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Amphiphilic Star Homo- and Block Copolymers of 2-(dimethylamino) Ethyl-Methacrylate via Atom Transfer Radical Polymerization

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Amphiphilic Star Homo- and Block Copolymers of 2-(dimethylamino) Ethyl-Methacrylate via Atom Transfer Radical Polymerization

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Three arm star homopolymers of 2-(dimethylamino) ethylmethacrylate (DMAEMA) monomer were efficiently prepared via atom transfer radical polymerization technique (ATRP). True ATRP was obtained by using N,N,N′,N′-tetramethylethylenediamine-(TMED)/CuBr catalytic system at 90, 100°C. However, lower temperatures saved more controlled ATRP. (DMAEMA) di-and tri- block copolymers were prepared in the same fashion as in the case of homopolymers but at 90°C. Several monomers were involved in such polymerization experiments such as styrene (St.), methylmethacrylate (MMA), methylacrylate (MA) and vinylacetate (VA). Di-and tri- block copolymers of (DMAEMA) were prepared by using MMA, St, MMA-VA and MMA-St homo- and copolymers, respectively as macroinitiators. Relatively low molecular weights were recorded via GPC. The structures of the formed polymers were proved using ^{1}H-NMR and IR. Thermal behavior of the prepared polymers was studied in each case. The bromine end group was converted into hydroxyl one via a selective reaction with silver oxide. The structure of the hydroxyl-ended polymer was confirmed through ^{1}H-NMR and IR.

Keywords: amphiphilic polymers; star polymers; ATRP; ^{1}H-NMR

In recent years, star polymers have attracted great attention due to their unique properties and important applications, in addition to the ease of preparation (1). Star polymers represent a considerable member of the nanostructured polymers (e.g. star, hyberbranched, comb, etc. (2)). Generally, the branched polymers have a smaller hydrodynamic dimension, lower solution and melt viscosities than the linear analogues with the same molecular weights (3). Therefore, star polymers are very important in the fabrication processes of polymer materials.

Additionally, they also contain a higher degree of end group functionalities which is quite important in specialized applications (4). Amphiphilic star-shaped block copolymers are attractive for medical uses as micellar drug delivery and thermoplastic hydrogels because of their expected very low critical aggregation concentration (CAC) so they can behave as unimolecular micelles (5). Amphiphilic block copolymers of (2-dimethylamino)-ethylmethacrylate (DMA EMA) form micelles and act as stabilizers in the dispersion polymerizations. Poly (DMAEMA) and quaternized poly-(DMAEMA) are temperature-sensitive water-soluble polymers which can be applied in the environmental protection, drug delivery systems, sensors, etc. (6, 7). DMAEMA has been polymerized in a controlled fashion via several techniques such as living anionic polymerization (8, 9) and group transfer polymerization (GTP) (10). However, each has drawbacks, whether with respect to the stringent experimental conditions which often make industrial applications difficult, or lead to incomplete polymerization processes. Therefore, the synthesis by living radical polymerization techniques has gained more interest, because of its tolerance to impurities, adventitious water, and high temperatures (11). Accordingly, poly(St-DMAEMA) block copolymers have been prepared by stable free radical polymerization (12). Among the other living controlled free radical polymerization techniques, since its discovery in 1995, ATRP has been considered as the best method known in the synthesis of functional polymers and novel molecular architectures with well-defined topologies (13). Also, through ATRP, the degree of branching in vinyl polymers can be effectively controlled (11). Recently, various amphiphilic block copolymers of DMAEMA have been prepared via ATRP (6, 7, 14). The nature of ATRP

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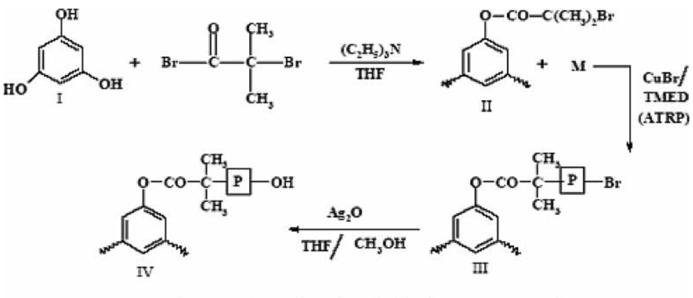

M, P = monomer and any polymeric unit whether homo- or copolymer.

