Synthesis and thermal degradation of amphiphilic 2-(diethylaminoethyl) methacrylate by Atom Transfer Radical Polymerization and its copolymers with isobornylmethacrylate

M. Fatih COŞKUN

Kadir DEMİRELLİ

University of Firat
Faculty of Science and Arts
Department of Chemistry
Elazığ- Turkey

Abstract

The atom transfer radical polymerization (ATRP) of 2-(diethylamino)ethyl methacrylate (DEAEMA) with isobornylmethacrylate (IBMA) were performed in bulk at 110 ^{o}C in the presence of cuprous(I)bromide (CuBr), and ethyl 2-bromoacetate. The structure of homo- and copolymers was characterized by IR, ^{1}H and ^{13}C-NMR techniques. For copolymerization system, their monomer reactivity ratios were obtained by using Kelen-Tüdös equations. Thermal analysis measurements of homo- and copolymers prepared by ATRP method were measured by TGA-50 and DSC-50. The initial decomposition temperatures of the obtained copolymers increased with increasing mole fraction of IBMA moiety. The average activation energy calculated for the first and the second decomposition stages of poly(DEAEMA) by MHRK method were 43.45 and 94.82 kj/mole, respectively. Thermal degradation of poly[2-(diethylamino)ethyl methacrylate] was investigated by programmed heating from ambient temperature to 350 ^{o}C under vacuum followed by the product collection, and using FT-IR spectra of partially degraded polymer. The cold ring fraction (CRF) of products volatile at degradation temperature but not at ambient temperature was identified by GS-MS, FT-IR. Based on degradation, the major products of CRF are tri ethylamine, [m/e:99(M^{+}), 86(base peak)], diethyl 2-hydroxyethylamine [m/e:17(M^{+}), 86(b.p)], 2-(diethylaminoethyl) methacrylate(monomer)[m/e:185(M^{+},very small),113,99, 86(b.p), 69,58].

Key words: ATRP, DEAEMA, IBMA, DSC, Monomer reactivity ratios, thermal degradation.

INTRODUCTION

Controlled/living vinyl addition polymerization giving a wide range of polymer structures is continuing to receive widespread attention(1). This allows the controlled synthesis of a range of polymeric structures such as block copolymers, graft copolymers, functional polymes, star polymers(2). In comparison to the other controlled radical polymerization processes, atom transfer radical polymerizations is mechanistically more complex. Thus, the catalyst reactivity depends on the ligand, the transition metal itself, and the initiating organic Halide(3). So far, copper-based systems seem to be the most efficient(4) when compared to the other transition metals such as iron(5), nickel(6), ruthenium(7), rhodium(8). The counterions are often chloride and bromide, and bromide normally yields higher rates(9).

Amphiphilic copolymers have attracted increasing interest in recent years because of their application as stabilizers, dispersants(10-12). Atom transfer radical polymerization (ATRP) tolerates a variety of functional groups on the monomers and has been succesfully applied toward the preparation of well-defined polymers such as subtituted (meth)acrylic esters, styrene, acrylonitrile(13-15). Particular interest has recently been focused on the controlled/living polymerization of tertiary amine monomers such as 2-(diethylamino)ethyl methacrylate (DEAEMA) and 2-(dimethylamion)ethyl methacrylate (DMAEMA) because their copolymers exhibit interesting associative behaviors(16-18). One of the major advantage of living radical procedures compared to living anionic or cationic polymerizations is the ability to prepare well-defined random copolymers. In traditional anionic or cationic procedures, there are numerous problems which normally preclude the succesfully synthesis of random copolymers. For example, monomer reactivity ratio can be extremely large in anionic systems, and so true random copolymerizations do not occur and block structures are obtained.

The finding that the reactivity ratios for monomers under living free radical conditions are essentially the same as under normal free radical conditions is also fundamentally important(19). The poly(n-alkyl methacrylate)s prepared via free radical polymerization method have been reported to degrade relatively easily to the monomers on heating(20). But, studies of thermal degradation on methacrylate polymers synthesized by ATRP method are marginal. Some of them are triblock copolymers based on bacterial poly[(R)-3-hydroxybutyrate] by atom transfer radical polymerization(21), poly-(butyl methacrylate)-block-poly(butyl acrylate)-block-poly-(butyl methacrylate) (PBMA-b-PBA-b-PBMA) triblock copolymers synthesized by atom transfer radical polymerization (ATRP)(22), Thermal degradation and synthesis of block copolymers of styrene and n-butyl methacrylate by atom transfer radical polymerization (23).

This work reports the ATRP of 2-(diethylamino)ethyl methacrylate (DEAEMA) with isobornylmethacrylate (IBMA) in presence of ethyl 2-bromoacetate (2-EBA) as initiator. The monomer reactivity ratios were determined by the Kelen-Tüdös procedure. Thermal analysis results are given as in comparison with each other for all polymers. The kinetics of thermal degradation otf poly(DEAEMA) was studied by thermogravimetric analysis (TG) in dynamic nitrogen gas at four different heating rates: 5,10,15,20 ^{o}C/min. Also, thermal behavior of poly[2-(diethylamino)ethyl methacrylate] was investigated by thermogravimetric analysis (TG) and by programmed heating from ambient temperature to 350 ^{o}C under vacuum followed by product collection.

Experımental Procedures

Materials

2-(Diethylamiono)ethyl methacrylate (DEAEMA)(Aldrich Chemical Co.) was purified by vacuum distillation. Isobornyl methacrylate (IBMA)was removed from inhibitor by washing with 5% aqeous NaOH. Cuprous(I)bromide, 2,2'-bipyridine (as ligand) and ethyl 2-bromoacetate (as initiator) (Aldrich Chemical Co.) was used as received.

Characterization techniques

FT-IR spectra were obtained on a Perkin Elmer Spectrum One FT-IR spectrometer. NMR spectra were recorded on a NMR (300 MHz) spectrometer at room temperature in $CDCI_3$. Thermogravimetric analysis (TGA) measurements were carried out under a nitrogen flow with a Shimadzu Mark TGA-50 thermobalance at a heating rate of 10 ^{o}Cmin^{-1}. The glass transition temperatures of polymers were measured by Shimadzu Mark DSC-50 from ambient temperature to 200 ^{o}C at a heating rate of 20 ^{o}Cmin^{-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 solvents were tetrahydrofurane (THF) and 5% triethyl amin, the flow rate was 1 ml.min^{-1}. Calibration was achieved with polystyrene.

