ISSN:1306-3111
e-Journal of New World Sciences Academy
2009, Volume: 4, Number: 2, Article Number: 3A0006

NATURE SCIENCES
Received: January 2009
Accepted: March 2009
Series : 3A
ISSN : 1308-7304
© 2009 www.newwsa.com

Adnan Kurt
Kadir Demirelli
University of Firat
adnankurt@firat.edu.tr
Elazig-Turkey

SYNTHESIS AND CHARACTERIZATION OF BLOCK COPOLYMERS OF ETHYL METHACRYLATE WITH STYRENE VIA ATRP

ABSTRACT

The homopolymer of ethyl methacrylate and diblock and triblock copolymer with styrene were accomplished by atom transfer radical polymerization method. Temperature studies indicated that the polymerizations occurred smoothly in bulk at 110°C and 130°C for ethyl methacrylate and Styrene. Of all polymers were characterized by FT-IR, ^{1}H-NMR, UV-VIS and DSC techniques. The percentage of styrene units in the diblock and triblock copolymers were obtained as 68 and 21 (by %), respectively. The T_g values for poly(EMA), poly(EMA-b-St) diblock and poly(EMA-b-St-b-EMA) triblock copolymer were determined as 73°C, 97°C and 78°C, respectively. The results obtained from GPC chromatograms showed that the polymerizations were controlled/living. The average molecular weight (Mn) and the molecular weight distribution of homo, diblock and triblock copolymers were found as 3100, 29300, 40000 and as 1,14, 1,17, 1,96, respectively.

Keywords: ATRP, Block Copolymerization, Synthesis, Characterization, Ethyl Methacrylate, Styrene

ATRP METODUYLA ETİL METAKRİLATIN STİREN İLE BLOK KOPOLİMERLERİNİN SENTEZİ VE KARAKTERİZASYONU

ÖZET

Etilmetakrilatın homopolimeri ve Stiren ile olan diblok ve triblok kopolimerleri atom transfer radikal polimerizasyon yöntemi ile gerçekleştirildi. Etilmetakrilat ve stirenin polimerizasyonu için gerekli sıcaklıkların sırasıyla 110°C ve 130°C olduğu yapılan sıcaklık çalışmalarından tespit edildi. ATRP şartlarında sentezlenen polimerler FT-IR, ^{1}H-NMR, UV-VIS ve DSC teknikleri ile karakterize edildi. Stiren birimlerinin diblok ve triblok kopolimer içindeki oranları sırasıyla %68 ve %21 olarak belirlenirken poly(EMA), poly(EMA-b-St) diblok ve poly(EMA-b-St-b-EMA) triblok kopolimeri için camsı geçiş sıcaklıkları 73°C, 97°C ve 78°C olarak ölçüldü. GPC kromatogramlarından elde edilen sonuçlara göre polimerizasyonların kontrollü-yaşayan karakterli olduğu belirlendi. Sayıca ortalama molekül ağırlıkları ve molekül ağırlık dağılımları sırasıyla 3100, 29300, 40000 ve 1,14, 1,17, 1,96 olarak tespit edildi.

Anahtar Kelimeler: ATRP, Blok Kopolimerizasyon, Sentez, Karakterizasyon, Etil Metakrilat, Stiren

1. INTRODUCTION (GİRİŞ)

The development of living radical polymerization for the synthesis of polymers with controlled architecture, molecular weight, and narrow polydispersity is among the most significant accomplishments in polymer chemistry in the last two decades [1 and 2]. One of the representative accomplishments obtained in the area of living radical polymerization should be atom transfer radical polymerization invented by Matyjaszewski and his friends [3 and 4]. Atom transfer radical polymerization is based on establishing a rapid dynamic equilibration between a minute amount of growing free radicals and a large majority of the dormant species. Atom transfer radical polymerization is a living radical polymerization system that has been demonstrated to successfully polymerized a series of vinyl monomers such as styrene as well as its derivative, acrylate, methacrylate and acrylonitrile [5, 6, 7, and 8]. It is proved that the application of ATRP has resulted in the synthesis of polymers with very narrow molecular weight distribution $M_w/M_n<1,1$. Irrespective of the number and types of monomers, which can be successfully polymerized, ATRP has also been shown to be more versatile with respect to the novel polymer architectures such as graft copolymers, block copolymers, branched and hyper branched polymers [9, 10, and 11].

