

Thermal Degradation of Block Copolymers of Ethyl Methacrylate with Styrene Synthesized by Atom Transfer Radical Polymerization Method

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Abstract

The thermal stabilities of the poly(ethyl methacrylate) [poly(EMA)], poly(ethyl methacrylate-b-styrene) [poly(EMA-b-St)] and poly(ethyl methacrylate-b-styrene-b-ethyl methacrylate) [poly(EMA-b-St-b-EMA)] were determined from thermo gravimetric analysis (TGA). For this purpose, the homo and block copolymers, poly(EMA), poly(EMA-b-St), poly(EMA-b-St-b-EMA) were heated from ambient temperature to 500°C at a heating rate of 10°C/min under nitrogen flow. Decomposition temperatures of poly(EMA), poly(EMA-b-St) and poly(EMA-b-St-b-EMA) were determined in a single step at about 257, 308 and 294°C, respectively. The thermal stability data and the residues at 450°C were also determined from TGA curves. On the other hand, the thermal degradation behaviors of the block copolymers were studied using thermogravimetry and a single line vacuum system consisting of a degradation tube with a condenser for product collection and a liquid nitrogen trap (-196°C). The products of degradation were collected at two different fractions, which are cold ring fraction (CRF) and volatile liquid fraction (VLF) trapped at -196°C. All the fractions of diblock and triblock copolymers were investigated by means of IR, ¹H-NMR, and GC-MS techniques. From analyzing of degradation products ethyl methacrylate and styrene are given as major products of degradation. In addition, the most important minor products are benzene, ethyl benzene and toluene.

Key Words: Thermal Degradation, Cold Ring Fraction (CRF), Volatile Liquid Fraction (VLF), Ethyl Methacrylate, Styrene.

Atom Transfer Radikal Polimerizasyon Metoduyla Sentezlenen Etil Metakrilatın Stiren ile Blok Kopolimerlerinin Termal Degradasyonu

Özet

Poli(etil metakrilat) [poly(EMA)], poli(etil metakrilat-b-stiren) [poly(EMA-b-St)] ve poli(etil metakrilat-b-stiren-b-etil metakrilat) [poly(EMA-b-St-b-EMA)] polimerlerin termal kararlılıkları termogravimetrik analiz (TGA) tekniği kullanılarak belirlendi. Bu amaçla, homo ve blok kopolimerler, poly(EMA), poly(EMA-b-St), poly(EMA-b-St-b-EMA) azot gazı atmosferinde 10°C/dak ısıtma hızında oda sıcaklığından 500°C'ye kadar ısıtıldı. Poly(EMA), poly(EMA-b-St) ve poly(EMA-b-St-b-EMA) polimerlerinin bozunma sıcaklıkları 257, 308 ve 294°C olarak ölçüldü. Ayrıca TGA eğrilerinden termal kararlılık verileri ve 450°C'deki artık oranları da belirlenmiştir. Öte yandan blok kopolimerlerin termal degradasyon davranışları da özel bir degradasyon sistemi kullanılarak araştırıldı. Bu amaçla ürün toplama özellikli bir soğutucunun takılı olduğu bir degradasyon tüpü ve -196°C'deki sıvı azot tuzağını içeren özel bir degradasyon düzeneği kullanıldı. Degradasyon ürünleri soğuk halka fraksiyonu (CRF) ve -196°C'de tutulan uçucu sıvı fraksiyonu (VLF) olmak üzere iki farklı fraksiyonda toplandı. Diblok ve triblok kopolimerlerin bütün degradasyon ürünleri FT-IR, ¹H-NMR, ve GC-MS teknikleri ile karakterize edildi. Bu ürünlerin analizinden etil metakrilat ve stiren başlıca degradasyon ürünleridir. Ayrıca, tespit edilen diğer önemli degradasyon ürünleri de benzen, etil benzen ve toluen bileşikleridir.

Anahtar Kelimeler: Termal Degradasyon, Soğuk Halka Fraksiyonu (CRF), Uçucu Sıvı Fraksiyonu (VLF), Etil Metakrilat, Stiren.