Sch. 1. Schematic representation of the used synthetic procedures.

always places a halogen group at the terminus of the polymer chain. Hence, the recent development in ATRP has been directed toward converting this end-group to various functionalities such as amine, azide and hydroxyl groups either in situ or in a post polymerization modification step (15). Consequently, Sawamoto et al. and Bielawski et al. successfully prepared keto end group functionalized polymers and telechelic polyacrylates with unsaturated ends (15). Herein, we report the synthesis of the three-arm star amphiphilic homopolymers, di-and tri- block copolymers of (DMAEMA) via ATRP by using three arm star 1,3,5-(2-bromo-2-methylpropionato) benzene based core as the initiator as represented in Scheme 1. Successive characterization of the formed polymers was carried out for better understanding of their behavior. Transformation of the bromine end groups into hydroxyl ones was targeted. Therefore, a trial was carried out on MMA-DMAEMA copolymer as an example where it was simply treated with silver oxide reagent to form the hydroxyl end.

1 Experimental

1.1 Materials

All chemicals were provided from Sigma-Aldrich Chemicals. The monomers, such as (MMA), (MA), (St) and (VA) monomers were purified via alumina column and stored under argon. The other chemicals were used as received.

Table 2. ATRP of three-arm star DMAEMA block copolymers

Polymer type	Time (h)	Conversion (%)	D	M_{nth}	M_{nGpc} g/mol
St-DMAEMA	23	66	1.68	14700	12886
MMA-DMAEMA	23	69	1.68	11625	9825
MMA-St-DMAEMA	25	32	2	20099	16397
MMA-VA-DMAEMA	25	37	1.85	18012	14059

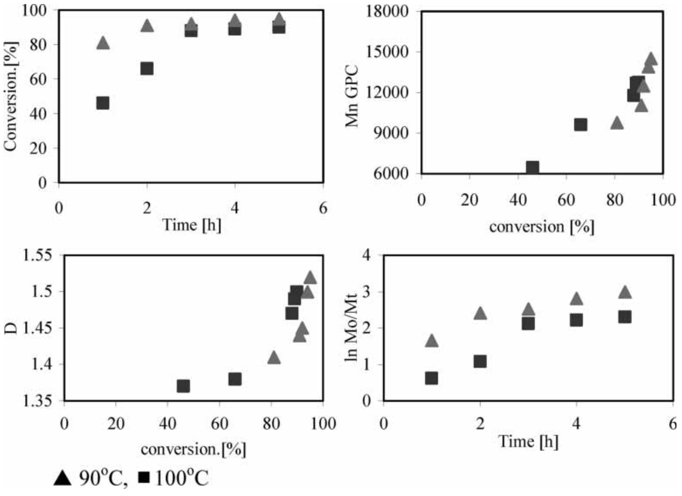

Fig. 1. Kinetic plots for the (DMAEMA) three-arm star homopolymers.

1.2 Measurements

^{1}H-NMR spectra were obtained from Varian Mercury-Oxford-300 MZ using $CDCL_3$ as a main solvent for the all samples. Molecular weights and polydispersities were measured on Agilent-1100 gel permeation chromatography (GPC) columns (Guard, 100, 10^4 and 10^5) coupled with G-1362 A differential refractometer using THF as the

Table 1. ATRP of three-arm star DMAEMA homopolymers

Entry	Temperature (°C)	Time (h)	Conversion (%)	$Ln(M_o/M_t)$	D	M_{nth}	$M_{n\ Gpc}$ g/mol
1	90	1	46	0.62	1.37	7804	6472
2	90	2	66	1.08	1.38	10948	9616
3	90	3	88	2.12	1.47	14407	11782
4	90	4	89	2.22	1.49	14564	12672
5	90	5	90	2.30	1.5	14721	12744
6	100	1	81	1.66	1.41	13306	9768
7	100	2	91	2.41	1.44	14879	11054
8	100	3	92	2.53	1.45	15036	12500
9	100	4	94	2.81	1.5	15350	13900
10	100	5	95	3.00	1.52	15507	14500

eluent with a flow rate of 1 ml min^{-1}. Standard polystyrenes and polymethylmethacrylates were used to calibrate the columns. FT-IR spectra were recorded on Bruker FT-IR IFS 113 V by using KBr pellets. Thermal analyses were carried out on a Shimadzu-DSC differential scanning calorimeter by using sample weight of 2 mg.

1.3 Synthetic Procedures

All the used synthetic routes can be summarized and represented as in Scheme (1).