2. RESEARCH SIGNIFICANCE (ÇALIŞMANIN ÖNEMİ)

In this article, we report the synthesis and characterization of poly(EMA), poly(EMA-b-St) diblock and poly(EMA-b-St-b-EMA) triblock copolymer by ATRP method.

3. EXPERIMENTAL METHOD (DENEYSEL YÖNTEM)

3.1. Materials (Malzemeler)

Ethyl methacrylate (EMA) (Aldrich) and Styrene (Aldrich) were distilled under vacuum after washing with 5% NaOH aqueous solution just before homo and copolymerization. Cuprous bromide (CuBr), 2,2′-bipyridyne and ethyl 2-bromo acetate (2-EBA) (analytical reagent) were used as received.

3.2. Instrumental Techniques (Enstrümantal Teknikler)

Infrared spectra were obtained on a Mattson 1000 FTIR spectrometer and obtained by polymeric film or liquid film on a salt plate. The UV–visible absorption spectra were obtained using T80 + UV/VIS Spectrometer (PG Instruments Ltd.) in the wavelength range of 200–500 nm. NMR spectra were recorded on a Jeol FX 90Q NMR spectrometer at room temperature using $CDCI_3$ as a solvent and TMS as an internal standard. Differential Scanning Calorimetry (DSC) measurements were carried out under nitrogen flow with heating rate of 20°C min^{-1}. Gel permeation chromatography (GPC) analyses were carried out using a high pressure liquid chromatography pump with Agilent 1100 system equipped with a vacuum degasser, a refractive index detector. The eluting solvent was tetrahydrofuran (THF), the flow rate was 1 ml min^{-1}. Calibration was achieved with polystyrene.

3.3. Atom Transfer Radical Polymerization of EMA (EMA'ın Atom Transfer Radikal Polimerizasyonu)

CuBr was first introduced to a glass tube. Then, the glass tube was sealed with a rubber septum and cycled twice between vacuum and argon. The monomer (EMA), initiator [ethyl 2-bromo acetate (2-EBA)] and ligand (2,2′-bipyridyne) were degassed by argon purging for 10 min before adding to the glass tube. The sealed tube was immersed in a preheated oil bath at 110°C. After the polymerization had carried out, the tube was removed from oil bath and the reaction mixture was

dissolved in chloroform, filtered, and the polymer was precipitated in methyl alcohol with 1% aqueous hydrochloric acid, and dried at 45°C under vacuum (Scheme 1.a).
^{1}H NMR (CDCI$_3$, ppm): 4,01 (-COOCH$_2$ protons in EMA units), 1,89 (CH$_3$ and CH$_2$ protons in main chain), 1,26 (CH$_3$ protons in EMA units).
FT-IR (cm^{-1}): 2970-2880 (aliphatic C-H stretching), 1727 (C=O stretching), 1455-1413 (aliphatic C-H bending), 1150 (asymmetric C-O stretch), 1030 (symmetric C-O stretch).

3.4. AB Type Diblock Copolymerization of PEMA with St (St'in PEMA ile AB Tip Diblok kopolimerizasyonu)

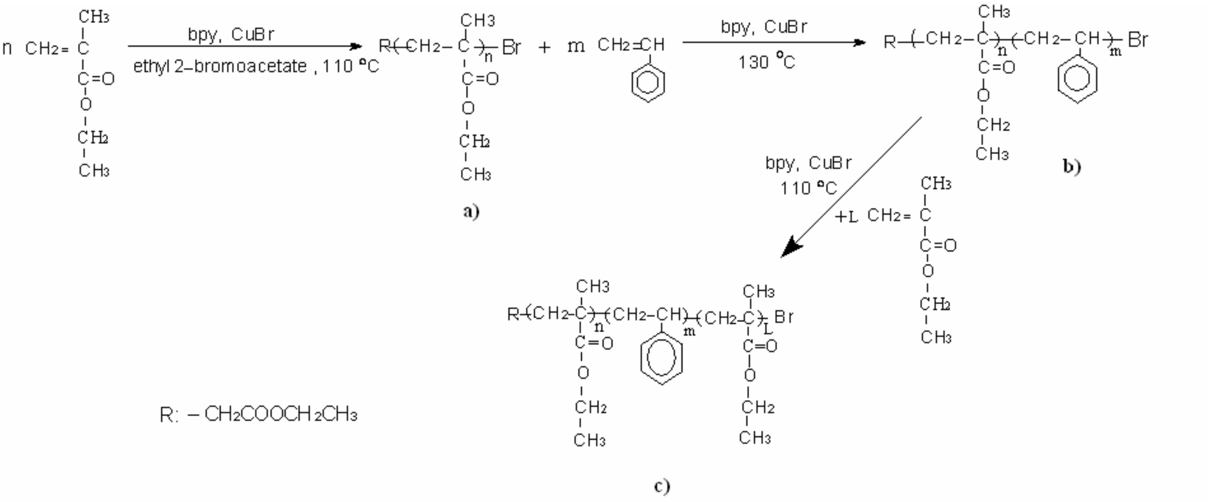
The diblock copolymer of PEMA with St was synthesized using PEMA as macroinitiator and Cu(I)Br complexed with 2,2'-bipyridine as catalyst in bulk polymerization of St. After the reaction was completed, the polymer was dissolved in chloroform and precipitated in methanol. The AB type diblock copolymer was dried under vacuum at 45°C (Scheme 1.b).
^{1}H NMR (CDCI$_3$, ppm): 6,98-6.3 (aromatic protons in St units), 3,95 (-COOCH$_2$ protons in EMA units), 1,56 (CH$_3$, CH$_2$ and CH protons in main chain), 0,98 (CH$_3$ protons in EMA units).
FT-IR (cm^{-1}): 3120-2881 (C-H stretching on aliphatic and aromatic group), 1727 (C=O stretching), 1605 (C=C stretching on aromatic ring), 1455-1413 (C-H bending on aliphatic group), 1150 (asymmetric C-O stretch), 1030 (symmetric C-O stretch).

