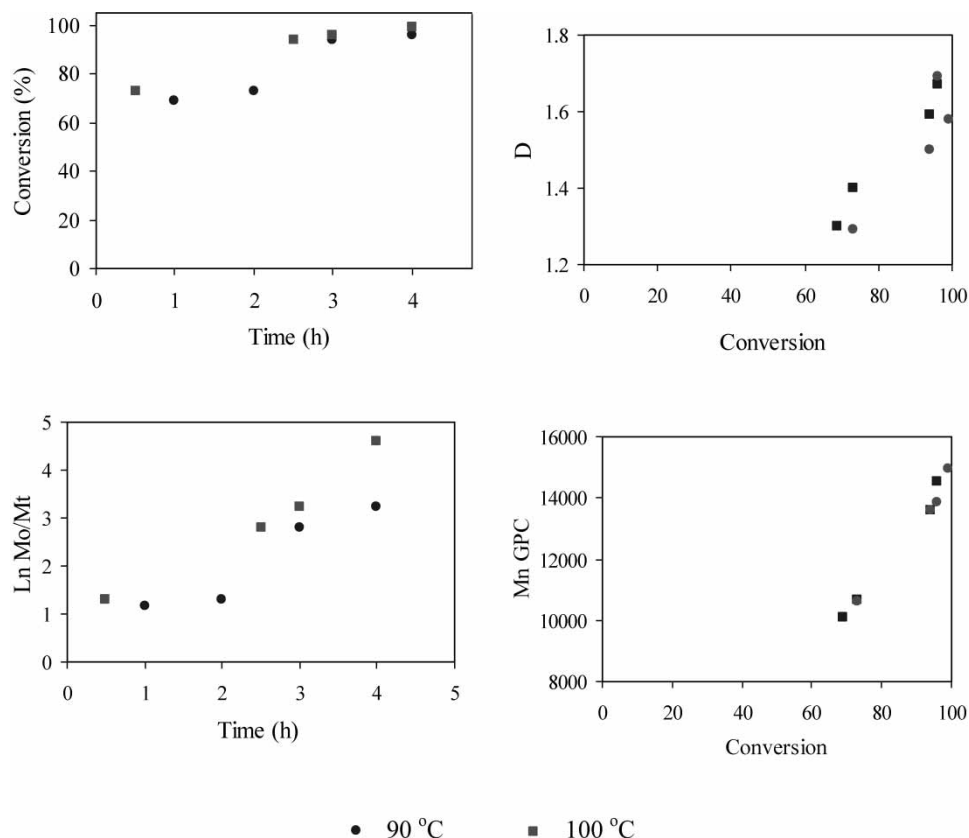


Figure 3. Kinetic plots for the n-BMA three-arm star homopolymers prepared via ATRP.

clear nanoscale domains. Successive thermal studies were carried out on the MMA star homo- and co-polymers and compared with the linear analogs. The linear MMA polymers were prepared via normal ATRP using benzhydrylbromide as initiator at comparable polymerization conditions of the star systems (17). The star polymers demonstrated observed thermal stability greater than that of the linear analogs as indicated in Table 4. Obviously, that behavior revealed the difference in T_g values

Table 3
ATRP copolymerization of MMA macroinitiator with St., MA and VA

Co-polymer	Time (h)	Temp.	Conv. (%)	Mn MMA (mI)	$M_{n\text{th}}$	$M_{n\text{GPC}}$	D
MMA-St	21.30	90	43	8334	14262	18816	1.49
MMA-MA	21.30	90	40	6479	11613	16485	1.68
MMA-VA	21.30	90	42	6751	11722	16213	1.75