The degradation products were analysed by Gas Chromatography-Mass Spectrometry (GC-MS) that is a Hewlett Packard system: HP-Agilent 5973 N GC-MS system with 6890 GC. ADB-5 MS column (30 m, 0.25 mm i.d., film thickness 0.25 µm) was used with helium as the carrier gas. The injector temperature was 250°C and the split flow was 1 ml/min. The GC oven temperature was kept at 70 °C for 2 min and programmed to 150 °C at a rate of 10 °C/min and then kept constant at 150 °C for 15 min. Afterwards, temperature of oven was increased to 240 °C at a rate of 5°C/min. MS were taken at 70 eV and a mass range of 35–425.

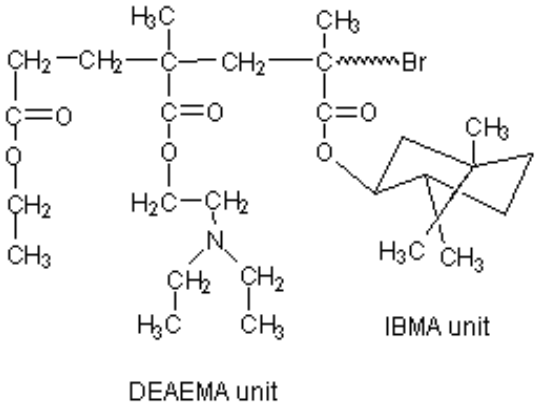
Atom transfer radical copolymerization of DEAEMA with IBMA

The general procedure for the copolymerization of DEAEMA with IBMA of six compositions was as follows: In all cases, predetermined amounts of monomers, ethyl 2-bromoacetate as initiator, 2,2'-bipyridine (bpy) as ligand and the adequate amount of CuBr as catalyst were added to a flask. The mixture was first degassed three times and sealed in vacuum (24). The flask was shaked until the mixture was dissolved and then immersed in an oil bath and heated to the required temperature (at 110^{o}C). After a given time, the flasks were openned and dichloromethane was added to the sample to dissolve the copolymer. The heterogene solution was filtered. The copolymers were isolated by precipitation in n-heptane cooled to -50 ^{o}C. The obtained polymer solution was passed over alumina to remove the catalyst, then the copolymers were precipitated with an excess of n-heptane cooled -50 ^{o}C. The copolymers isolated were passed from column to romove CuBr. Then, the copolymers were dried under vacuum at 40 ^{o}C for 24 h. The conversion of the copolymerization to determine monomer reactivity ratio at low ratios was under 15% .

RESULTS AND DISCUSSION

Characterization of copolymers

The ^{1}H-NMR spectra of poly(DEAEMA) and copolymers prepared by ATRP method in various feed ratios of DEAEMA and IBMA are shown in Figure 1. The signal at 4.06 ppm is assigned to -CH_2- protons adjacent to oxygene in OCH_2CH_2N of DEAEMA unit. The ^{1}H-NMR spectra of poly(DEAEMA-co-IBMA) showed signals at 4.06 ppm (-CH_2- protons adjacent to oxygene ın OCH_2CH_2N, 2H) and at 4.33 (OCH-, 1H) in IBMA units. The DEAEMA units in the copolymer system increased from 14 to 80%. Hence, intensities of signals at 4.06 ppm also increased. The other signals are in good agreement with structure of copolymer showed as in Scheme 1. The ^{13}C-NMR spectrum of poly(DEAEMA0.33-co-IBMA) is shown in Figure 2. As it is seen in ^{13}C-NMR spectrum of polymer illustrates, the most characteristic signals were obtained at 177 ppm (C=O in two units), 62 ppm (quaternar C in IBMA unit), 48 and 51 ppm (-CH_2- adjacent to nitrogene and oxygene for DEAEMA unit, respectively).



Scheme 1

The gel permeation chromatographs (GPC) of some polymers synthesized by ATRP are shown in Figure 3. The polymers obtained have slightly broader molecular weight distribution. And GPC results are given in Table 1. Relatively straight kinetic lines in the semilogarithmic plot were obtained suggesting fast initiation and negligible termination (Figure 4). Unlike ATRP of styrene or acrylates which is usually carried out at 90 to 110 ^{o}C [25,26], polymerization of DEAEMA can be accomplished at much lower temperatures. In particularly, well-controlled polymers with low polydispersity can be prepared at room temperature. Matyjaszewski and et all have recorded that has adsorbtion of poly(DEAEMA) on the GPC column and addition of 1 vol % triethylamine to the GPC eluent (THF) did not minimize these effects[27].

Table 1. GPC results in copolymers prepared via ATRP method

Entry	time(h)	M_n	Mw/Mn
Poly(DEAEMA)	6	30.800	2.08
Poly(DEAEMA)	12	34.300	1.82
Poly(DEAEMA)	18	36.000	1.86

Monomer reactivity ratios

The atom transfer radical random copolymerization of DEAEMA and IBMA initiated by ethyl 2-bromoacetate for various ratios of DEAEMA to IBMA has been carried out. The copolymer compositions were determined by using ^{1}H-NMR spectra. ^{1}H-NMR spectroscopy has been used extensively to evaluate the microstructure of methacrylate copolymers. The monomer sequence distribution of these copolymers was also calculated theoretically from the monomer reactivity ratios and compared with the experimental data obtained by ^{1}H-NMR (28,29). In this study, the copolymer compositions were also analyzed with ^{1}H-NMR spectra. Figure 1 shows ^{1}H-NMR spectra of poly(DEAEMA) and poly(DEAEMA-co-IBMA) prepared by ATRP in various compositions.

The signals centered at 4.0 ppm 4.33 ppm are assigned to aliphatic protons adjacent to oxygene in DEAEMA and IBMA units, respectively. Thus, the mole fractions of DEAEMA and IBMA in the copolymer were determined from the ratio of the signal intensities of methylene and methine protons in 4.06 ppm 4.33 ppm, respectively. Table 2 shows data obtained on the copolymerization. Copolymer compositions have been calculated from the following equation:

$$\frac{\text{Integral heights of } OCH_2 \text{ protons in DEAEMA units}}{\text{Integral heights of } OCH \text{ protons in IBMA units}} = \frac{2m_1}{m_2}$$

Where, m_1 and m_2 are mole fraction of DEAEMA and IBMA in copolymer, respectively.