3.5. ABA Type Triblock Copolymerization of Poly[EMA-b-St] with EMA (Poli[EMA-b-St]'in EMA ile ABA Tip Triblok Kopolimerizasyonu)

Triblock copolymer of poly[EMA-b-St] with EMA was synthesized using poly[EMA-b-St] as macroinitiator and Cu(I)Br complexed with 2,2'-bipyridine as catalyst in bulk polymerization of EMA. After the reaction was completed, the polymer was dissolved in chloroform and precipitated in methanol. The ABA type triblock copolymer was dried under vacuum at 45°C (Scheme 1.c).
^{1}H NMR (CDCI$_3$, ppm): 7,06-6,36 (aromatic protons in St units), 4,12 (-COOCH$_2$ protons in EMA units), 1,87-1,25 (CH$_3$, CH$_2$ and CH protons in main chain), 0,92 (CH$_3$ protons in EMA units).
FT-IR (cm^{-1}): 3120-2881 (C-H stretching on aliphatic and aromatic group), 1727 (C=O stretching), 1605 (C=C stretching on aromatic ring), 1455-1413 (C-H bending on aliphatic group), 1150 (asymmetric C-O stretch), 1030 (symmetric C-O stretch).

4. RESULTS AND DISCUSSION (BULGULAR VE TARTIŞMA)

To accomplish of a homopolymer of ethyl methacrylate a controlled/living radical process was carried out by atom transfer radical polymerization method using ethyl 2-bromo acetate (2-EBA) as initiator and CuBr/bpy as catalyst system. The ^{1}H-NMR spectrum of poly(EMA) homopolymer was illustrated in Figure 1. Also, the diblock and triblock copolymers were performed using same catalyst system and related macroinitiators mentioned above. The molar ratio of compounds in ATRP system were applied as 1:1:2:100 for initiator(or macroinitiators):Cu(I)Br:bpy:monomers, respectively.



Scheme 1. Synthesis of block copolymers
(Şema 1. Blok kopolimerlerin Sentezi)

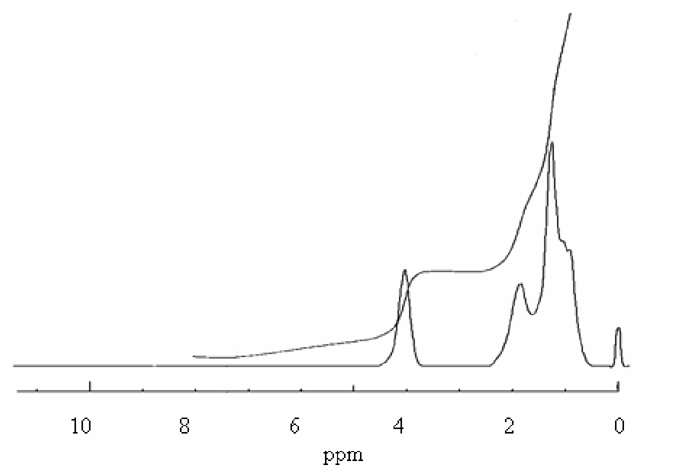


Figure 1. ^{1}H-NMR spectra of poly(EMA)
(Şekil 1. Poli(EMA)'ın ^{1}H-NMR spektrumu)