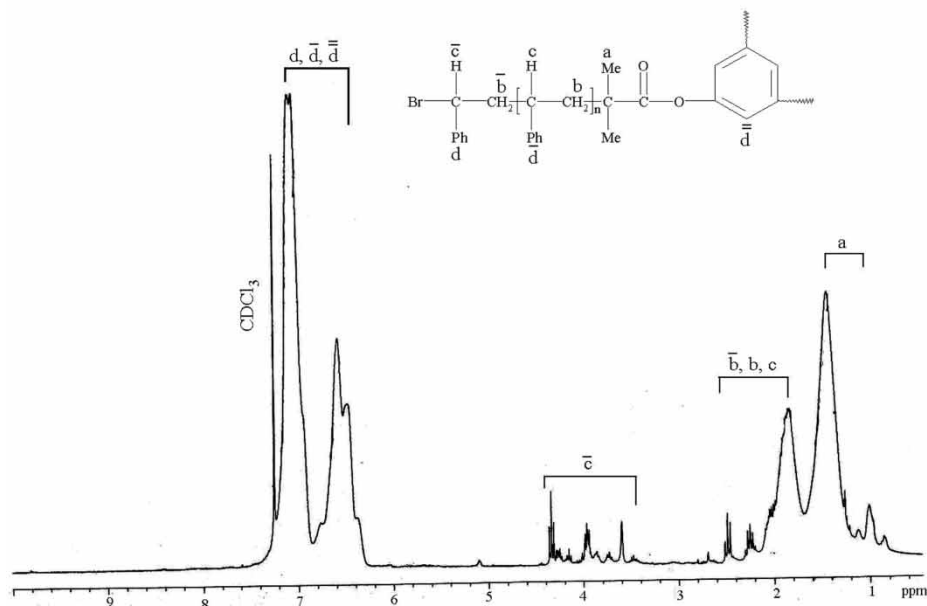
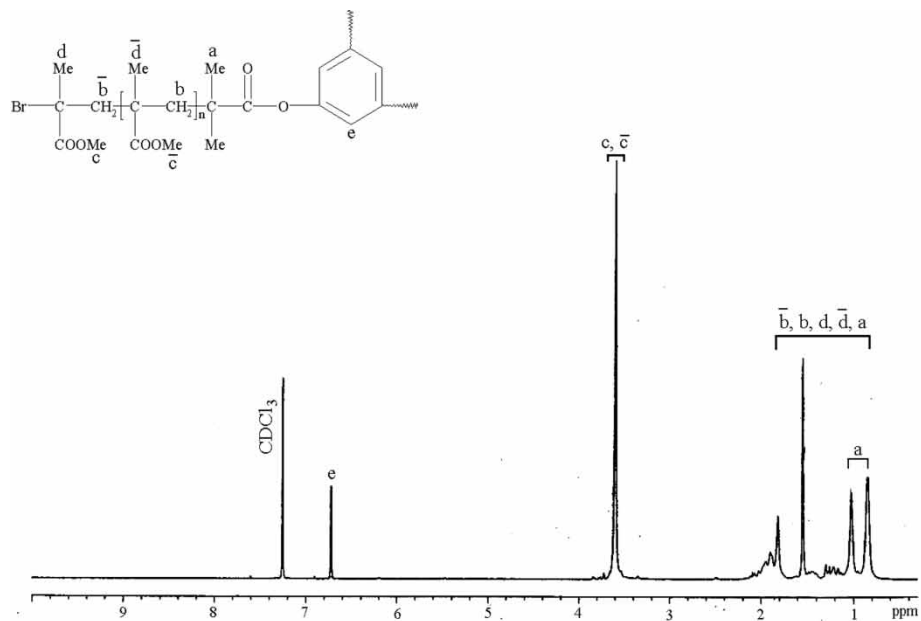


Figure 4. ¹H-NMR spectra of MMA and St. three-arm star homopolymers.

between the linear and the star polymers (e.g., T_g for MMA linear was 110°C and increased to 119.8°C for the star one). The same situation was found in the case of the copolymers (e.g., T_g of the MMA-St linear copolymer was 94°C whereas, that of the star one was 129.3°C).

