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Synthesis and Characterization of Tertiary Butyl Methacrylate Ethylmethacrylate Copolymers Using Atom Transfer Radical Polymerization

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ABSTRACT

Atom transfer radical polymerization (ATRP) conditions with Cu(I)Br/2,2'- bipyridine as catalyst system where employed for 1,3,5-(2-Bromo-2-metelpropiyonato)benzene (BMPB) as initiator, three-armed star homopolymer of t- butyl methacrylate (t-BMA) monomer, and t-BMA and Ethyl methacrylate (EMA) three-armed poly (t-BMA-co-EMA) star copolymer were synthesized at 110 °C. The homo and copolymers were characterized by FT-IR, 1H-NMR techniques. The compositions of the copolymers were calculated from 1H-NMR spectra. The molecular weight and molecular weight distribution were obtained by Gel Permeation Chromatography (GPC). The thermal behavior of three-armed homopolymer of t-BMA and its copolymers with EMA were studied by thermogravimetric analysis (TGA). The glass transition temperature (Tg) of three-armed poly(t-BMA-co-EMA) were measured by differential scanning calorimetry (DSC).

Keywords: Atom transfer radical polymerization , Three-armed polymer, Ethyl methacrylate.

1.INTRODUCTION

Atom transfer radical polymerization (ATRP) is currently used as a suitable method for the polymerization of a wide range of monomeric derivatives such as substituted styrenes, methacrylates and acrylonitrile (Matyjasweski at al., 1997). The monomer participation mechanism proceeds by using alkyl halides, transition metals, ligands as initiators in the ATRP mechanism. Thus, polymerization continues in a controlled manner until all monomer units in the environment are exhausted. It is also possible to synthesize star polymers with a multi-arm growth outward from a certain center as well as controlled synthesis of linear, homo and copolymers branched in various ways, graft copolymers, diblock and multi-block copolymers by ATRP (Matyjasweski, 1998). The atomic transfer radical polymerization method has been used successfully in the preparation and determination of copolymers with various components and topological structures such as random, block, graft, and star, and the end functionalities of the monomers can be very well controlled.

The ATRP method can be used to polymerize a wide range of monomers with growing radicals that can stabilized such as styrene, acrylate, methacrylate, acrylamide, methacrylamide and acrylonitrile (Angot at al., 2006). Since the polymers obtained by ATRP have active halogen atoms at the chain ends, such polymers can also be used as macro initiators. Such macro initiators can be used successfully in chain extension with ATRP to form new di-block, tri-block, and graft copolymers . Multifunctional initiators in order to produce polymers with uniform arms, low molar mass distribution, and controllable molar masses: all the initiation sites must be equally reactive and have the same rate of initiation. Furthermore, the initiation rate must be higher than the propagation rate (Matmour at al., 2008). Although copper-based ATRP is still regarded as the most important catalyst system today, other transition metals such as Ru, Fe, Ni, Pd and Pt are also successfully used.

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In this article, a three-armed star t-BMA homopolymer was initially obtained via ATRP method with a three-armed 1,3,5- (2-Bromo-2-methylpropionato)(BMPB) benzene initiator using a three-armed t-BMA monomer, and then (t-BMA-co-EMA) three-armed star copolymers were synthesized via ATRP method.

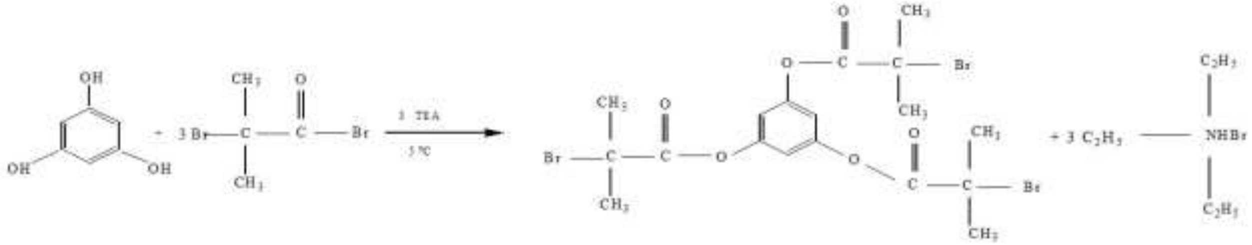
2.EXPERIMENTAL DETAILS

2.1.Materials

EMA, t-BMA (Aldrich) was washed with %5 NaOH and dried over $MgSO_4$ overnight and distilled under vacuum. Ethyl alcohol, chloroform, dichloromethane, diethylether, deuterated chloroform (d-chloroform) (Aldrich). 1,3,5-trihydroxybenzene, triethylamine, 2-bromo, 2-methyl propionylbromide, ethyl alcohol, n-hexane, CuBr and 2,2'-bipyridine (Fluka). Magnesium sulphate ($MgSO_4$), calcium chloride ($CaCl_2$) (Aldrich).