1. Introduction

Thermal degradation studies of polymers are necessary as many applications depend on their

thermal stability. In order to accomplish this goal, many techniques have been used including pyrolysis mass spectrometry, thermal volatilization analysis, thermogravimetric

analysis coupled to fourier transform infrared spectroscopy, etc. [1]. In the case of homopolymers or block copolymers, there are two main patterns of breakdown: depolymerization or side group (substituent) reactions. During depolymerization, the distinctive feature is the absence of residues at high temperatures, i.e. all the degrading products, e.g. monomers, dimers, chain fragments, etc. have essentially the same composition as the repeating unit. In most cases, the polymer molecular weight will fall rapidly as degradation proceeds and often, but not invariably, there is only one stage of degradation as the temperature is gradually raised. Side group or substituent reactions can lead to a more complex pattern of degradation. The main features include the presence of products of different compositions from the original repeating unit and the presence of a residue char at high temperature, in the absence of air [2-5]. Under these circumstances, more than one stage of degradation is normally observed as the temperature is gradually increased [6].

In this article, the thermal degradation of block copolymers was reported. The products of degradation have been investigated by using FT-IR, ¹H-NMR, TGA and GC-MS techniques. Of all data were given as compared with each other.

2. Experimental

2.1. Materials

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.

2.2. Instrumental techniques

Infrared spectra were obtained on a Mattson 1000 FTIR spectrometer and obtained by

polymeric film or liquid film on a salt plate. NMR spectra were recorded on a Jeol FX 90Q NMR spectrometer at room temperature using CDCl₃ as a solvent and TMS as an internal standard. Thermogravimetric analyses were recorded on a TGA-50 instrument. The thermal stability measurements were carried out under nitrogen flow with heating rate of 10°C min⁻¹. The identification of degradation products were supplied by gas chromatography and mass spectrophotometer (GC-MS) instrument.

2.3. Atom transfer radical polymerization

For homo polymerization of EMA the catalyst, copper(I) bromide and ligand 2,2'-bipyridyne were first placed in a round bottom flask and three cycles of nitrogen pressurization followed by vacuum were applied to remove air and moisture from the flask. The deoxygenated monomer and initiator, ethyl methacrylate and ethyl 2-bromo acetate (2-EBA), was added into flask, respectively. The mixture was stirred at room temperature until it becomes homogeneous. The flask was placed in an oil bath at 110°C. After the polymerization had carried out, the flask 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. The same procedure and amount of chemicals for synthesizes of poly(EMA-b-St) diblock and poly(EMA-b-St-b-EMA) triblock copolymer were applied except of macro initiators and polymerization temperatures. While the diblock copolymer of poly(EMA) with St was synthesized at 130°C using poly(EMA) as macroinitiator, the triblock copolymer of poly(EMA-b-St) with EMA was synthesized at 110°C using poly(EMA-b-St) as macroinitiator. The molar ratio of compounds in this polymerization system were applied as 1:1:2:100 for initiator (or macroinitiators): Cu(I)Br: bpy: monomers, respectively.

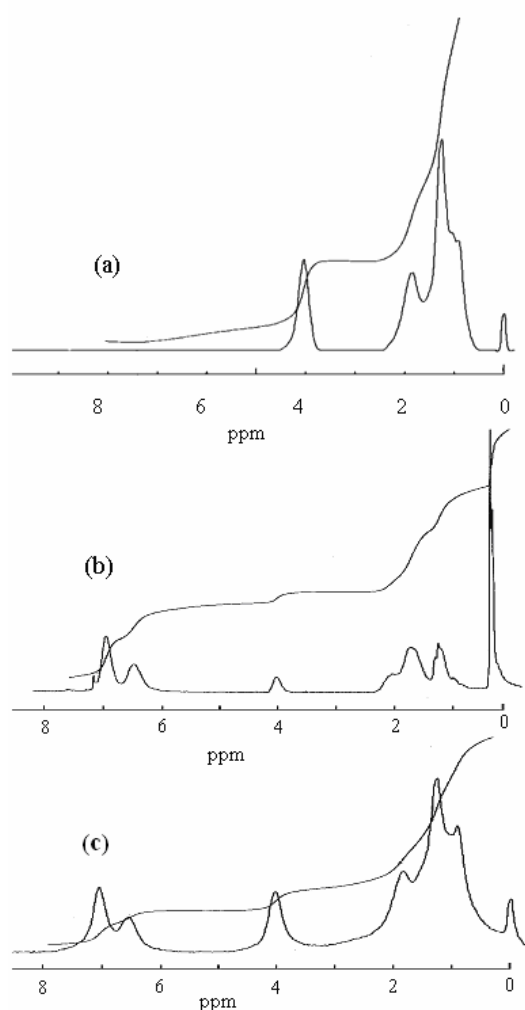


Figure 1. $^1\text{H-NMR}$ spectra of a) poly(EMA), b) poly(EMA-b-St), c) poly(EMA-b-St-b-EMA)