Table 2. Copolymerization of DEAEMA and IBMA at various monomer feeds[a] and copolymer characteristics

Sample No	M_1[b]	Intensitiy of -OCH_2- protons in DEAEMA unit	Intensitiy of -OCH- protons in IBMA unit	m_1[C]
1[a]	0.90	10	1	0.84
2	0.80	8	1	0.80
3	0.65	15	3	0.71
4	0.50	11	5	0.52
5	0.35	8	8	0.33
6	0.20	4	8	0.20
7	0.10	2	6	0.14

a: Conditions of polymerization; [DEAEMA]:[IBMA]:[CuBr]:[bpy]=90:10:1:2, at 110°C
b: Mole fraction of DEAEMA in Feed, c: Mole fraction of DEAEMA in copolymer

Table 3. Kelen-Tüdös parameter for the copolymerization of DEAEMA and IBMA

Sample No	$F=M_1/M_2$	$f=m_1/m_2$	$G=F(f-1)/f$	$H=F^2/f$	$\eta=G/(\alpha+H)$	$\xi=H/(\alpha+H)$
1	9.00	5.25	7,28	15,42	0.44	0.93
2	4.00	4.00	3,00	4,00	0.59	0.79
3	1.85	2.44	1,09	1,40	0.44	0.57
4	1.00	1.08	0,07	0,92	0.03	0.47
5	0.54	0.49	-0,56	0,59	-0.34	0.36
6	0.25	0.25	-0,75	0,25	-0.58	0.19
7	0.11	0.16	-0,57	0,07	-0.51	0.06

[a]M_1= Mole fraction of DEAEMA in feed; M_2= mole fraction of IBMA in feed, m_1=mole fraction of DEAEMA in copolymer, m_2= mole fraction of IBMA in copolymer.

$\alpha=(H_{min}\ H_{max})^{1/2}=1.03$, H_{min}: lowest value of H, H_{max}: highest value of H

It is well known that monomer reactivity ratios can offer the message of relative reactivity of comonomers. To estimate the relative reactivity of DEAEMA and IBMA in the atom transfer radical copolymerization, the Kelen-Tüdös (30) equation was which are $\eta=(r_1 + r_2/\alpha)\xi - r_2/\alpha$ (The notation descriptions and the calculation results are summarized in Table 3) used. The plots of η versus ξ are shown in Figure 5. Using the slope and intercept of the straight line, the monomer reactivity ratios of DEAEMA and IBMA were determined as r_1=0.76 (r_1=monomer reactivity ratio of DEAEMA) and r_2=0.70. Monomer reactivity ratio of IBMA is quite similar to that of DEAEMA. Apparently, the values of monomer reactivity ratios indicate that the growing radicals with IBMA ends were added to DEAEMA monomer in slightly higher tendency, but the radicals with DEAEMA end have a slightly higher tendency to be added to IBMA. Distributions of the monomeric units along the copolymer chains are random, and they are slightly richer in IBMA units. The copolymer composition equals the monomer feed with a random placement of the two building blocks along the copolymer chain. Such a behavior is referred to as random.

Differential Scanning Calorimetry (DSC) Measurements

The glass transition temperatures of the copolymers of DEAEMA and IBMA prepared by ATRP were measured by DSC. Representative DSC curves of the copolymers heated at 20 ^{o}C/min to 200 ^{o}C are shown in Figure 6. The Tg values of poly(DEAEMA) and poly(IBMA) were measured as 0 ^{o}C and 200 ^{o}C, respectively. The unique transition observed for DEAEMA-IBMA copolymer system corresponds to the glass transition of the soft DEAEMA segments and appears at lower temperatures. The feature may be attributed to miscibility of both types of segments. The Tg's of all the copolymers synthesized by ATRP methods are also represented in Table 4. The glass transition temperatures of copolymers measured by an reference enhancement in the IBMA unit are between 15-184 ^{o}C. The plots of the Tg values versus mole fraction of DEAEMA in the copolymers are shown in Figure 7. Tg's values obtained of the copolymers indicates a slightly negative deviation with respect to linearity that can be associated with a slightly lower free volume.

Table 4 DSC measurements of homo- and copolymer system

Polymers	T_g (^{o}C)
Poly(IBMA)	200
Poly(DEAEMA0.14-co-IBMA)	184
Poly(DEAEMA0.20-co-IBMA)	161
Poly(DEAEMA0.33-co-IBMA)	125
Poly(DEAEMA0.52-co-IBMA)	100
Poly(DEAEMA0.71-co-IBMA)	56
Poly(DEAEMA0.80-co-IBMA)	33
Poly(DEAEMA0.84-co-IBMA)	15
Poly(DEAEMA)	0

Thermogravimetric study

The some of thermogravimetric curves obtained from room temperature to 500 ^{o}C, heating rate 10 ^{o}C/min, nitrogen flow for poly(DEAEMA), poly(IBMA) and poly(DEAEMA-co-IBMA) are given in Figure 8 for comparisons to each other. The decomposition of poly(DEAEMA) is produced in two steps. At the first step, the temperature is 220 ^{o}C. The second stage, more rapid weight loss is observed and this is attributed to the degradation reaction by either of the side chain decomposition or the random chain scission in the backbone. The temperature at which weight loss begins for the DEAEMA-IBMA copolymers are lower than that for poly(IBMA). The thermal stability of copolymer increases with the increasing IBMA unit in copolymer system. TGA results of the polymers are summarized in Table 5.

Table 5 TGA data for the homo- and copolymers prepared by ATRP method

Polymers	$^{a}T_i$ (^{o}C)	T%50 (^{o}C)	%Weigth loss at 300 ^{o}C	%Weigth loss at 350 ^{o}C	%Weigth loss at 400^{o}C
Poly(DEAEMA)	220	348	13	51	63
Poly(IBMA)	260	275	86	92	6
Poly(DEAEMA84% -co- IBMA)	222	348	13	52	62
Poly(DEAEMA52%-co- IBMA)	236	325	16	64	76
Poly(DEAEMA14%-co- IBMA)	260	307	38	78	86

a: Initial decomposition temperature

The activation energy of decomposition of poly(DEAEMA)

The activation energy on the thermal decomposition of poly(DEAEMA) was determined by thermogravimetric analysis. The activation energy of the decomposition process is determined by multiple heating rate kinetics (MHRK). The degradation occurred in a two stages up to a weight loss 20% and 80%. Thus, the series of experiments were run at different heating rates, ΔE could be obtained from slope of the graphic of heating rate vs. 1/T. Figure 9 shows the weight loss vs. temperature for poly(DEAEMA) at different heating rates. The lines showed in Fig 10a and 10b are obtained by plotting heating conversion levels.