1.4 Preparation of Three-Arm Star Initiator

1,3,5-(2-bromo-2-methylpropionato) benzene-based initiator (II) was synthesized from 1,3,5- trihydroxybenzene (I) as in the literature (16, 17) and as previously indicated in Scheme 1.

1.5 General Polymerization Experiment

Under argon atmosphere, a dry vial was charged with CuBr, ligand, monomer and anisole, then sealed, flushed with argon and placed in a thermostated oil bath at 90 or 100°C. A solution of initiator (II) in anisole was successively added

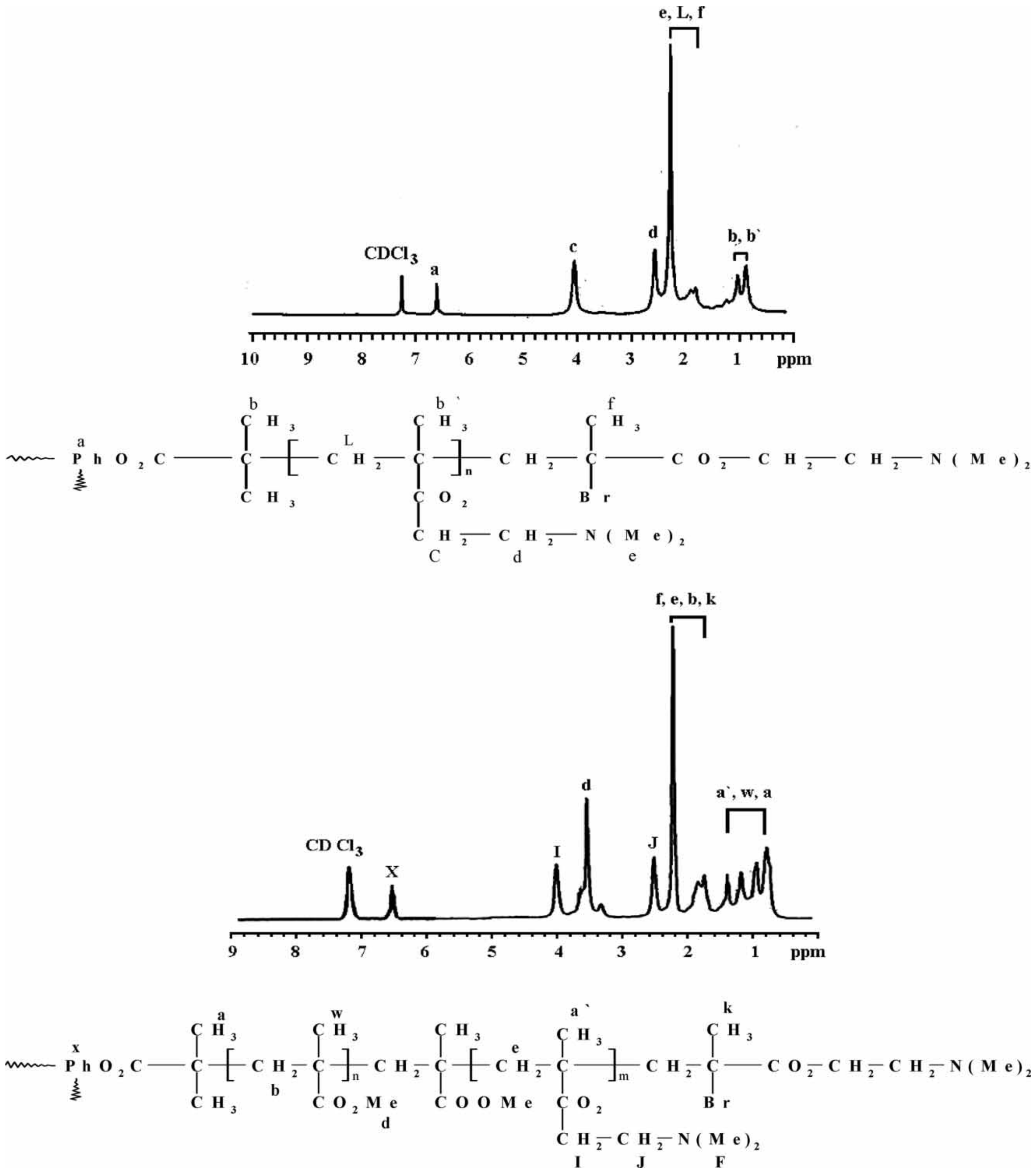

Fig. 2. ^{1}H-NMR spectra of three arm star homo-(DMAEMA) and MMA-(DMAEMA) copolymers.

and the polymerization started. The reactants were added in molar ratio (ligand : CuBr : initiator : monomer = 6 : 3 : 1 : 100). The copolymerization experiments were conducted at 90°C in anisole. The conversion was gravimetrically determined. The molecular weight M_{nGpc} and the polydispersity of the resulting polymer (III) were recorded by passing its solution in THF through alumina column then GPC measurements were carried out.