3. Results and Discussion

The characterization was confirmed by FT-IR and $^1\text{H-NMR}$ techniques. The most characteristic FT-IR absorption bands for poly(EMA) were attributed to the band at 1727 cm^{-1} for C=O ester group stretching, at $1455-$

1413 cm^{-1} for aliphatic C-H bending, at 1150 and 1030 cm^{-1} for asymmetric and symmetric C-O stretching, respectively. These bands were also observed for diblock and triblock copolymer except that the band at 1605 cm^{-1} for C=C stretching on aromatic ring in St units, which was appeared in diblock and triblock copolymer but wasn't seemed in homopolymer. Figure 1 shows the $^1\text{H-NMR}$ spectra for polymers in which the spectra for diblock and triblock copolymers show signals at $7.06-6.36\text{ ppm}$ (aromatic ring protons in St units), 4.12 ppm ($-\text{COOCH}_2$ protons in EMA units), $1.87-1.25\text{ ppm}$ (CH_3 , CH_2 and CH protons in main chain), 0.92 ppm (CH_3 protons in EMA units). Especially, the signal at 4.12 ppm attributed to $-\text{COOCH}_2$ protons in EMA units was observed as a weak intensity in poly(EMA-b-St) while it was middle in poly(EMA-b-St-b-EMA). Similar to this approach the signals at $7.06-6.36\text{ ppm}$ were observed as a strong intensity in diblock copolymer.

3.1. Thermogravimetric study

The thermogravimetric curves for poly(EMA), poly(EMA-b-St), poly(EMA-b-St-b-EMA), which are obtained from room temperature to 500°C at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen flow, are illustrated in Figure 2 as compared with each other. Decomposition temperatures of poly(EMA), poly(EMA-b-St) and poly(EMA-b-St-b-EMA) were determined in a single step at about 257 , 308 and 294°C , respectively. The thermal stability data and the residues at 450°C of polymers are summarized in Table 1.

Table 1. TGA data for homo and block copolymers

Polymers	aT_i	bT_f	$^cT_{\%50}$	%Weight loss at 300°C	%Weight loss at 350°C	%Weight loss at 400°C	Residue at 450°C (%)
Poly(EMA)	257	382	325	13	88	95	4
Poly(EMA-b-St-b-EMA)	294	435	371	2	29	78	3
Poly(EMA-b-St)	308	450	405	1	15	46	4

a)Initial decomposition temperature, b)Final decomposition temperature, c)Decomposition temperature at 50%

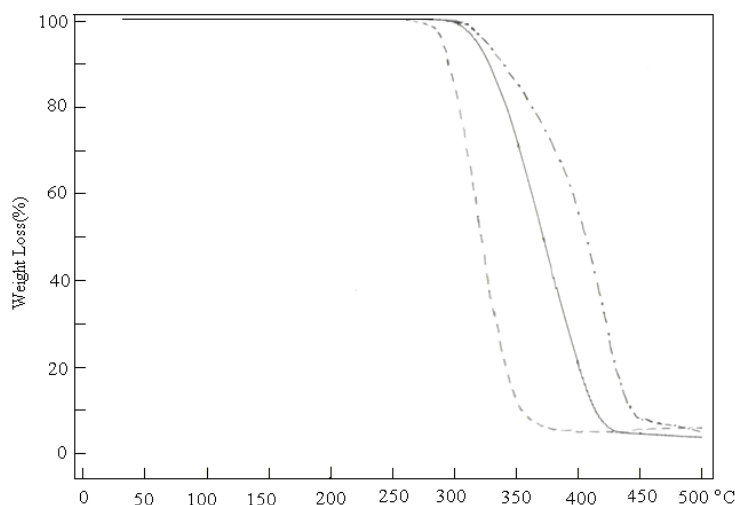


Figure 2. TGA trace for poly(EMA)(dashed line), poly(EMA-b-St-b-EMA)(continuous line), poly(EMA-b-St)(dotted line)