From the slopes, the average activation energy calculated for the first and the second stages by MHRK Method were 43.45 and 94.82 kj/mole, respectively. It was found that the thermal degradation of poly(DEAEMA) have two separate decomposition regions. The first decomposition region was considerably result in depolymerization primarily. This reaction followed first-order kinetics and had the activation energy of 43.45 kjoul/mol. The second decomposition region was the thermal degradation for the corresponding polymethacrylic anhydride. In this region, the fragmentation of anhydride ring's structure in polymethacrylic anhydride constitutes the major decomposition reaction with the activation energy of 94.82 kjoul/mol. This is much more lower than that of polymethacrylic acid which was determined as 169.5 kjoul/mole by Ho et al. (31). TG curves are based on weight loss, however, not on the individual products formed during degradation. Activation energies for the thermal degradation of poly(DEAEMA) are shown in Table 6.

Table 6: The activation energies for the thermal degradation of poly(DEAEMA)

Weight loss (%)	Activation energy (kj/mol)	
5	30.5	
10	38.0	
15	47.5	
20	57.8	
Average	43.45	(for the first stage)
55	66.12	
60	103.42	
65	124.2	
70	91.20	
80	89.20	
Average	94.82	(for the second stage)

Changes in IR spectra during degradation

The film of poly(DEAEMA) on a salt plate was partially heated under Ar flow at 10^{o}C/min heating rate, to 200, 250, 270, 300, 320, 350, 370, 400, 420 and 450^{o}C. The spectra were recorded at each heating stage as shown in Figure 11 those of heated to 320, 350, 370, 400, 420 and 450^{o}C in comparison of C=O bands. The IR spectrum of poly(DEAEMA) heated to 320^{o}C is similar to that of the original poly(DEAEMA) although thermogravimetry suggested a weight loss of 20% at 320^{o}C. Although there is not an important change in IR spectrum, 20% weight loss formed may be an evidence of depolymerization. The IR spectrum of the polymer heated to 350^{o}C shows some new peaks at 1022, 1763 and 1804 cm^{-1}, which are the evidence of a six membered cyclic anhydride structures. Formation of a six membered cyclic anhydrides has been observed in thermal degradation of many polymethacrylate esters (32-34). The degradation of polymers in many methacrylate ester polymers such as poly(phenacyl methacrylate)(34), poly(1-phenoxycarbonylethyl methacrylate(35), poly(methyl methacrylate)(36) starts generally with depolymerization above 200 ^{o}C. As the temperature increases intensities of peaks corresponding to cyclic anhydride increased, and intensity of ester carbonyl peak (1731 cm^{-1}) decreased, and above 400^{o}C new peaks at 1674, 1646 and 1598 cm^{-1} appeared, of which two are due to olefinic structures, and the last is probably an evidence of aromatization.

Product identification studies

The degradation was carried out in a single-line system consisting of a degradation tube with a condenser, product collection, and a rotary pump. 250 mg of the polymer was heated at rate of 10^{o}C/min from ambient to 350^{o}C, and the degradation products were collected on inner surface of condenser (Cold ring fraction, CRF) and at a trap in liquid nitrogen (volatile fraction, VF)(-196^{o}C). The both fractions were analyzed by the FT-IR and GC-MS techniques. The FT-IR spectrum of VF showed some characteristic peaks at 3380 cm^{-1} (O-H), 1756 cm^{-1}, 1727 cm^{-1}(C=O), 1696 cm^{-1}(C=O in amide and/or acid), 1667 cm^{-1} and 1646 cm^{-1} (C=C). The FT-IR spectrum of CRF showed similar bands with that of VF, except some additional bands at 3050 cm^{-1}, 1717 cm^{-1} and 1696-1626 cm^{-1}. GC-MS studies showed that VF and CRF contain similar products but in different compositions. These are: three ethylamine [m/e:99(M^{+}), 86(b.p)], diethyl 2-hydroxyethyl amine[m/e: 117(M^{+}), 86(b.p)], 2-(diethylaminoethyl) methacrylate (monomer)[m/e: 185(M^{+}, very small), 113, 99, 86(b.p), 69, 58].

CONCLUSION

The homo- and random copolymers of DEAEMA with IBMA have been synthesized by the ATR polymerization method with ethyl 2-bromoacetate as initiator. ^{1}H, ^{13}C-NMR and FT-IR techniques revealed the presence of both monomeric units in the copolymer chain. The monomer reactivity ratios were calculated using the feed composition and copolymer composition. For the copolymerization systems in six different feed ratios, monomer reactivity ratios of them were found using the K-T method. In this copolymerization system, two monomers have a tendency to form random copolymer because the value of $r_1.r_2$ is at around 0.53. In case of poly(DEAEMA-co-IBMA), initial decomposition temperature of copolymers increased with an increasing in IBMA content. TG measurements were to investigate the kinetics of poly(DEAEMA) thermal degradation. The average activation energy calculated for the first and the second stages by MHRK method were 43.45 kj/mole and 94.82 kj/mole, respectively.

ACKNOWLEDGEMENT

The authors wish to thank the Fırat University Research Fund (FUBAP-1095) for financial support of this work.