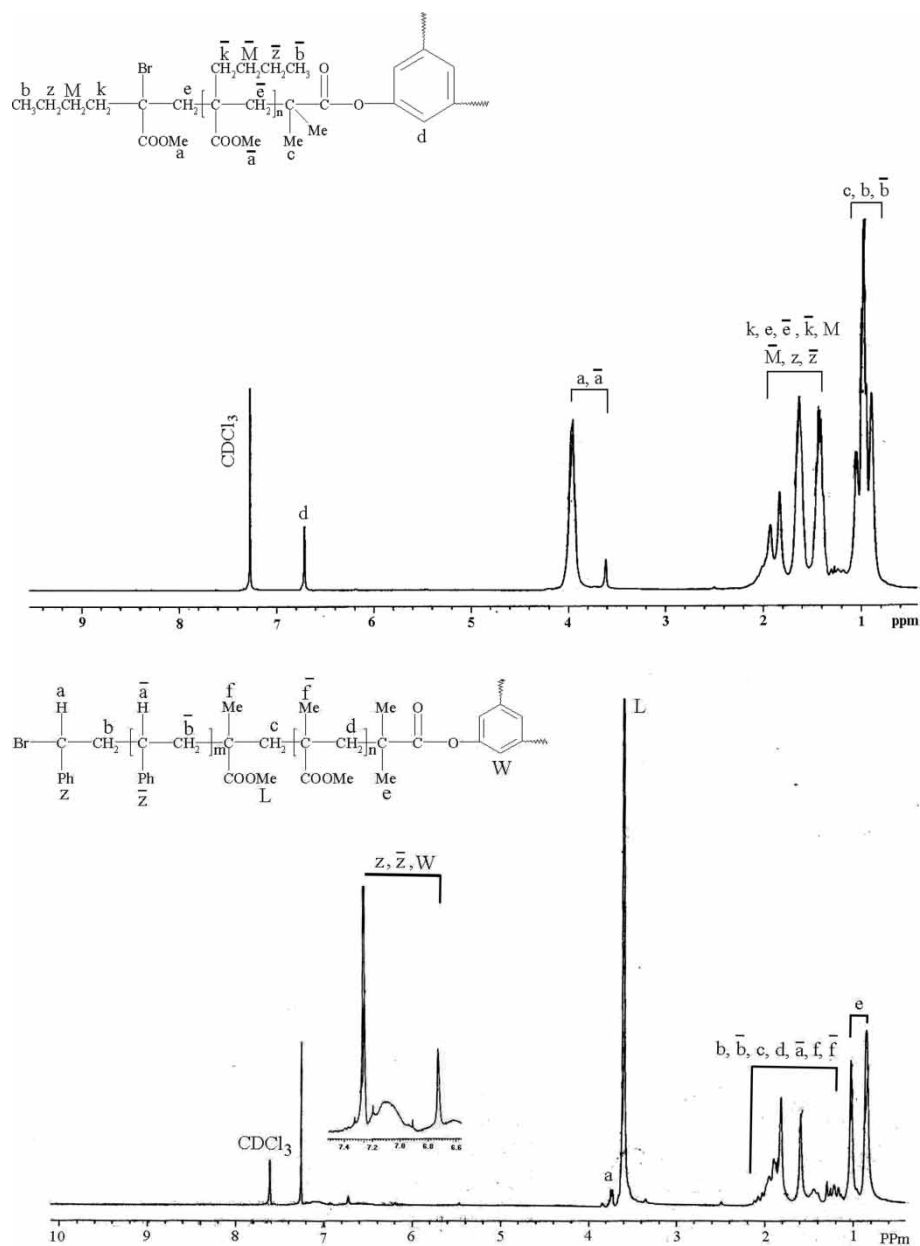


Figure 5. ¹H-NMR spectra of the three-arm star n-BMA homopolymer and MMA-St copolymer.

Conclusions

Some of the three-arm star homo- and copolymers were prepared via ATRP, using core-first methodology and a trifunctional initiator was used. Several studies were carried out to evaluate their behavior. Kinetically, linear kinetic plots were observed