3.3. Product identification studies

Two main fractions, cold ring fraction (CRF) and volatile liquid fraction (VLF) trapped at -196°C (in liquid nitrogen), were taken from degradation of block copolymers. All fractions were investigated by FT-IR, $^1\text{H-NMR}$ and GC-MS. The IR spectra of these fractions were illustrated in Figure 3. The most characteristic signals of CRF of diblock copolymer (Figure 3a) are signals at $3120\text{-}2820\text{ cm}^{-1}$ (aliphatic and aromatic C-H stretch), 1728 cm^{-1} (C=O stretch), 1627 cm^{-1} (aliphatic C=C), 1600 cm^{-1} (aromatic C=C); $^1\text{H-NMR}$ spectrum (Figure 4a) of the

same fraction shows signals at 7,26 ppm (aromatic ring protons), 5,77-5,13 ppm ($\text{CH}_2=\text{CH}_2$, $-\text{CH}=\text{CH}-$), 4,20 ppm ($-\text{COOCH}_2$ protons, small). While the IR spectrum of CRF of triblock copolymer (Figure 3b) is showing strong C=O band at 1727 cm^{-1} and vinylic C=C at 1627 cm^{-1} , its $^1\text{H-NMR}$ spectrum (Figure 4b) shows signals at 7,27 ppm (aromatic ring protons), 5,80-5,25 ppm (vinylic $\text{CH}_2=\text{C}$), 4,20 ppm ($-\text{COOCH}_2$ protons, strong). These data suggest the presence of EMA and St monomers. Also, IR and $^1\text{H-NMR}$ spectra for VLF of diblock and triblock copolymers have been presented and its structures similar to CRF's.

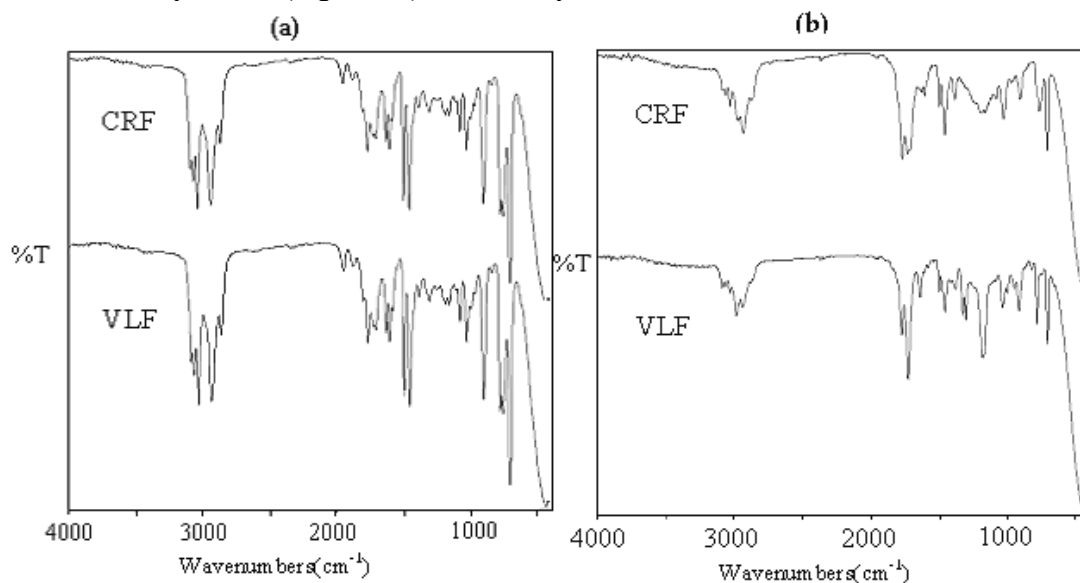


Figure 3. IR spectra of the cold ring fractions (CRF) and volatile liquid fractions (VLF) collected during degradation for a) poly(EMA-b-St), b) poly(EMA-b-St-b-EMA)