REFERENCES

1. Webster, O.W., Lıvıng polymerızatıon methods (1991), Science, 251(4996), pp-887-893.
2. Hawker, C. J., "Living" free radical polymerization: A unique technique for the preparation of controlled macromolecular architectures, (1997), Acc Chem. Res, 30(9): pp-373-383.
3. Kickelbick, G, Reinöhl, U., Ertel., T.S., Bertagnolli, H. Matyjaszewski K., ACS Symp.Ser. 2000, 768211.
4. Queffelec J., Gaynor S.G., Matyjaszewski K., Optimization of atom transfer radical polymerization using Cu(I)/tris(2-(dimethylamino)ethyl)amine as a catalyst, (2000), Macromolecules, 33 (23): pp-8629-8639.
5. Ando, T., Kamigaito M., Sawamoto M., Iron(II) chloride complex for living radical polymerization of methyl methacrylate , (1997), Macromolecules, 30 (16): pp-4507-4510.
6. Granel. C., Dubois P., Jerome R., Teyssie, P., Controlled radical polymerization of methacrylic monomers in the presence of a bis(ortho-chelated) arylnickel(II) complex and different activated alkyl halides, (1996), Macromolecules, 29 (27): pp-8576-8582.
7. Kato, M., Kamigato M., Sawamoto M., Higashimura T., Polymerızatıon Of Methyl-Methacrylate wıth the Carbon-tetrachlorıde dıchlorotrıs(Trıphenylphosphıne)Ruthenıum(II) methylalumınum Bıs(2,6-dı-tert-butylphenoxıde) Inıtıatıng System - Possıbılity of Lıvıng Radıcal Polymerızatıon, (1995), Macromolecules 28 (5): pp-1721-1723.
8. Moineau G, Granel C, Dubois P, Jerome R, Teyssie P. Controlled radical polymerization of methyl methacrylate initiated by an alkyl halide in the presence of the Wilkinson catalyst, (1998), Macromolecules 31 (2): pp-542-544.
9. FischerH.,The persistent radical effect: A principle for selective radical reactions and living radical polymerizations, 2001, Chemıcal Revıews, 101 (12): pp-3581-3610
10. Price, C. In Developments in Block Copolymers-1; Goodman, I., Ed.; Applied Science: London, 1982.
11. Baines, F. L.; Armes, S.P.; Billingham, N.C.;Tuzar, Z. Micellization of poly(2- (dimethylamino)ethyl methacrylate-block-methyl methacrylate) copolymers in aqueous solution (1996), Macromolecules, 29 (25): 8151-8159. **[**
12. Hamley, I.W. In Block copolymers; Oxford University Press: Oxford,1999.
13. Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T., polymerızatıon of methyl-methacrylate wıth the carbon-tetrachlorıde dıchlorotrıs(trıphenylphosphıne)ruthenıum(ıı) methylalumınum bıs(2,6-dı-tert-butylphenoxıde) ınıtıatıng system - possıbılity of lıvıng radıcal polymerızatıon, (1995), Macromolecules 28 (5): pp-1721-1723.
14. Matyjaszewski, K.; Xia, J.H. Atom transfer radical polymerization, (2001), Chem Rev, 101 (9): pp-2921-2990. .
15. Kamigaito, M.; Audo, T.; Sawamoto, M. Metal-catalyzed living radical polymerization (2001), Chem Rev, 101 (12): pp-3689-3745.
16. Gohy, J.F.; Creutz, S.; Garcia, M.; Mahtig, B.; Stamm, M.; Jeröme, R. Aggregates formed by amphoteric diblock copolymers in water, (2000), Macromoleculs, 33 (17): 6378-6387.

17. Anderson, B.C.; Mallapragada, S.K., Synthesis and characterization of injectable, water- soluble copolymers of tertiary amine methacrylates and poly(ethylene glycol) containing methacrylates, (2002), Biomaterials, 23 (22): pp-4345-4352.
18. Gan LH, Ravi P., Mao BW, Tam KC., Controlled/living polymerization of 2-(diethylamino) ethyl methacrylate and its block copolymer with tert-butyl methacrylate by atom transfer radical polymerization , (2003), Journal of Polymer Scıence Part A-Polymer Chemıstry 41 (17): pp-2688-2695.
19. Hawker C.J., Bosman A.W., Harth E., New polymer synthesis by nitroxide mediated living radical polymerizations, (2001), Chem Rev 101 (12): pp-3661-3688.
20. Razga J, Petranek J., Thermal-degradatıon of poly-2-hydroxyethyl methacrylate by pyrolysıs-gas chromatography, (1975), European Polymer Journal, 11 (12): pp-805-808.
21. Zhang XQ, Yang H, Liu QW, Zheng Y, Xie HF, Wang ZL, Cheng RS, Synthesis and characterization of biodegradable triblock copolymers based on bacterial poly[(R)-3-hydroxybutyrate] by atom transfer radical polymerization, (2005), Journal of Polymer Scıence Part A-Polymer Chemıstry, 43 (20): pp-4857-4869.
22. Martin-Gomis L, Fernandez-Garcia M, de la Fuente JL, et al., Physical properties of PBMA-b-PBA-b-PBMA triblock copolymers synthesized by atom transfer radical polymerization, (2003), Macromolecular and Physıcs, 204 (16): pp-2007-2016.
23. Demirelli K, Kurt A, Coskun M, Thermal degradation and synthesis of block copolymers of styrene and n-butyl methacrylate by atom transfer radical polymerization (2004), Polymer-Plastics Technology and Engineering, 43 (4): pp-1245-1263.
24. Moschogıannı P, Pispas S., Hadjichristidis N., Multifunctional ATRP initiators: Synthesis of Four-Arm Star Homopolymers of Methyl Methacrylate and Graft Copolymers of Polystyrene and Poly(t-butyl methacrylate), (2001), J Polym Sci A: Polym Chem 38:650.
25. Wang, J.S.; Matyjaszewski, K., Controlled Lıvıng Radıcal Polymerızatıon - Atom-Transfer Radıcal Polymerızatıon In The Presence Of Transıtıon-Metal Complexes (1995) J. Am.Chem.Soc. 117,5614.
26. Matyjaszewski, K., Pattern, T.E., Xia J., Controlled/"living" radical polymerization. Kinetics of the homogeneous atom transfer radical polymerization of styrene (1997) J. Am.Chem.Soc. 119,674.
27. Zhang, X., Xia, J., Matyjaszewski, K., Cotrolled/"Living" Radical polymerization of 2-(dimethylamino)ethyl Methacrylate, (1998) Macromolecules,31,5167-5169.
28. Simionescu CI, Barboiu V., Simionescu BC, Talmaciu V, Sava C., On the copolymerı- zatıon model and mıcrostructure of methyl acrylate - styrene radıcal copolymer - ınfluence of $ZnCl_2$, (1986), Journal of Polymer Science Part A Polymer Chem, 24 (5): pp-851-860.
29. Uebel JJ, Dinan FJ., A Reassessment of The H-1-NMR Spectra of Styrene Methyl-Methacrylate co-Polymers, (1983), Journal of Polymer Sci: Part A-Polymer Chem 21 (8): 2427-2438 1983
30. Tüdös, F., Kelen, T. Analysıs of lınear methods for determınıng copolymerızatıon reactıvıty ratıos, 1. New Improved Lınear Graphıc Method, (1975), Journal of Macromole- cular Scıence-Chemıstry, A 9 (1): pp-1-27.
31. Ho BC, Lee YD, Chin WK, Thermal-degradatıon of polymethacrylıc acıd (1992), Journal of Polymer Scıence Part A-Polymer Chemıstry, 30 (11): pp-2389-2397.
32. Coskun M., Soykan C., Ahmedzade M. and Demirelli K., Preparation and thermal degradation of poly(*p*-substituted phenacyl methacrylates), (2001), *Polym. Degrad. Stab* **72**, 69.
33. Demirelli K., Coskun M. and Dogru M., Preparation and thermal degradation of 4-benzene sulfonylbenzyl methacrylate, (2000), Polym. Degrad. Stab **69**,237.
34. Soykan C, Ahmedzade M, Thermal degradation of poly(phenacyl methacrylate) (2002), Polymer Degradatıon And Stabılıty, 78 (3): pp-497-503.
35. Demirelli K, Kurt A, Coskun M, Atom transfer radical polymerization of 1-phenoxy carbonylethyl methacrylate monomer, (2004), European Polymer Journal, 40 (3): pp-451-457.
36. McNeıll IC, Neıl D, Degradatıon of Polymer Mıxtures 3. Poly(Vınyl Chloride)/ Poly(methyl methacrylate) mıxtures, Studıed By Thermal Volatilizatıon Analysıs and Other Technıques - Nature of Reactıon Products and Mechanısm of Interactıon of Polymers, (1970), European Polymer Journal, 6 (4): 569.