2.2.Synthesis of the 1,3,5-(2-Bromo-2-metelpropiyonato) benzene macroinitiator

In obtaining 1,3,5-(2-bromo-2-methylpropionato) benzene (Scheme 1), 1,3,5-tri-hydroxybenzene and triethylamine at three times molarity were added to a three-necked flask, and the mixture was cooled to 0-5 °C. 2-bromo, 2-methyl propionylbromide diluted in THF was added dropwise to the reaction medium with a dropping funnel. The reaction continued for 24 hours. The organic phase was filtered, washed with water then dried over anhydrous $MgSO_4$. The solvent in the organic phase was removed by evaporator. The residue was dissolved in hot ethyl alcohol and allowed to crystallize in cold.



Scheme 1. Syntesis of the 1,3,5-(2-Bromo-2-metelpropiyonato) benzen macroinitiator

2.3.Polymerization of three-armed t-BMA

2.3.1.ATRP in bulk

The monomer, metal halide, ligand and initiator ratios used in the three-armed star homopolymerization were respectively; [t-BMA: CuBr: bpy: initiator [1,3,5-tri-(2'-bromo-2'-methylpropionato)benzene] = 300: 3: 6: 1. Before polymerization, the polymerization tube was vacuumed and purged with argon gas. Then, the tube was filled with the required amount of CuBr, ligand (2,2'-bipyridine, bpy), and [1, 3, 5-tri-(2'-bromo-2'-methylpropionato)benzene] as a three-armed initiator. The polymerization tube was again purged with argon gas. t-BMA was then added and the tube was purged with argon gas. The mouth of the tube was closed with a plastic cover. The tubes were immediately left in the oil bath, which had previously been set at a temperature of 110 °C for the reaction medium. After 48 hours the tube was removed from the oil bath and cooled to room temperature. The polymer solution was diluted by adding some acidic ethanol (into ethanol with 1% aqueous hydrochloric acid) into the cooling tube. The resulting polymer solution was filtered and precipitated with n-hexane. The dissolution and precipitation process was repeated 2-3 times to remove the unreacted monomers and other impurities from the medium. The triple-armed polymer yield reaction is shown in (scheme 2.).

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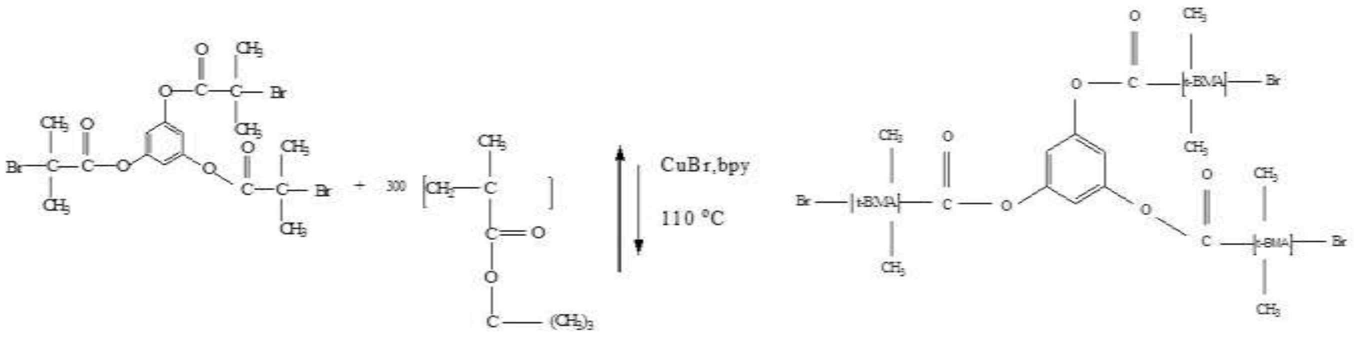
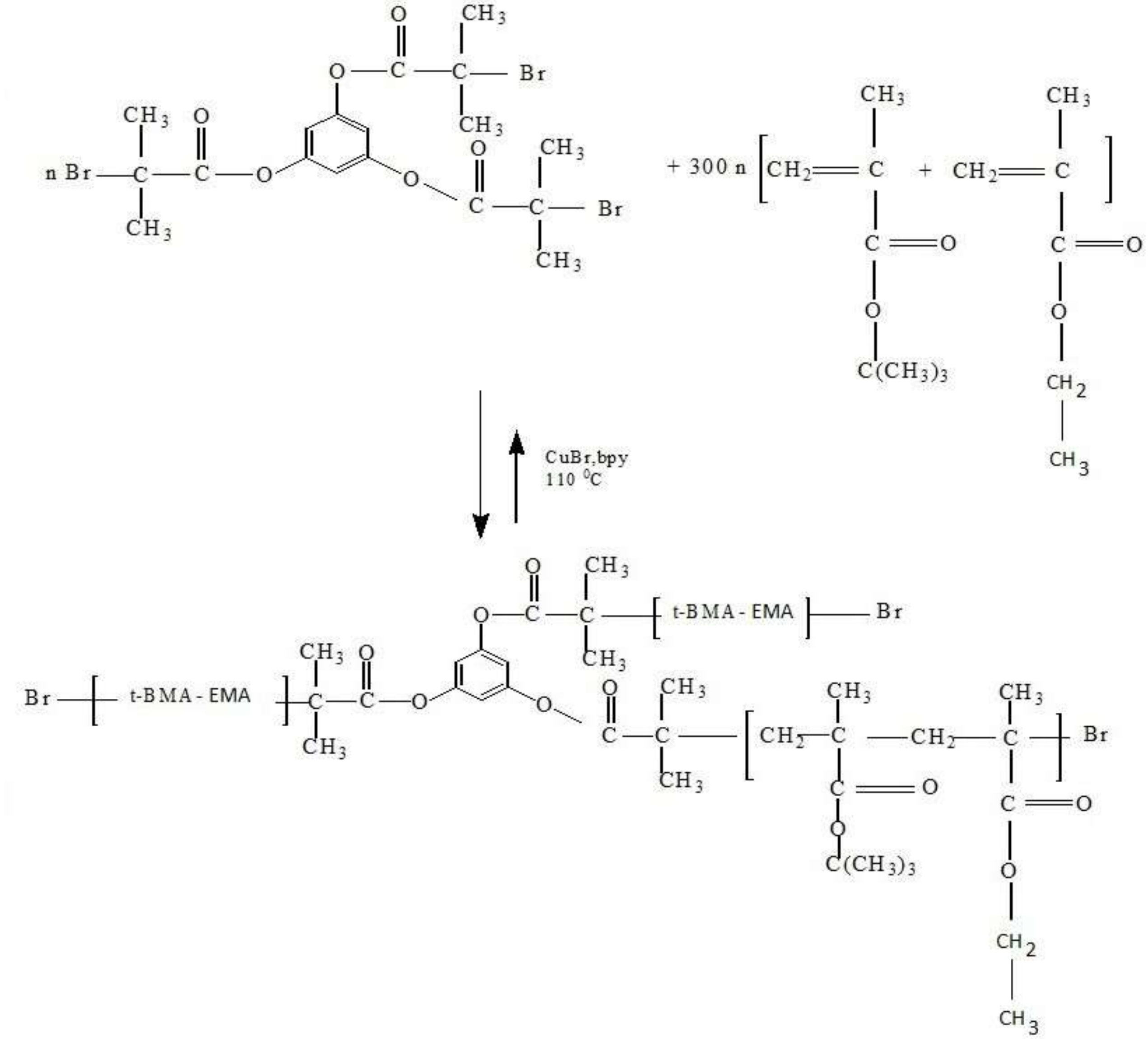