4.1. Copolymer Composition (Kopolimer Bileşimi)

The compositions of diblock and triblock copolymers were determined by ^{1}H-NMR technique. The ^{1}H-NMR spectra of diblock and triblock copolymers were illustrated in Figure 2a and 2b. The characterization was carried out by the signals observed at 6,3-6,98 ppm for aromatic protons in St units and observed at 3,95 ppm for methylene protons adjacent to ester group in EMA units. By comparing the integration of aromatic peak to methylene peak, the percentage of styrene units in the diblock and triblock copolymers were obtained as 68 and 21 (by %), respectively.

4.2. Molecular Weights and Polydispersities (Molekül Ağırlıkları ve Polidispersiteler)

The molecular weight and molecular weight distribution of all polymers were obtained from a high pressure liquid chromatography pump with Agilent 1100 system equipped with a vacuum degasser, a refractive index detector. The average molecular weight (Mn) and the polydispersity index of homo, diblock and triblock copolymers were found as 3100, 29300, 40000 and as 1,14, 1,17, 1,96, respectively. The predictable molecular weight and narrow molecular weight distribution were given in Table 1 and the GPC chromatograms were illustrated in Figure 3. From these data, it can be suggested that the controlled/living polymerization was performed [10]. Also, the resulting copolymers posses relatively narrow polydispersities. This suggest that the contribution of chain breaking and transfer as well as termination reactions during copolymerization may be observed but this state can be neglected until higher polymerization conversation [12].

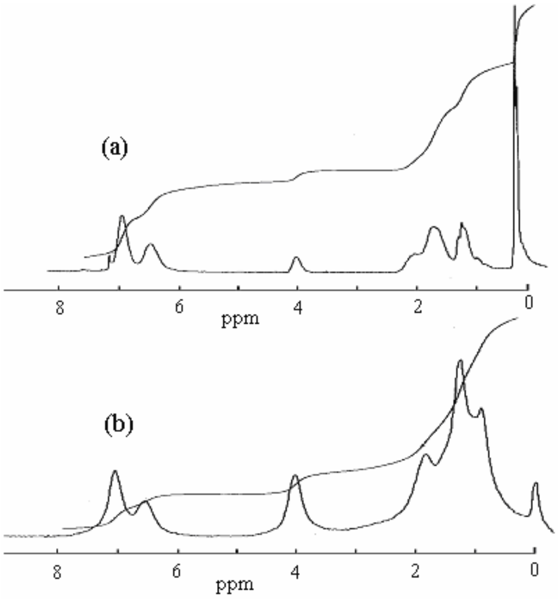


Figure 2. ^{1}H-NMR spectra of a) diblock and b) triblock copolymers
(Şekil 2. ^{1}H-NMR spektrumları a) homopolimer, b) diblok ve c) triblok kopolimer)

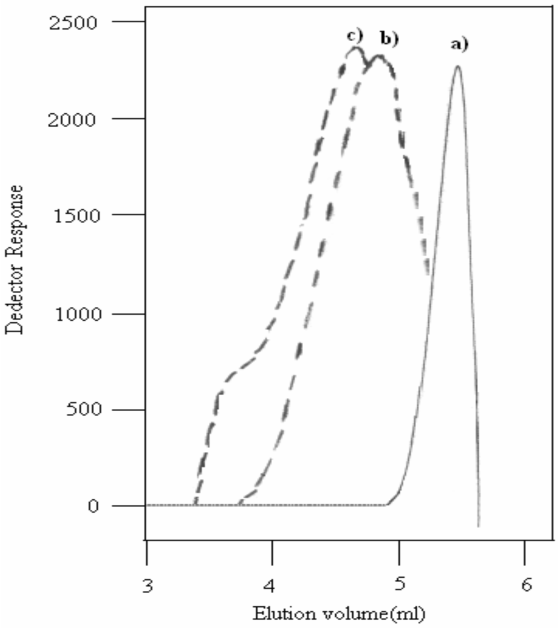


Figure 3. GPC curves of a) homopolymer, b) diblock and c) triblock copolymers
(Şekil 3. GPC eğrileri a) homopolimer, b) diblok ve c) triblok kopolimer)