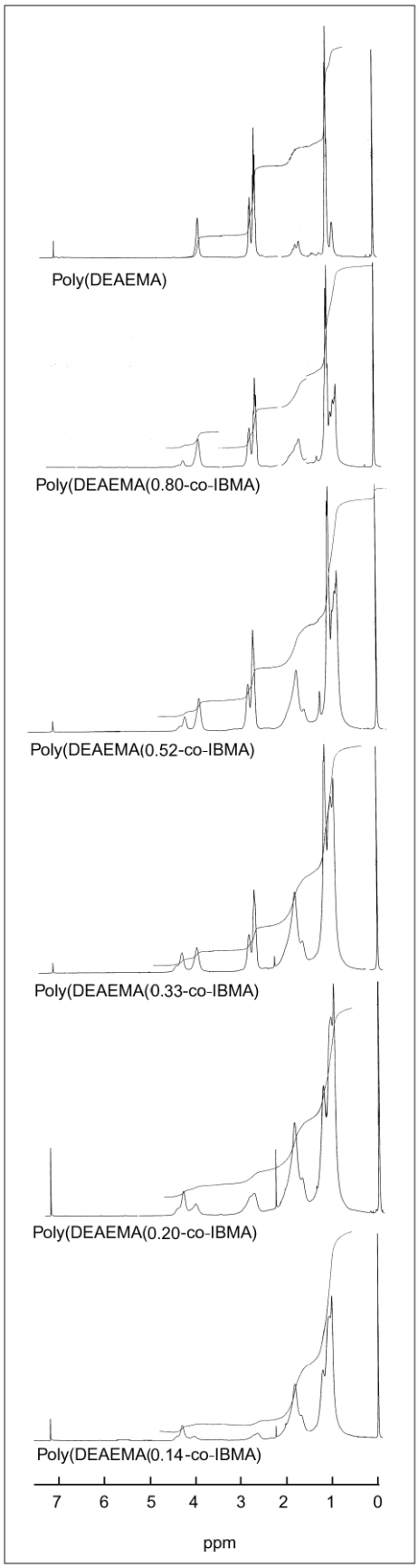


Figure 1 ^{1}H-NMR spectra of Poly(DEAEMA), DEAEMA and IBMA copolymer systems

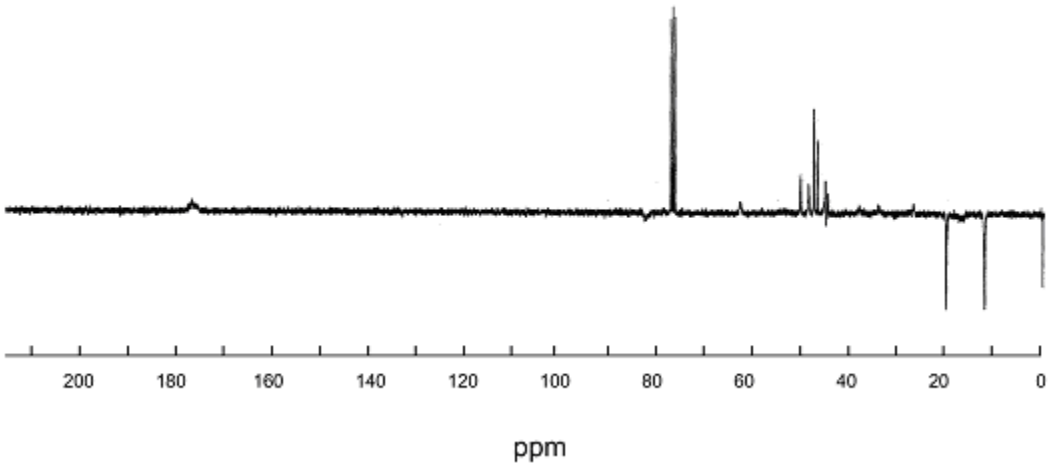


Figure 2 ^{13}C-NMR spectrum of poly(DEAEMA-co-33% IBMA)

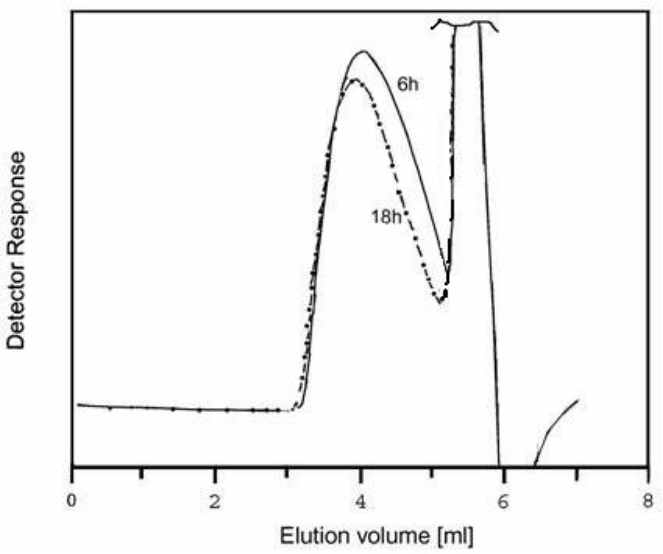


Figure 3 GPC traces of poly(DEAEMA) prepared in the solution poymerization for two different times.