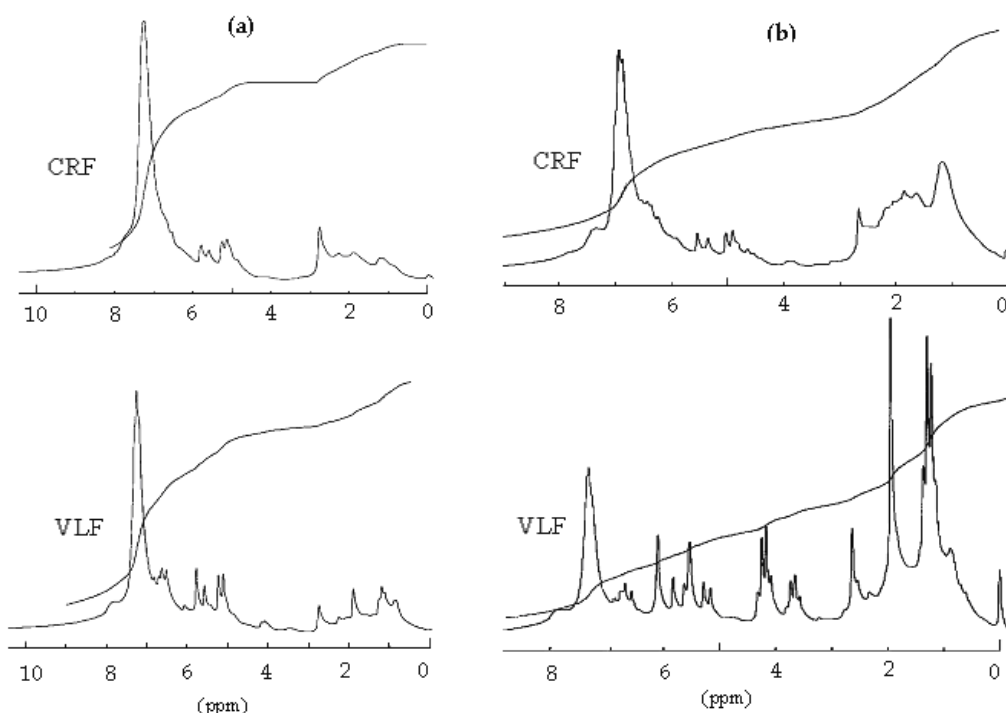


Figure 4. ^1H -NMR spectra of CRF and VLF trapped at -196°C during degradation; a) poly(EMA-b-St), b) poly(EMA-b-St-b-EMA)

The product identification studies in CRF and VLF of block copolymers were performed by GC-MS. The gas chromatograms of CRF and VLF were shown in Figure 5. The main products of degradation for diblock and triblock

copolymers were given in Table 2 and Table 3, respectively.

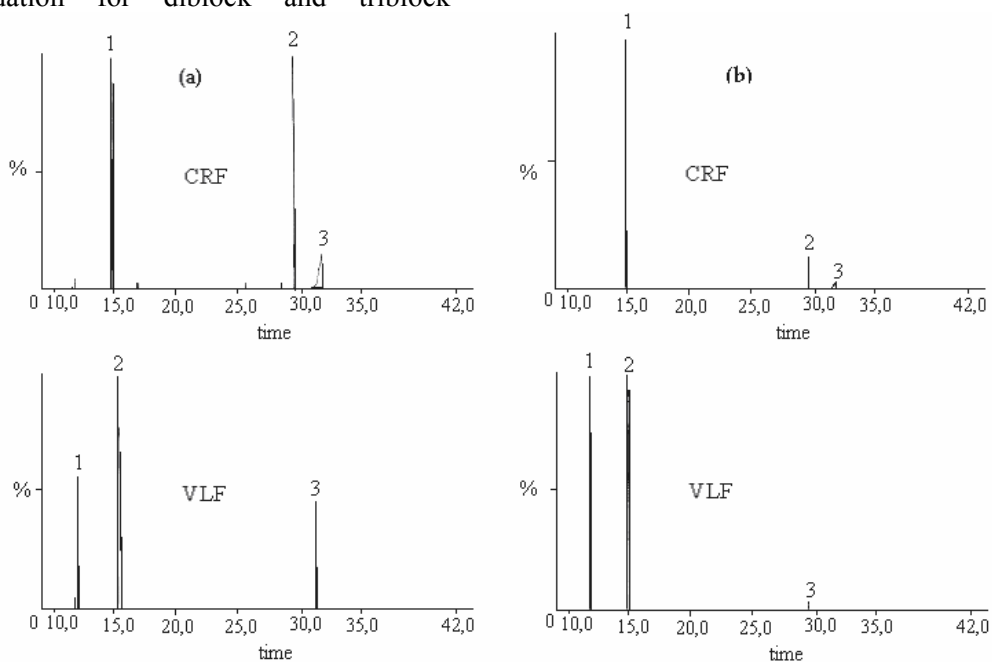


Figure 5. The gas chromatograms of CRF and VLF; a) poly(EMA-b-St), b) poly(EMA-b-St-b-EMA)