Table 1. The molecular weights and molecular weight distribution of polymers.
(Tablo 1. Polimerlerin molekül ağırlıkları ve molekül ağırlık dağılımları)

Polymers	Mn	Mw	Mv	Mz	Polydispersity
Poly(EMA)	3100	3600	3600	4100	1,14
Poly(EMA-b-St)	29300	34200	34200	39400	1,17
Poly(EMA-b-St-b-EMA)	40000	78900	78900	172800	1,96

4.3. UV–Visible Absorbance Curves of Samples (Örneklerin UV-Görünür Absorbans Eğrileri)

UV–visible absorbance curves of poly(EMA), poly[EMA-b-St] and poly[EMA-b-St-b- EMA] were shown in Figure 4. The curve for poly(EMA) (Figure 4.a) shows strong UV absorption at 297 and 308 nm, which is attributed to the presence of aliphatic polymer backbone and ester group based on n-π* transitions, respectively. The curve for poly[EMA-b-St] (Figure 4.b) shows UV absorption at 345 nm which is attributed to the presence of conjugate C=C bonded at St units in copolymers based on π-π* transitions [13]. From Figure 4, it can be seen that the small absorption at 308 nm for EMA units in diblock copolymer shifts towards higher absorption in triblock copolymer at same wavelength. Similar to this shifting, it is observed that the middle intense absorption at 345 nm for St units in diblock copolymer shifts towards the more small absorption in triblock copolymer at 345 nm. These results showed that EMA units were determined excessive in triblock copolymer while the St units were excessive in diblock copolymer.

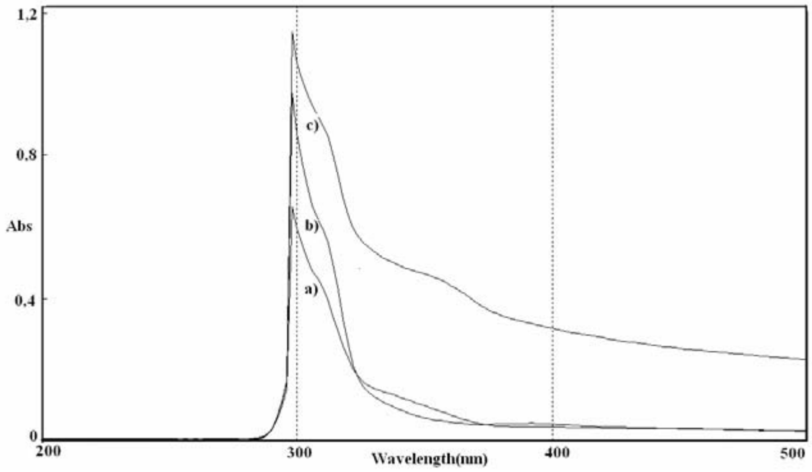


Figure 4. UV curves of a) homopolymer, b) triblock and c) diblock copolymers
(Şekil 4. UV eğrileri a) homopolimer, b) diblok ve c) triblok kopolimer)

4.4. Differential Scanning Calorimetry (DSC) (Diferansiyel Taramalı Kalorimetre (DSC))

Representative DSC curves of poly(EMA), poly[EMA-b-St] and poly[EMA-b-St-b- EMA] were shown in Figure 5. The heating rate was maintained at 20°C/min. under nitrogen flow. While the T_g value of poly(EMA) is 73°C, the value of diblock and triblock copolymer were found as 97°C and 78°C, respectively. From these results it was observed that there wasn’t a phase separation between EMA and St units in block copolymer chains. The reason of high Tg value at diblock copolymer according to homo and triblock copolymer is a high ratio of St units (69%) in copolymer composition.

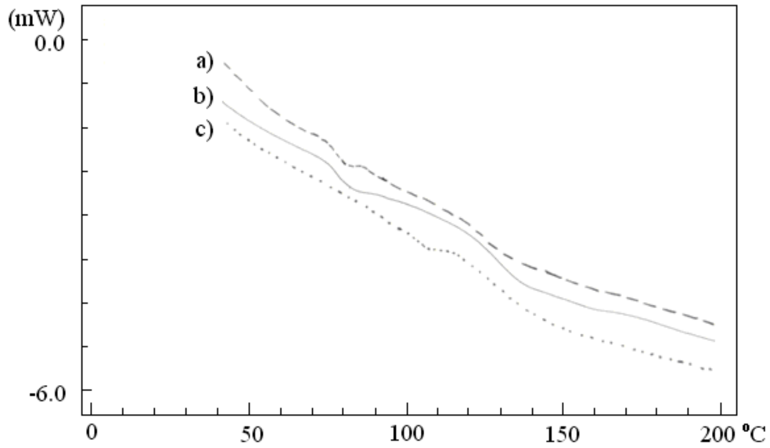


Figure 5. DSC trace of a) poly(EMA), b) poly(EMA-b-St-b-EMA), c) poly(EMA-b-St)
(Şekil 5. DSC eğrileri a) poly(EMA), b) poly(EMA-b-St-b-EMA), c) poly(EMA-b-St)