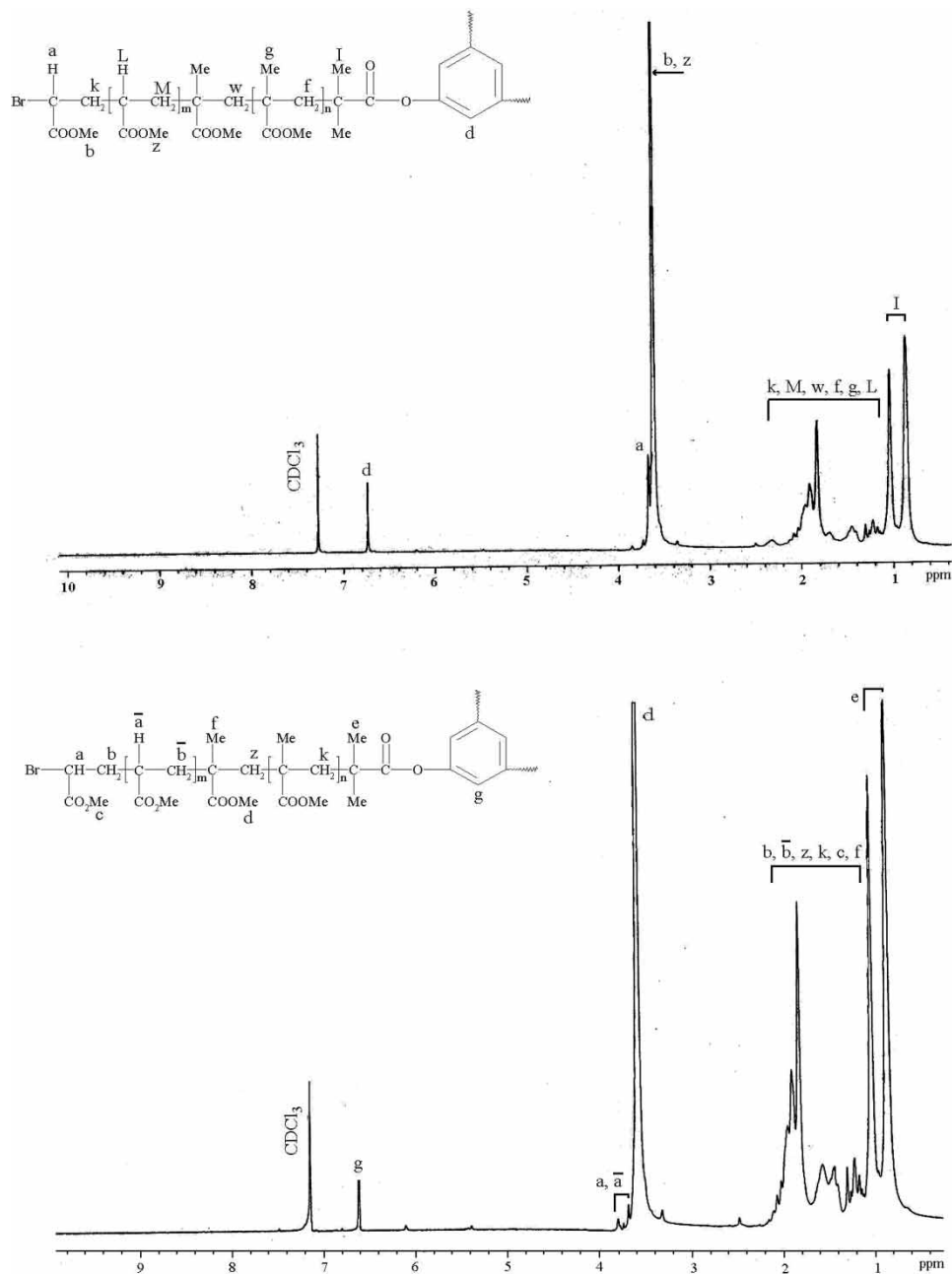


Figure 6. ¹H-NMR spectra of the three arm star MMA-MA and MMA-VA copolymers.

where conversion increased linearly with time. Higher polydispersity values were observed at higher conversions, especially in the case of styrene due to the monomer steric effect. Although higher polydispersities were recorded, uniform well-defined structures were obtained and proved through ¹H-NMR. Nano structures were clearly