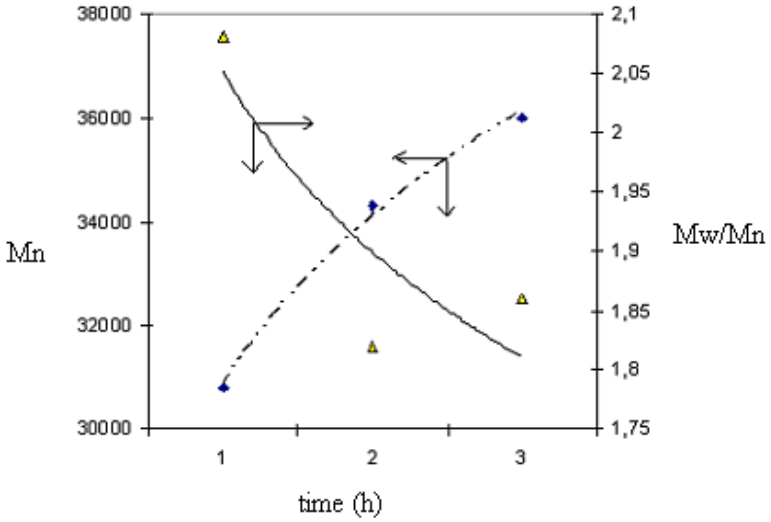


Figure 4 The plot of Mn and polydispersity versus time

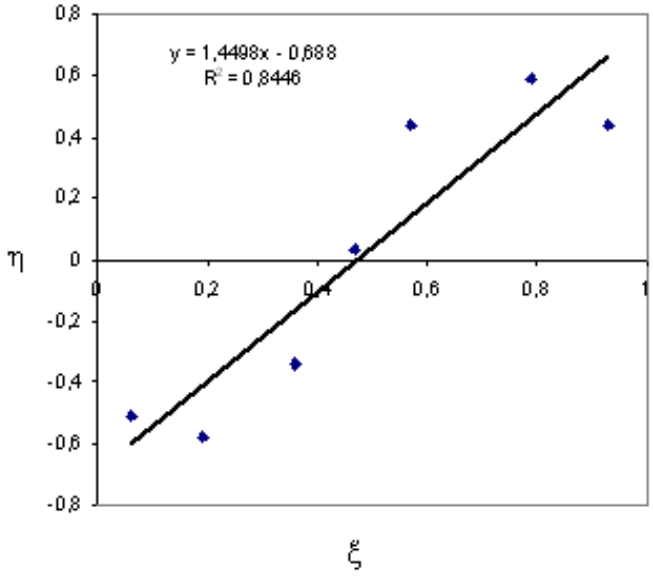


Figure 5 Kelen-Tüdös plot for DEAEMA and IBMA copolymer systems

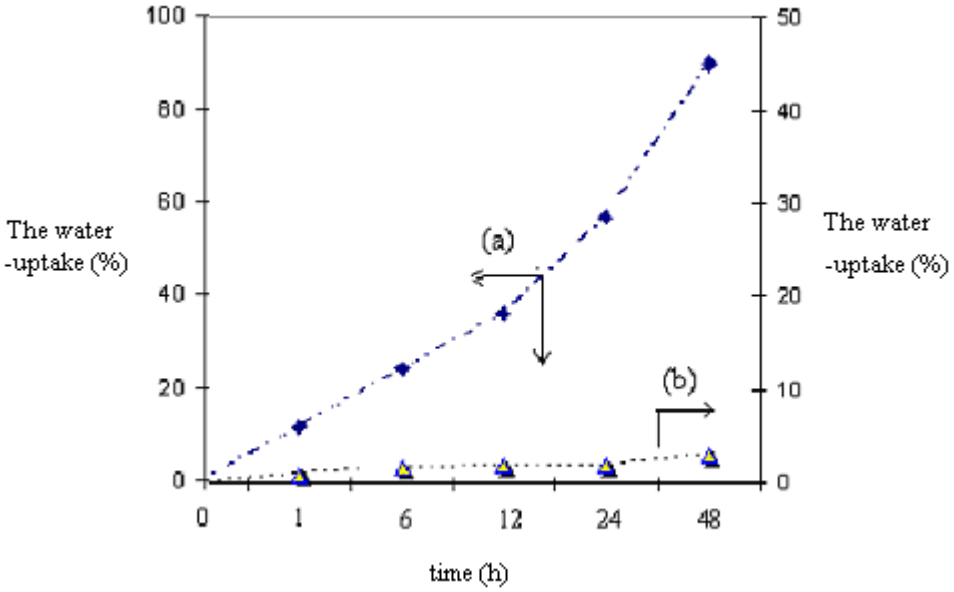


Figure 6 The capacity of water-uptake versus time for a) poly(DEAEMA), b) poly(DEAEMA0.15-co-IBMA)