5. CONCLUSIONS (SONUÇLAR)

Homopolymer of EMA and its block copolymers with St were synthesized using CuBr/bpy as the catalyst system and ethyl 2-bromo acetate (2-EBA) and C-Br-end-group polymers as initiator and macroinitators at 110°C and 130°C by atom transfer radical polymerization. Of all polymers were characterized by FT-IR, ^{1}H-NMR and UV spectroscopy. The molecular weight and molecular weight distributions were determined by GPC and from its results, it was seen that the polymerization was controlled/living. From the glass transition temperature results, it was observed that there wasn’t a phase separation between EMA and St units in block copolymer chains. The reason of high Tg value at diblock copolymer according to homo and triblock copolymer is a high ratio of St units (69%) in copolymer composition.

REFERENCES (KAYNAKLAR)

1. Hawker, C.J., Bosman, A.W., and Harth, E., (2001). New polymer synthesis by nitroxide mediated living radical polymerizations. *Chem Rev,* 101 (12), 3661-3688.
2. Matyjaszewski, K. and Xia, J.H., (2001). Atom transfer radical polymerization. *Chem Rev,* 101 (9), 2921-2990.
3. Wang, J.S. and Matyjaszewski, K., (1995). Controlled living radical polymerization - atom-transfer radical polymerization in the presence of transition-metal complexes. *J Am Chem Soc,* 117 (20), 5614-5615.
4. Kato, M., Kamigaito, M., Sawamoto, M., and Higashimura, T., (1995). Polymerization of methyl-methacrylate with the carbon - tetrachloride dichlorotris (triphenylphosphine) ruthenium(II) methylaluminum bis(2,6-di-tert-butylphenoxide) initiating system - possibility of living radical polymerization. *Macromolecules,* 28 (5), 1721-1723.
5. Wang, J.S. and Matyjaszewski, K., (1995). Controlled living radical polymerization - halogen atom-transfer radical polymerization promoted by a Cu(I)Cu(II) redox process. *Macromolecules,* 28 (23), 7901-7910.

6. Patten, T.E. Xia, J.H., Abernathy, T., and Matyjaszewski, K., (1996). Polymers with very low polydispersities from atom transfer radical polymerization. ***Science,*** 272 (5263), 866–868.
7. Matyjaszewski, K., Patten, T.E., and Xia, J.H., (1997). Controlled/''living'' radical polymerization. Kinetics of the homogeneous atom transfer radical polymerization of styrene. ***J Am Chem Soc,*** 119 (4), 674–680.
8. Percec, V. and Barboiu, B., (1995). Living radical polymerization of styrene initiated by arenesulfonyl chlorides and Cu-I(bpy)(N)Cl. ***Macromolecules,*** 28 (23), 7970–7972.
9. Gaynor, S.G., Edelman, S., Matyjaszewski, K., (1996). Synthesis of branched and hyperbranched polystyrenes. ***Macromolecules,*** 29 (3), 1079–1081
10. Demirelli, K., Kurt, A., and Coskun, M., (2004). Atom transfer radical polymerization of 1-phenoxycarbonyl ethyl methacrylate monomer. ***European Polymer Journal***, 40 (3), 451-457.
11. Demirelli, K., Kurt, A., Coskun, M.F., and Coskun, M., (2006). Characterization and synthesis of three-armed copolymers of phenoxycarbonylmethyl methacrylate and ethyl methacrylate via atom transfer radical polymerization. ***Journal of Macromolecular Science-Pure and Applied Chemistry***, A43 (3), 573-587.
12. Bibiao, J., et al., (2006), Modification of the halogen end groups of polystyrene prepared by ATRP. ***European Polymer Journal***, 42 (1), 179-187.
13. Calcagno, L., Compagnini, G., and Foti, G., (1992). Structural modification of polymer films by ion irradiation. Nucl. Instrum. Methods. ***Phys. Res. B***, 65 (1–4), 413–422.