Scheme 2. Polymerisation of three-armed t-BMA

2.4.Copolymerization of t-BMA with EMA

2.4.1.ATRP in bulk

A series of copolymers were prepared in different percent compositions such that the total molar amounts of t-BMA and EMA monomers were 0.02 moles. Copolymers were synthesized by Atom Transfer Radical Polymerization (ATRP) method. In the ATRP reaction, the catalyst, ligand, initiator, and monomer ratios were [CuBr]: [bpy]: [1,3,5-tri-(2'-bromo-2'-methylpropionato)benzene] : [monomers] = 3:6:1:300. The copolymerization tubes were submerged in an oil bath previously set at 110 °C. After 48 hours the tubes were removed from the oil bath and cooled to room temperature. The polymer mixture was diluted by adding some acidic ethanol (into ethanol with 1% aqueous hydrochloric acid) to the cooling tubes. The polymer solution was filtered and the filtrate was precipitated with n-hexane. The dissolution and precipitation process was repeated 2-3 times to remove the unreacted monomers from the medium. The resulting polymer was dried at room temperature and then dried in an incubator at 40 °C for 24 hours. FT-IR, ^{1}H-NMR , GPC, TGA, DSC techniques were used to characterize the copolymers obtained. The triple-armed copolymer yield reaction is shown in Scheme 3.



Scheme 3. Triple-armed copolymer yield reaction poly(t-BMA-co-EMA)

2.5.Instrumental techniques

Infra-red spectra were recorded using a Mattson 1000 FT-IR spectrophotometer. The spectra were obtained by polymeric film or liquid film on a salt plate, cold ring fraction. ^{1}H and ^{13}C-NMR spectra of the products were taken from Jeol FX 90 Q 90 MHz NMR spectrometer using TMS as an internal standard and chloroform-d as a solvent. The TG curves were obtained using a shimadzu TGA-50 thermobalance. Programmed heating at 10 °C/min and under dynamic nitrogen atmosphere were employed. The DSC curves were obtained using a shimadzu DSC-50 thermobalance programmed heating at 20 °C/min.