Table 2. Identification by GC-MS of CRF and VLF products from degradation of diblock copolymer

Fraction	No	%	Assignment	m/e of major in MS
CRF	1	73,91	CH ₂ =CH(Ph)	(M-1), 103(b.p), 87, 65, 51,
	2	22,10	CH ₂ =C(Ph)CH ₂ CH ₂ (Ph)	M ⁺ , 208, 193, 178, 165, 130, 115, 104, 91(b.p), 78, 65, 51
	3	3,48	CH ₂ =C(Ph)CH ₂ CH ₂ (Ph)	(M-1), 207, 178, 165, 129, 117, 115, 103, 91(b.p), 77, 65, 51
VLF	1	11,63	CH ₂ =C(CH ₃)COOCH ₂ CH ₃	M ⁺ , 114, 99, 96, 86, 71, 69 (b.p), 55, 41
	2	80,13	CH ₂ =CH(Ph)	(M-1), 103(b.p), 97, 87, 77, 65, 50
	3	7,90	CH ₂ =C(Ph)CH ₂ CH ₂ (Ph)	M ⁺ , 208, 193, 178, 164, 151, 130, 115, 104, 91(b.p), 78, 65, 51

Table 3. Identification by GC-MS of CRF and VLF products from degradation of triblock copolymer

Fraction	No	%	Assignment	m/e of major in MS
CRF	1	85,23	CH ₂ =CH(Ph)	(M-1), 103(b.p), 89, 78, 63, 51,
	2	6,64	CH ₂ =C(Ph)CH ₂ CH ₂ (Ph)	M ⁺ , 208, 193, 178, 165, 130, 115, 104, 91(b.p), 78, 65, 51
	3	6,21	CH ₂ =C(Ph)CH ₂ CH ₂ (Ph)	(M-1), 207, 178, 165, 129, 117, 15, 103, 91(b.p), 77, 65, 51
VLF	1	51,86	CH ₂ =C(CH ₃)COOCH ₂ CH ₃	M ⁺ , 114, 99, 96, 86, 71, 69(b.p), 55, 41
	2	47,61	CH ₂ =CH(Ph)	(M-1), 103(b.p), 97, 87, 77, 65, 50
	3	0,17	CH ₂ =C(Ph)CH ₂ CH ₂ (Ph)	M ⁺ , 208, 193, 178, 164, 151, 130, 115, 104, 91(b.p), 78, 65, 51

*Ph: phenyl

3.4. The mechanism of degradation

The volatile product composition of degradation of their copolymers or polystyrene prepared by free radical polymerization method has been studied by some workers [7,8]. Depropagation is reported to involve only macroradicals and the same radical is involved in a competing backbiting intramolecular transfer reaction, which leads to dimer, trimer, etc. [9]. In this study, monomer evolution (EMA or St), which are evidence of depolymerization, is characteristic during degradation of block copolymers prepared by ATRP method. While CRF_d of diblock copolymer gives dimer of styrene (25%) and styrene (73.9%), its VLF_d shows styrene and EMA, 80% and 11.6%, respectively. On the other hand, the CRF_t of triblock copolymer shows styrene and EMA, 85% and 13%, respectively. The same products

were detected at VLF_t, 47% and 52%, respectively. Detection of monomers in CRFs and VLFs indicates that depolymerization is an important reaction in thermal degradation of block copolymers as was observed in thermal degradation of many poly methacrylic esters [10-12].

The chain fragments, formed as a result of transfer reactions, are an important fraction of degradation products. It contains some side chain decomposition at block copolymers whose evidence is presence of ethyl methacrylate. The other most important minor products, such as toluene, ethyl benzene, and benzene, are presented. Of all these decomposition mechanisms are summarized in Scheme 1. Most of the degradation products of diblock copolymers are similar to products formed from thermal degradation of triblock copolymers [13].

involves random backbone scissions, followed by depolymerization of the secondary radical end and intra- and intermolecular transfer of the primary radical end.

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