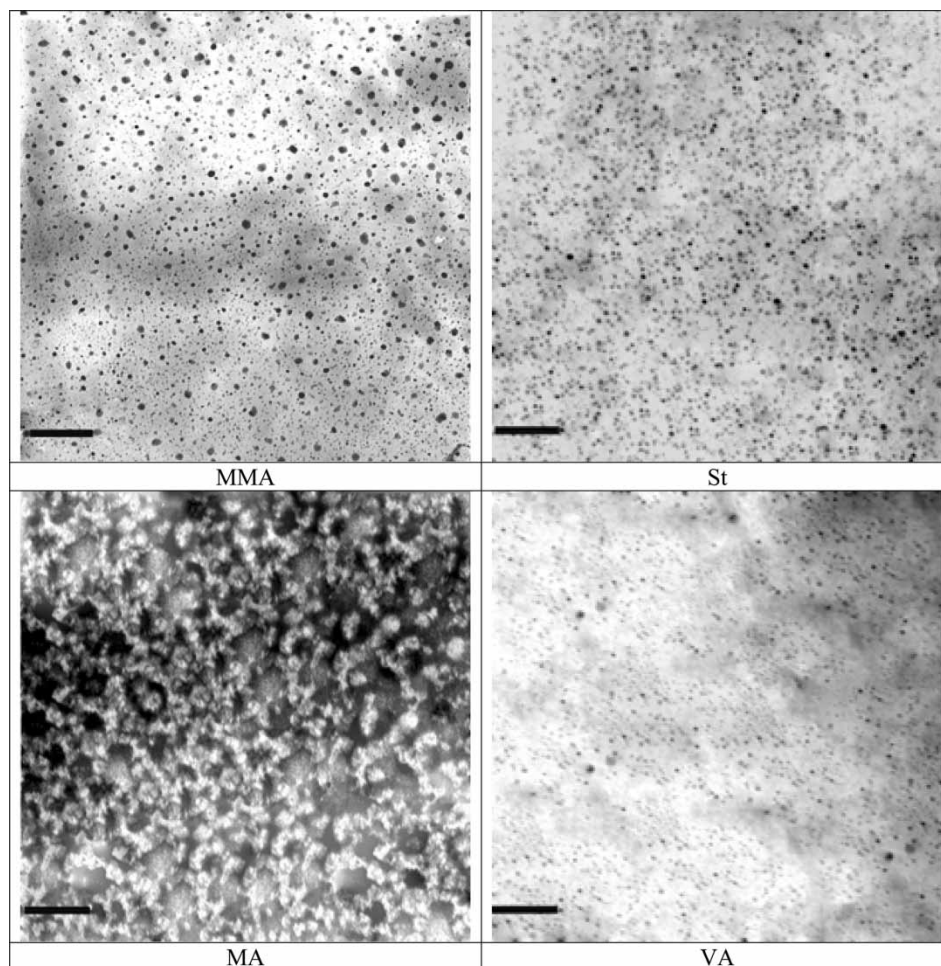


Figure 7. TEM images of three-arm star MMA homopolymer and MMA-copolymers with St, MA and VA, respectively. (Black bar = 150 nm).

Table 4
The thermal behavior of some three arm star polymers and their linear analogs

Entry	Polymer type	Time (h)	Conv. (%)	$M_{n,th}$	$M_{n,GPC}$	D	T _g (°C)	ΔC_p (J/g)
C1	MMA	0.5	63	6308	7658	1.2	119.8	-0.878
C2 ^a	MMA	2.20	61	6107	9663	1.29	110	0.437
C3	MMA-MA	21.30	40	11613	16485	1.68	128	-0.315
C4	MMA-VA	21.30	42	11722	16213	1.75	128.7	-0.826
C5	MMA-St	21.30	43	14262	18816	1.49	129.3	-1.74
C6 ^a	MMA-MA	24	42	7743	6349	1.596	54.7	0.387
C7 ^a	MMA-VA	48	34	6355	7878	1.645	97.8	0.557
C8 ^a	MMA-St	24	24	4899	7392	1.76	94	0.439

^aLinear polymers initiated with benzhydrylbromide initiator.

shown by TEM. Higher thermal stability was recorded, whether in the case of MMA star homo- or copolymers, compared to the linear analogs. Briefly, star polymers showed brilliant advantages, which could be widely utilized industrially or in various research fields.

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