3.RESULT AND DISCUSSION

In this study, 1,3,5-(2’- bromo-2’-methylpropionato) benzene was synthesized at 0-5 °C with 1,3,5-tri-hydroxybenzene (THB) and 2-bromo-2-methylpropionylbromide in the presence of triethylamine (TEA) according to the method described [20]. Structure of 1,3,5- (2'-bromo-2'-methylpropionato) benzene was supported by the appearance of the ester C═O stretching vibration at 1764 cm $^{-1}$ in FT-IR and aromatic ring protons at 6.98 ppm in ^{1}H-NMR and CH_3 signals at 2.04 ppm **(fig 1.).** For this purpose, conversion percentages were calculated with the ratio of integral heights of the protons at 5.6;6.2 ppm in the monomer to the integral heights of the other aliphatic protons in the monomer and polymer structures.

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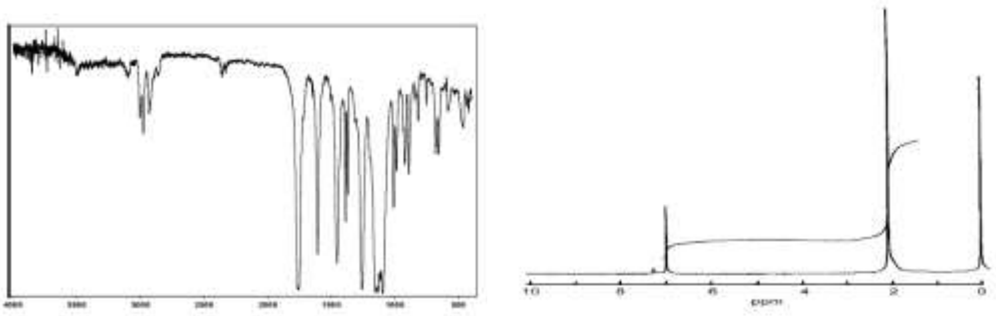

(a) (b)

Fig. 1. a. 1,3,5-tri-(2-bromo-2-metilpropiyonato)benzen'in FT-IR spektrumu, b. 1,3,5-tri-(2'-bromo-2'-metilpropiyonato)benzen'in ^{1}H- NMR Spektrumu

The relationship between time and % conversion of t-BMA polymerization at 110 °C with 1,3,5- (2'-Bromo-2'-methylpropionato) benzene as initiator and CuBr/bpy as catalyst system. % conversion determined ^{1}H- NMR (fig. 3). The copolymer was determined from the integrated proton NMR spectrum by comparing the integration of CH_2 proton peak to the total monomer and polymer peak integration :

$$\frac{H_2C\text{=Proton peak Integration}}{\text{Monomer and polymer peak integration}} = \frac{2m_2}{12m_2+14m_1} \qquad (1)$$

Where m_1 is mol franction of H_2C and m_2 is mol franction of monomer and polymer. % Conversion is achieved in 48 hours (table 1). The % conversion versus time curve in atom transfer radical polymerization of t-BMA is in a linear form indicating that the polymerization kinetics is in the first order (fig. 2.)

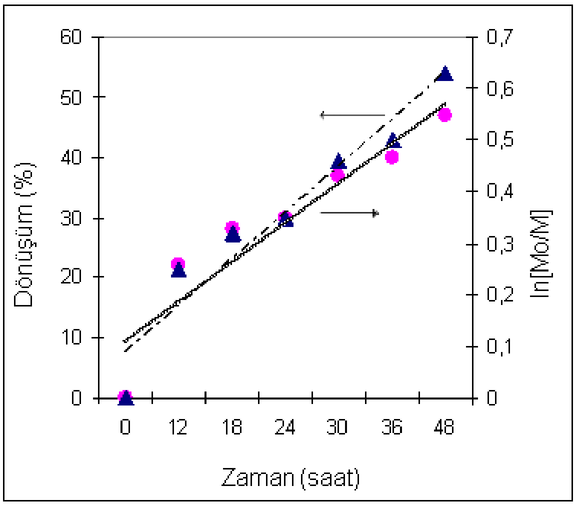

Fig. 2. % Conversion of t-BMA polymerization

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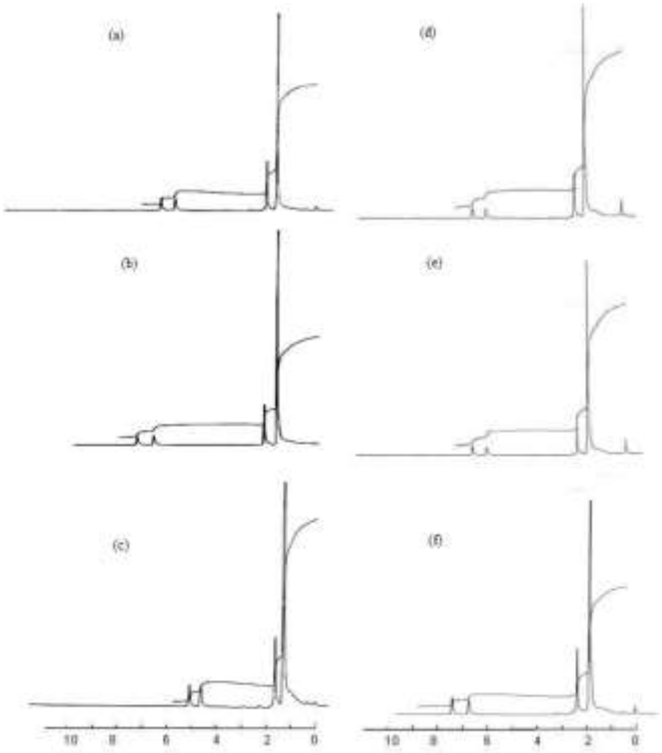

Fig. 3. The ^{1}H-NMR spectra % Conversion of t-BMA polymerization a. 12h, b.18h, c.24h, d. 30h, e. 36h, f. 48h.