1.6 Transformation of Bromine End Group into Hydroxyl

The transformation will be via a silver oxide reagent as the following:

Step (1) Formation of Silver Oxide Reagent

Warm solutions of equimolar amounts of NaOH and $AgNO_3$ (~0.3 mol) in 170 ml H_2O were added together. The resulting solution was stirred vigorously and allowed to stand until the coagulation of the precipitated silver oxide was complete. The silver oxide was washed by decantation with plenty of hot distilled H_2O. The final residual liquid was drained to obtain the damp silver oxide as the desirable reagent.

Step (2) Hydroxylation

The damp silver oxide was added to a solution of polymer (III) (0.15 mol) in THF where 10 ml MeOH were added.

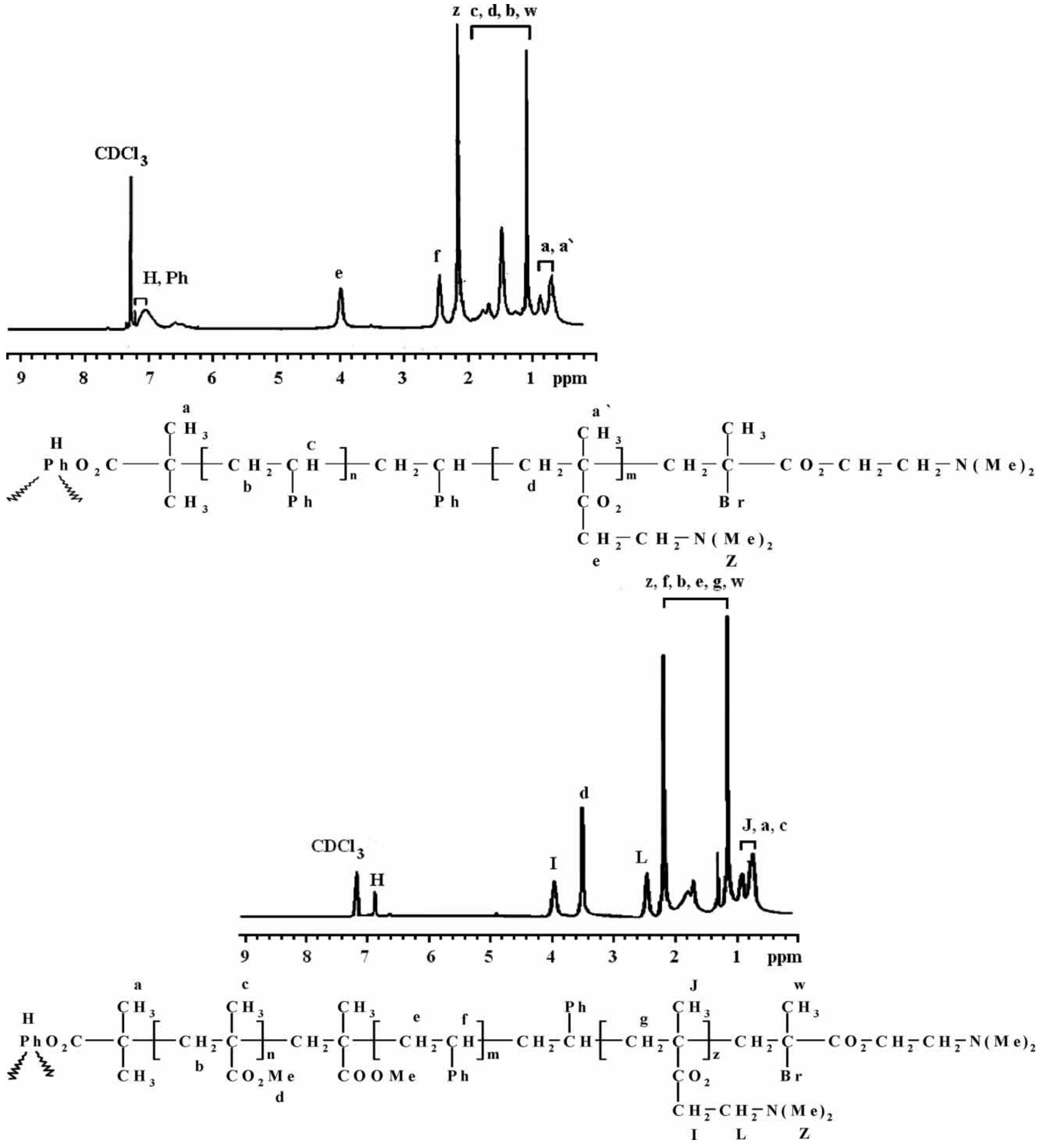

Fig. 3. ^{1}H-NMR spectra of three arm star St-DMAEMA, MMA-St-DMAEMA di- and tri- block copolymers, respectively.

The reaction mixture was stirred under inert atmosphere for 2 h and then filtered off the silver salts. The filtrate was collected and the solvent was evaporated *in vacuo*. The hydroxyl ended polymer (IV) was obtained and characterized via IR and ^{1}H-NMR.

2 Results and Discussion

The three-arm star benzene based core initiator (II) was involved in the preparation of the three-arm star (DMAEMA) amphiphilic homo-, di- and tri- block copolymers (III) with other different monomers such as (St), (MMA), (MA) and (VA) as previously illustrated in Scheme 1, Table 1, and Table 2. As shown in Table 2, three-arm star (MMA) and (St) homopolymers were used as macroinitiators in synthesizing (DMAEMA) di-block copolymers. However, in the case of tri-block copolymers, MMA-VA and MMA-St copolymers were involved as the macroinitiators. Generally, true ATRP was carried out by using a (TMED)/CuBr catalytic system. The general behavior of the prepared polymers was successively investigated. First, kinetic studies were performed in the case