Table 1 The poly(t-BMA) three-armed polymers (by ATRP)

Time (h)	% Transformation	ln [Mo/M]
12	22	0,25
18	28	0,32
24	30	0,35
30	37	0,46
36	40	0,50
48	47	0,63

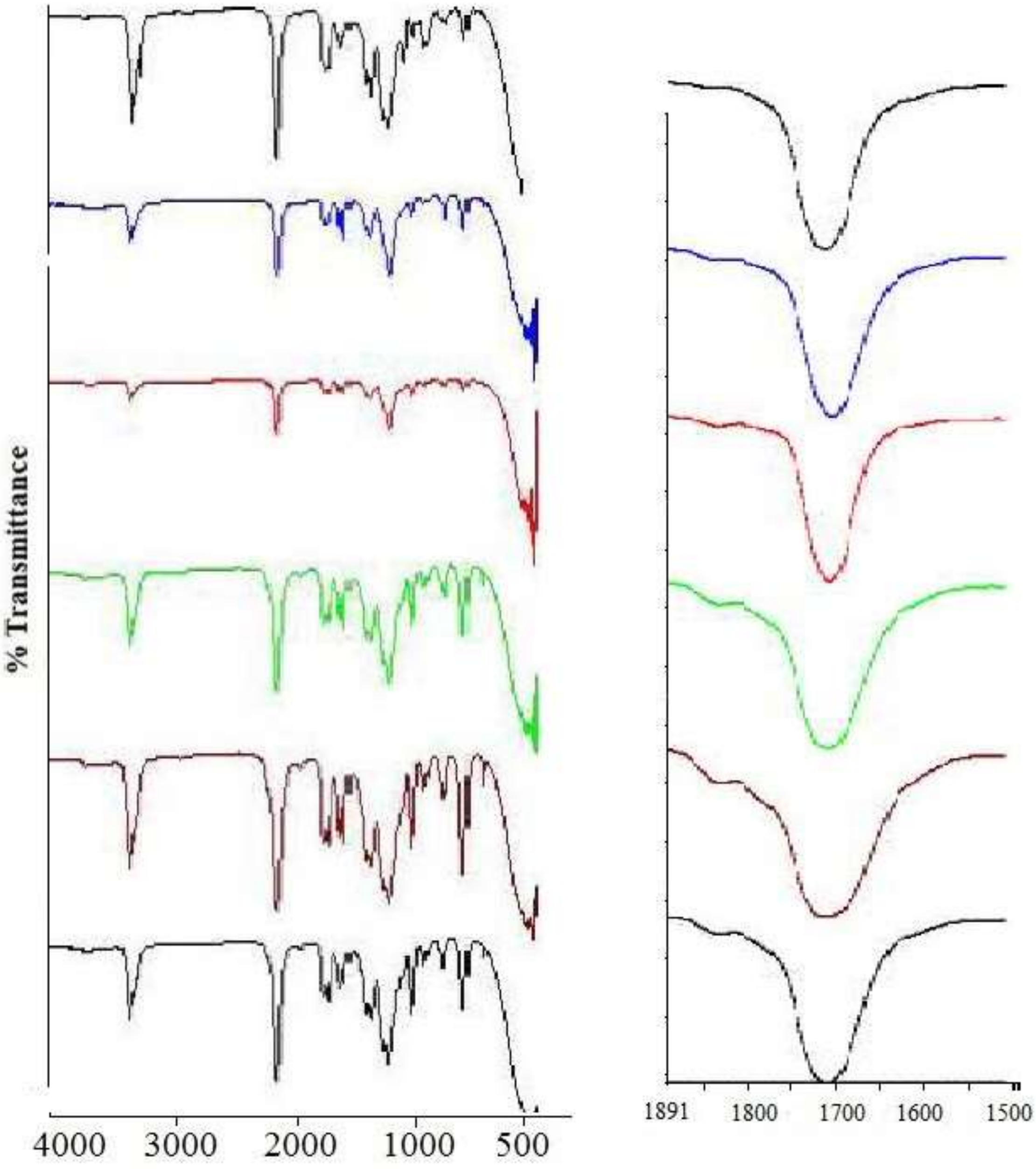

Fig. 4. The FT-IR spectrum of the three-armed copolymer poly(t-BMA-co-EMA)

Using 1,3,5-(2-bromo-2-methylpropionato)benzene initiator, atom transfer radical polymerization of t-BMA was performed at 110 °C with (CuBr):(bpy):(initiator)=[3:6:1]. Three-armed poly(t-BMA-co-EMA) was characterized by FT-IR and ^{1}H-NMR techniques. The FT-IR spectrum of the three-armed copolymer is shown in fig. 4. The C=O bands characteristic for copolymers were observed at around 1725 cm $^{-1}$. A small band observed around 1785 cm $^{-1}$ in the FT-IR spectra of a series of three-armed copolymers prepared by t-BMA and EMA using the ATRP method is characteristic of Br ended t-BMA, or the C=O tension in the other unit is characteristic of all three groups. The ^{1}H-NMR spectra of the copolymers of the three-armed poly(t-BMA-co-EMA) in varying proportions are given in Fig. 5**.** In each copolymer, the signal at 4.0 ppm showed the -CH$_2$ proton adjacent to oxygen in EMA units and the signal at 1.4 ppm showed -C(CH$_3$) protons in t-BMA unit. As the EMA units increase in the copolymer series, the 4.05 ppm signals are exacerbated, while the 1.4 ppm signals are getting weaker.

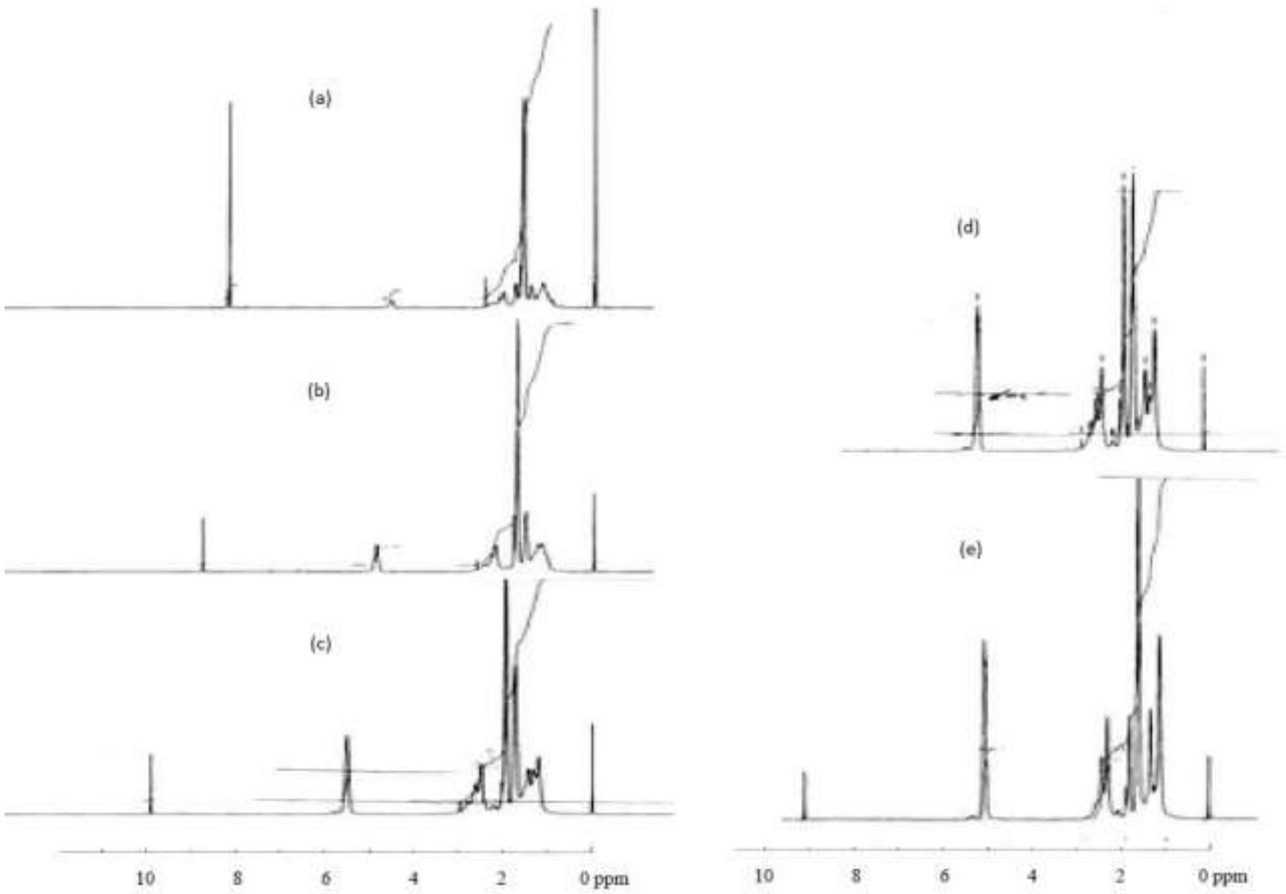

Fig.5.The ^{1}H-NMR spectra of three-armed poly(t-BMA-co-EMA) copolymers in varying proportions (a) poly(t-BMA0.90-ko-EMA), (b) (t-BMA0,75-ko-EMA), (c) poly(t-BMA0,50-ko-EMA), (d) poly(t-BMA0,25-ko-EMA), (e) poly(t-BMA0,10-ko-EMA)

3.1.Some physical parameters of the polymers

Weight-average molecular weight of poly(PCMA), as was given in Table 2, were determined by GPC using THF as standard and solvent, respectively. GPC curves in the poly(t-BMA-co- EMA) system (Fig. 6.)