of (DMAEMA) homopolymers at 90 and 100°C (Table 1, Figure 1). The conversions increased linearly up to 90% and 95% in relatively fast reactions (i.e., 5 h) at both 90 and 100°C, respectively. General linear kinetic plots were observed at both temperatures. The GPC measurements recorded higher polydispersities (D) and lower molecular weights (M_{nGpc}) than the theoretical ones (M_{nth}) especially at low temperatures as indicated in Table 1. However, this discrepancy is not surprising and is consistent with the formation of star shaped polymers, which have hydrodynamic volumes lower than those of linear polymers of comparable molecular weight (18). On the other hand, the low molecular weights may be attributed to the adsorption of DMAEMA polymers on the GPC column as previously reported (6, 8). The increase of polydispersities with conversions may be ascribed to some kind of termination especially at higher conversions in addition to the steric hindrance of the resulting polymers especially in case of the copolymers (19). General controlled ATRP processes were observed where the structures of the prepared polymers were proved with ^{1}H-NMR as indicated in Figures (2–4). IR presented additional evidence for the di- and tri block copolymers as in Figures (5, 6) where ν(C-H) aliphatic (e.g. CH_3, CH_2 and CH groups) appeared with various intensities in the region of 2772 to 2996 cm^{-1}. Also, ν(C=O) of the ester group appeared at 1730–1740 cm^{-1}. However, ν(C-H) aromatic appeared as a very obvious band at 3440 cm^{-1}. There was a greater increase in the intensity of the ν(C-H) aliphatic bands in the case of the tri-block copolymers than that of the di-block ones.

In a successive work, the bromine end group was converted to a hydroxyl one for future use of those polymers in medical applications in our research group. The MMA-DMAEMA copolymer was taken as an example where it was treated

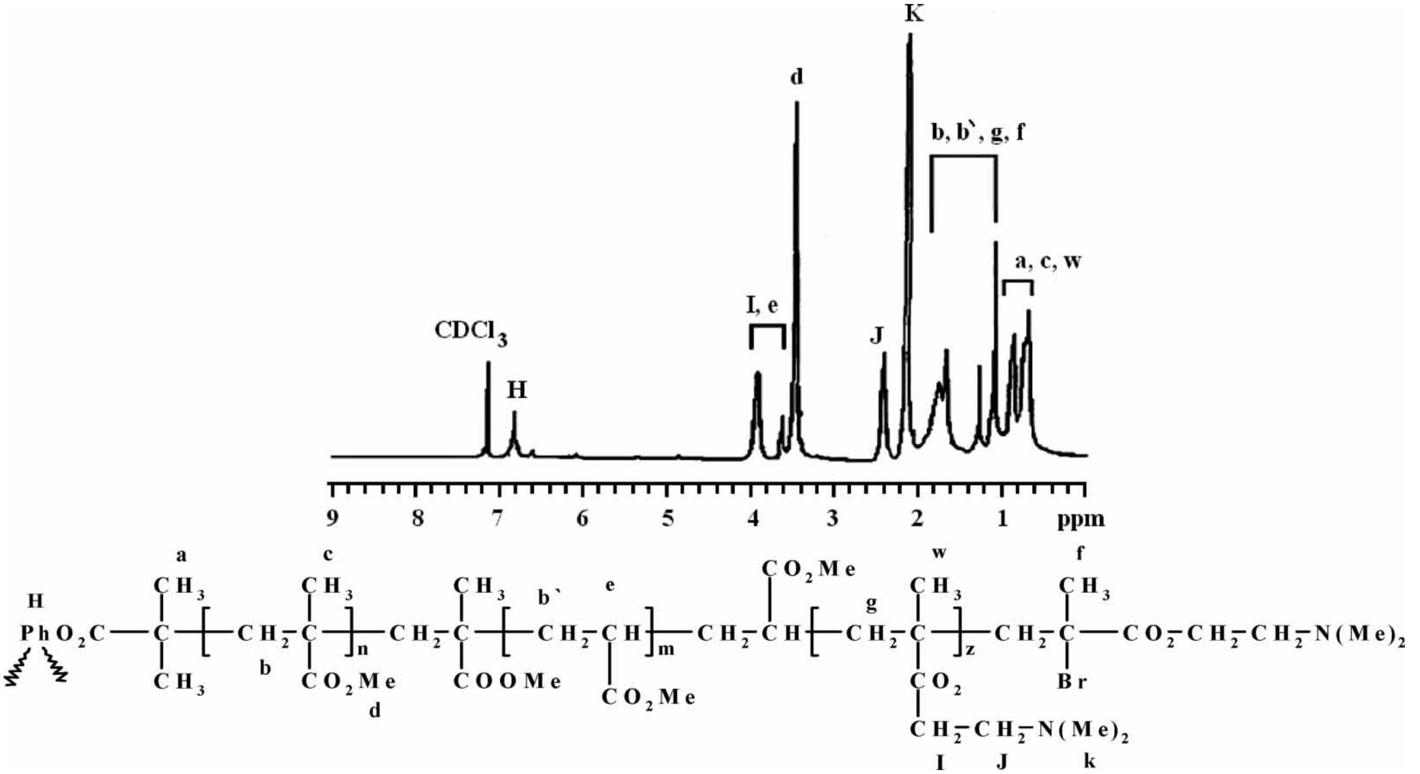

Fig. 4. ^{1}H-NMR spectra of three arm star MMA-VA-DMAEMA tri block copolymer.

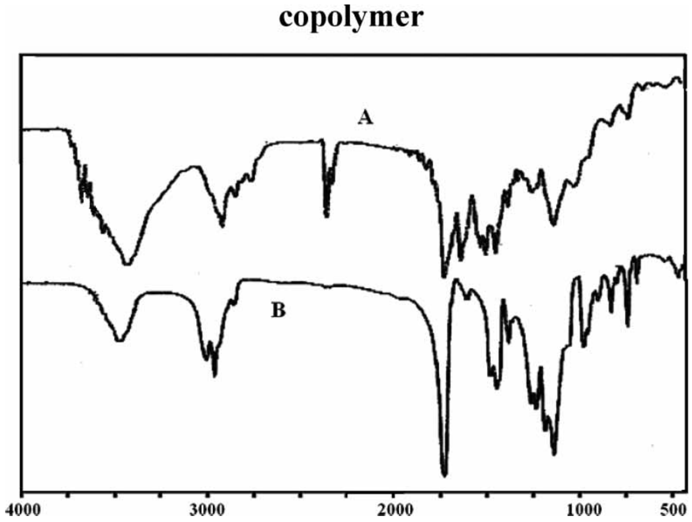

Fig. 5. IR of (A) MMA-DMAEMA and (B) St-DMAEMA three-arm star di-block copolymers.