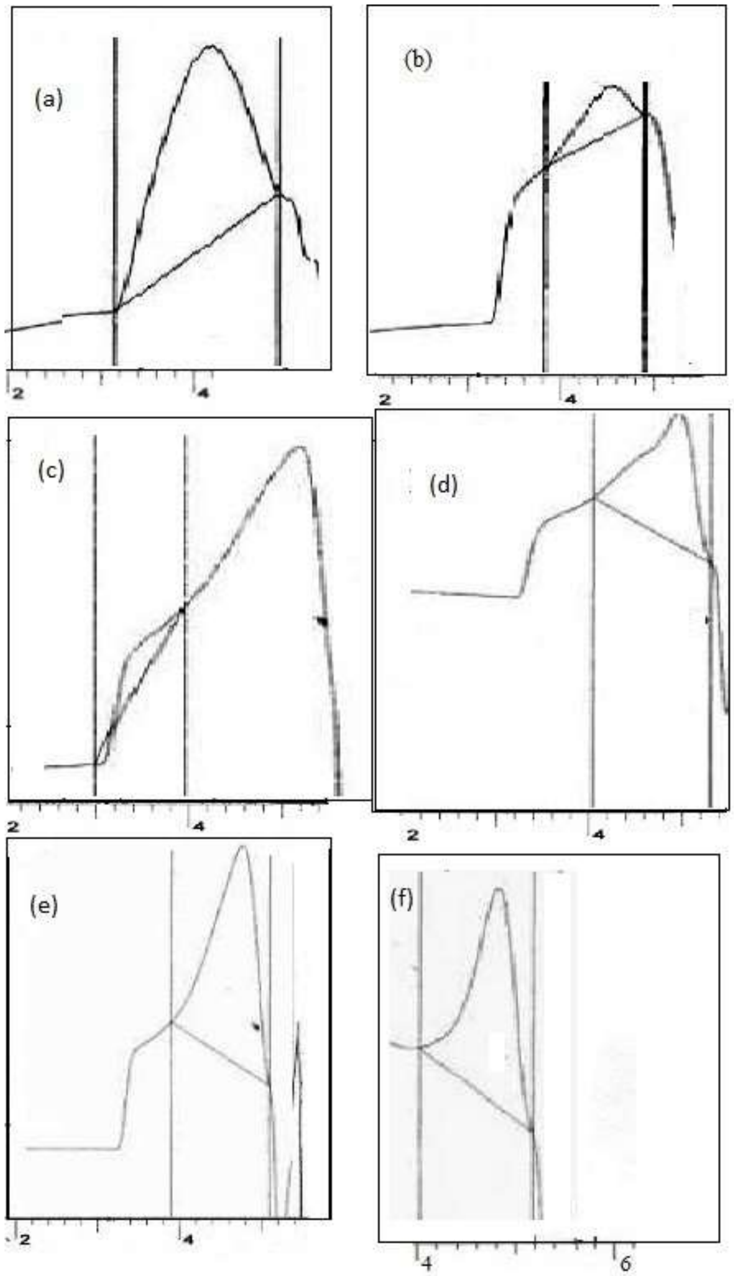

Fig. 6. GPC curves of The poly(t-BMA-co-EMA) three-armed polymers (by ATRP),(a)poly(t-BMA 0,90-co-EMA), (b) poly(t-BMA 0,75-co-EMA),(c) poly(t-BMA 0,50-co-EMA), (d) poly(t-BMA 0,35-co-EMA),(e) poly(t-BMA 0,25-co-EMA), (f) poly(t-BMA 0,10-co-EMA)

Table 2.GPC data of the poly(t-BMA-co-EMA) copolymer series

%polymer compount	Mn (g/mol)	Mw(g/mol)	Mv(g/mol)	Mw/Mn
Poly (t-BMA 0,90-co-EMA)	46000	7700	7700	1,59
Poly (t-BMA 0,75-co-EMA)	210000	230000	230000	1,09
Poly (t-BMA 0,50-co-EMA)	8700	16000	16000	1,18
Poly (t-BMA 0,35-co-EMA)	10000	17000	17000	1,7
Poly (t-BMA 0,25-co-EMA)	10000	17000	17000	1,7
Poly (t-BMA 0,10-co-EMA)	9900	14700	14700	1,48

3.2.Thermogravimetric study

The thermal degradation behaviors of the copolymers were compared using TGA curves (Fig. 7).In three copolymer series, it was observed that the thermal stability of copolymers increased as t-BMA units increased. The TGA results are summarized in Table 3.