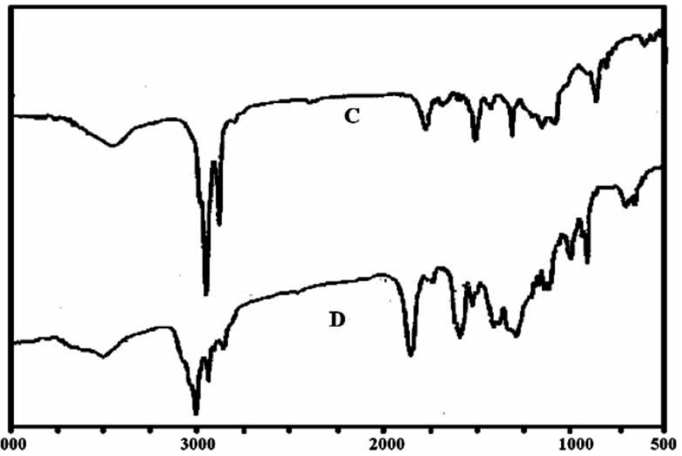

Fig. 6. IR of (C) MMA-St-DMAEMA and (D) MMA-VA-DMAEMA three-arm star tri-block copolymer.

with silver oxide reagent under mild conditions. The expected structure of the formed hydroxyl ended polymer was confirmed with ^{1}H-NMR as in Figure 7. IR showed an additional band, which was referred to as ν(O-H) at 3650-3675 cm^{-1} as in Figure 8.

Thermal stability of some polymers was studied by (TGA) in a temperature range (0–400°C) with a heating rate of 10°C/min by using N_2 gas as inert atmosphere. As shown in Figure 9, TGA showed that homo DMAEMA polymers had relatively good thermal stability up to 200°C, and then the degradation started till maximum. MMA-DMAEMA and St-DMAEMA copolymers displayed thermal stability up to 180°C and then it started to degrade at 200°C. However, MMA-St-DMAEMA and MMA-VA-DMAEMA tri-block copolymers showed thermal stability up to 120–140°C. As shown in Table 3, DSC measurements recorded increasing of the T_g values from 57.4°C with respect to homo DMAEMA polymers to 67 and 71°C, respectively for MMA-DMAEMA and St- DMAEMA copolymers. On the other hand, T_g became 91.4°C and 102.4°C for MMA-St-DMAEMA and MMA-VA-DMAEMA tri-block copolymers, respectively.

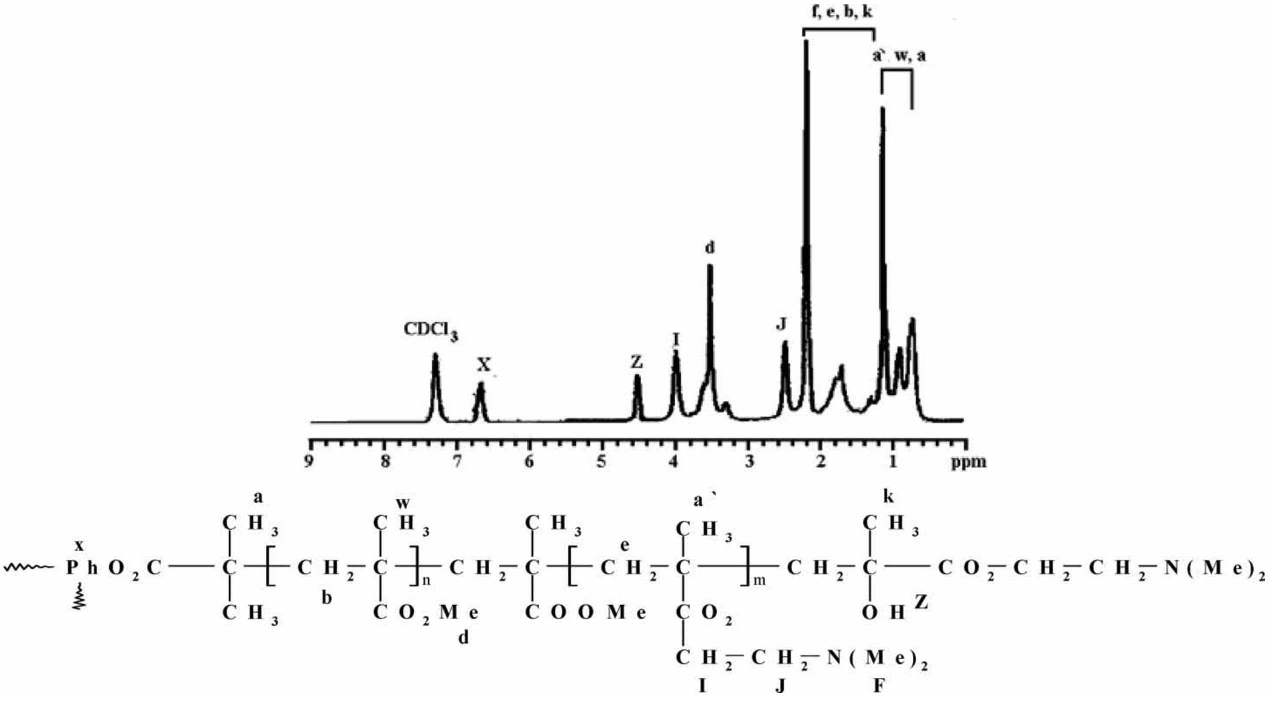

Fig. 7. ^{1}H-NMR spectra of three-arm star MMA-(DMAEMA)-OH block copolymer.

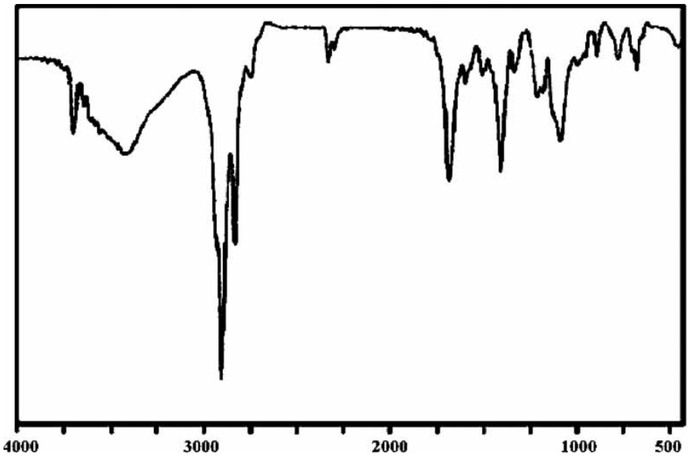

Fig. 8. IR of three-arm star MMA-DMAEMA-OH block copolymers.

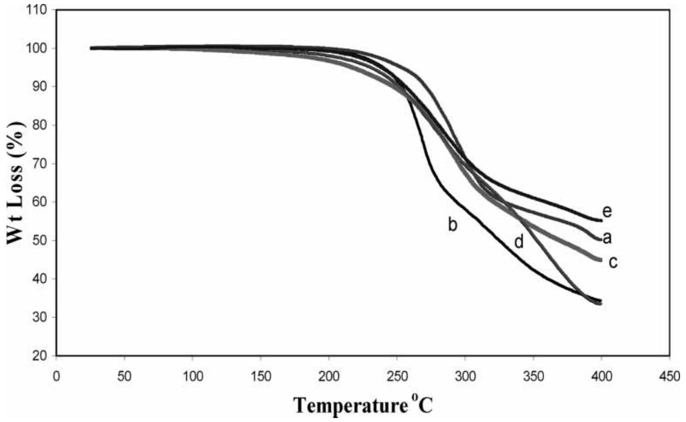

Fig. 9. TGA analyses for (a) DMAEMA, (b) St-DMAEMA, (c) MMA-St-DMAEMA, (d) MMA-VA-DMAEMA, (e) MMA-DMAEMA star polymers.

Table 3. Thermal behavior of the DMAEMA homo- and block copolymers

Polymer type	M_{nth}	M_{nGpc} g/mol	D	T_g (°C)
St-DMAEMA	14700	7892	1.68	71
MMA-DMAEMA	11625	6861	1.68	67
MMA-St-DMAEMA	20099	6989	2	91.4
MMA-VA-DMAEMA	18012	5952	1.85	102.4
DMAEMA	8146	5765	1.38	57.4

3 Conclusions

DMAEMA homo-and block copolymers were successfully obtained via ATRP processes under reasonable conditions. Linear kinetic plots were observed up to 95% conversions. Low GPC molecular weights were detected because of the adsorption of DMAEMA polymers on the column in addition to the nature of the star polymers themselves. ^{1}HNMR confirmed the controlled structures of the formed polymers indicating the true ATRP processes. IR provided further evidences on the formation of the di- and tri- block copolymers. The copolymerization increased the glass transition temperatures of the formed polymers than that of the homopolymers. Hydroxyl ended polymer was easily obtained via selective reaction with silver oxide. The amphiphilic DMAEMA hydroxyl ended polymer can be involved in various applications as has already planned in our research group.

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