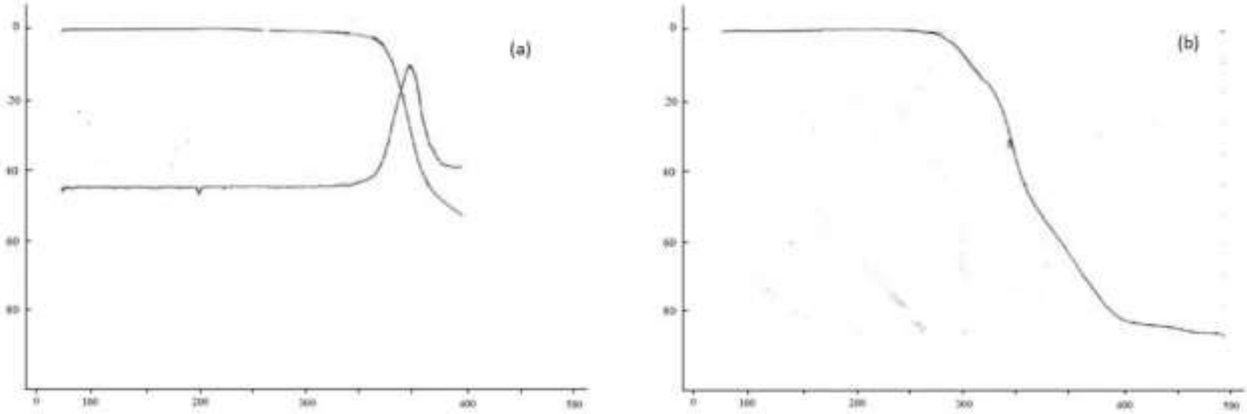

Fig. 7. The TG curves of the poly (t-BMA-co-EMA) ; a. poly(t-BMA 0,10-co-EMA), b. poly (t- BMA 0,35-co-EMA), heated in dynamic nitrogen at 10 °C/min to 500 °C.

Table 3. TGA data of copolymers

Copolymers	[a] Ti (°C)	T %50 (°C)	% residue at 300°C	% residue at 350°C	% residue at 400°C
poly (t-BMA 0,10-co-EMA)	215	290	57	-	-
poly (t-BMA 0,35-co-EMA)	190	310	42	73	94

[a]Ti : Initial decompositiontemperature

3.3.Differential scanning calorimetry (DSC)

Representative DSC curves of poly(t-BMA-co-EMA) (by ATRP) shown in Fig. 8. The heating rate was maintained at 20 °C/min. The measurement of glass transition temperature values is given in table 4. The T_g value of the copolymer was found some different 83°C and 102°C. The large number of chain ends do permit more flexibility by occupying a large free volume.

3.4. The Dıscussion of Degradation For Polymers

When TGA data were evaluated, it was observed that the thermal stability of t-BMA units residual copolymers increased in the copolymer series. In the copolymer series, as the EMA units increased in number average molecular weight changed from 46000 to 9900, while polydispersity ranged from 1.68 to 1.16. The appearance of a shoulder or two distinct regions on the GPC chromatogram may be attributed to the fusion of some arms resulting in the cessation of growth, or the increase in molecular diversity due to the growth of other arms. In other words, t-BMA monomers means high molecular weight in copolymerization, whereas high polydispersity means uncontrolled polymerization, which is due to star-star pairing as a result of the radical-radical combination (Martına at al., 2001; Arehart and Matyjaszewski, 1999; Stenzel-Rosebaum at al., 2001). This demonstrates that the copolymerization achieved under ATRP conditions does proceed in a controlled manner, while end-transfer reactions and side reactions such as chain breaks during ATRP are neglected. Chen et al. (Yuan and Pan, 2002) also noted that side reactions such as termination, chain transfer and chain breakage can be neglected during copolymerization until high polymerization conversion. The T_g value of the copolymer was found some different 83 °C and 102 °C. The large number of chain ends do permit more flexibility by occupying a large free volume. Three-armed poly(t-BMA-co-EMA) was characterized by FT-IR and ^{1}H-NMR techniques. The FT-IR spectrum of the three-armed copolymer is shown in fig. 4. The C=O bands characteristic for copolymers were observed at around 1728 cm $^{-1}$. A small band observed around 1780 cm $^{-1}$ in the FT-IR spectra of a series of three-armed copolymers prepared by t-BMA and EMA using the ATRP method is characteristic of Br ended t-BMA, or the C=O tension in the

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4. CONCLUSION

As a result, this study that three-armed star polymers can be successfully synthesized by the controlled polymerization method (ATRP) using multifunctional initiator. This study showed that complex structured macromolecules can be synthesized in two or three steps without any modification in polymer end group. Structures of synthesized polymers are defined by spectroscopic methods. They will have important place for nanotechnology.

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