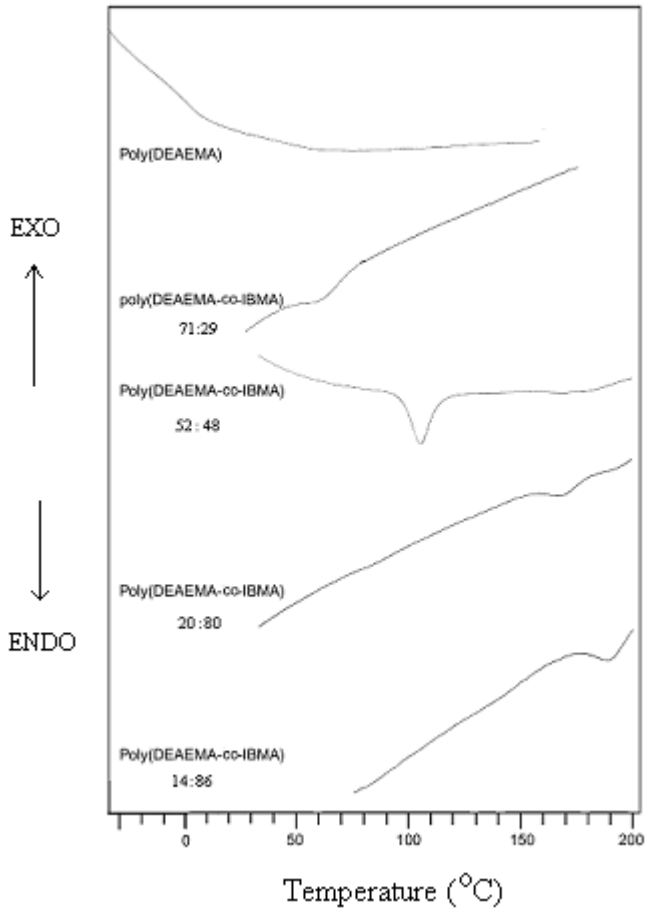


Figure 7 DSC curves of poly(DEAEMA) and DEAEMA and IBMA copolymer system

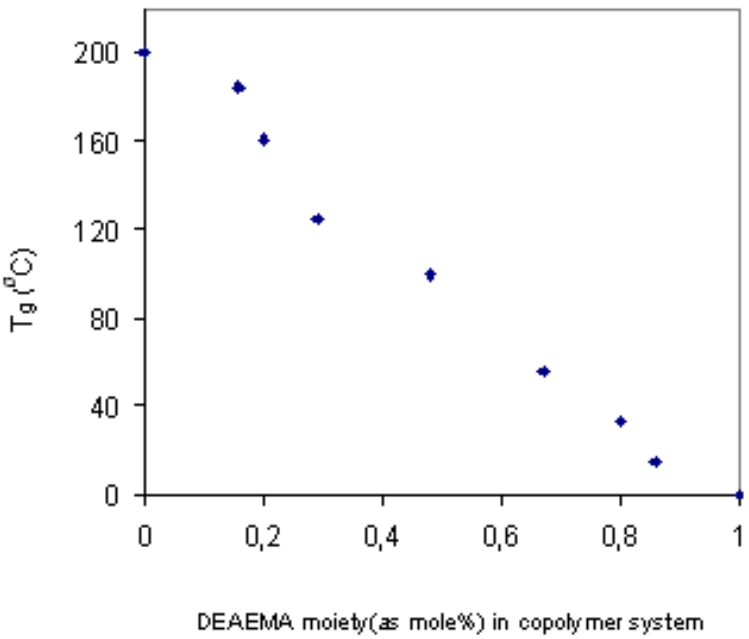


Figure 8 Tg change versus DEAEMA moiety in copolymer system

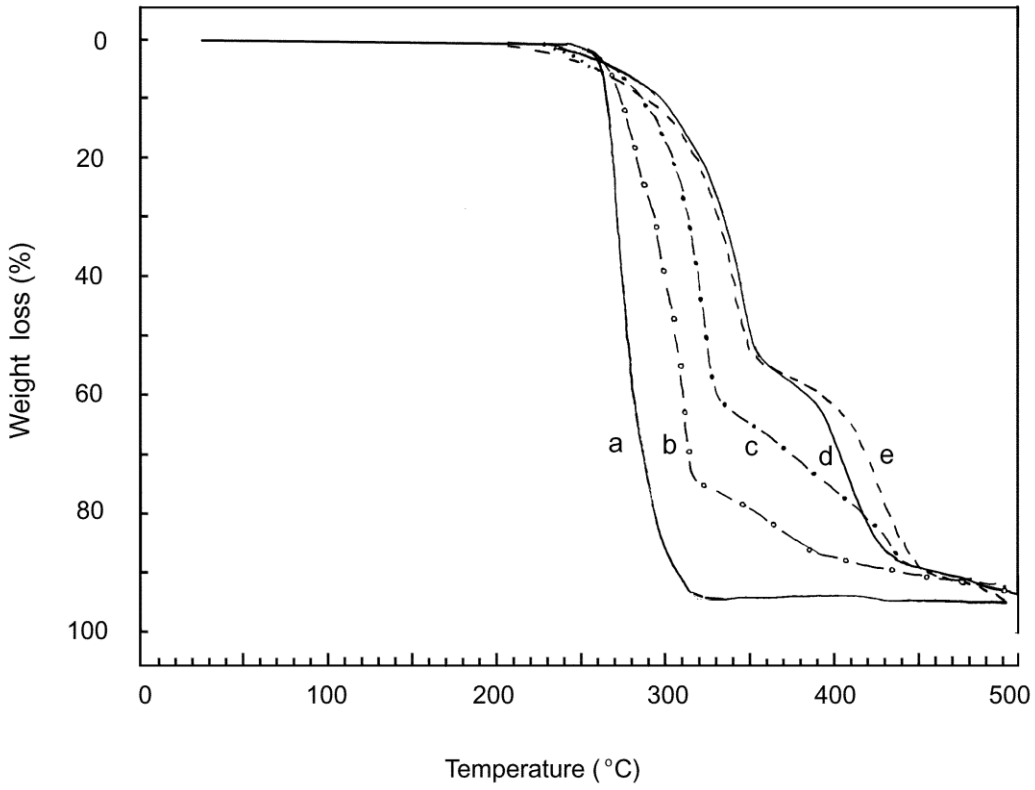


Figure 9 TGA curves of a) poly(IBMA), b) poly(DEAEMA), b) poly(DEAEMA0.84-co-IBMA) c) poly(DEAEMA0.52-co-IBMA), d) poly(DEAEMA0.33-co-IBMA), e) poly(DEAEMA)

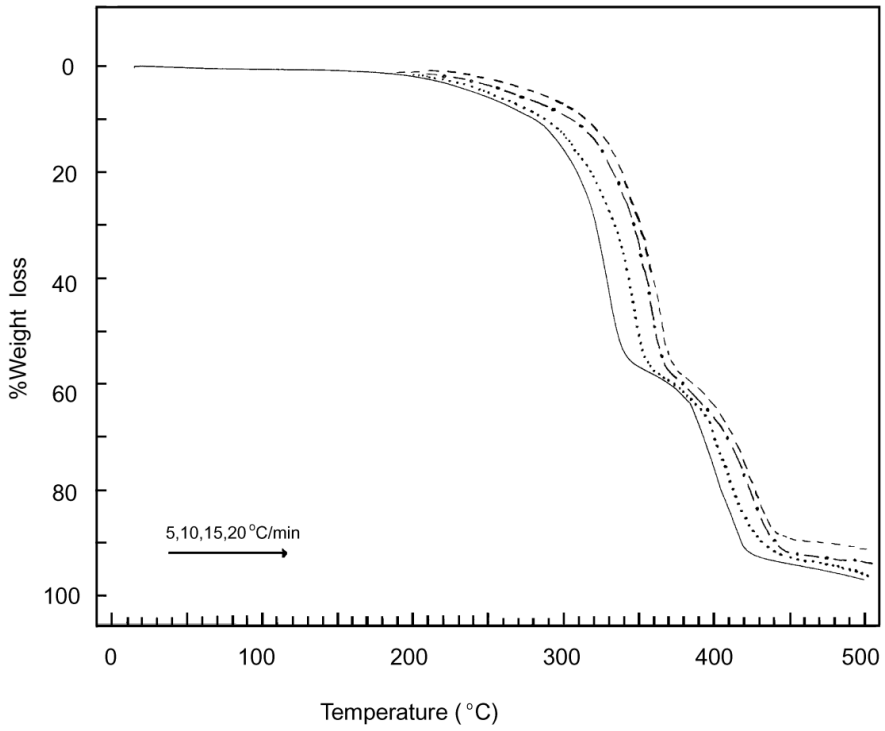


Figure 10 TGA curves of poly(DEAEMA) heated at various heating rates

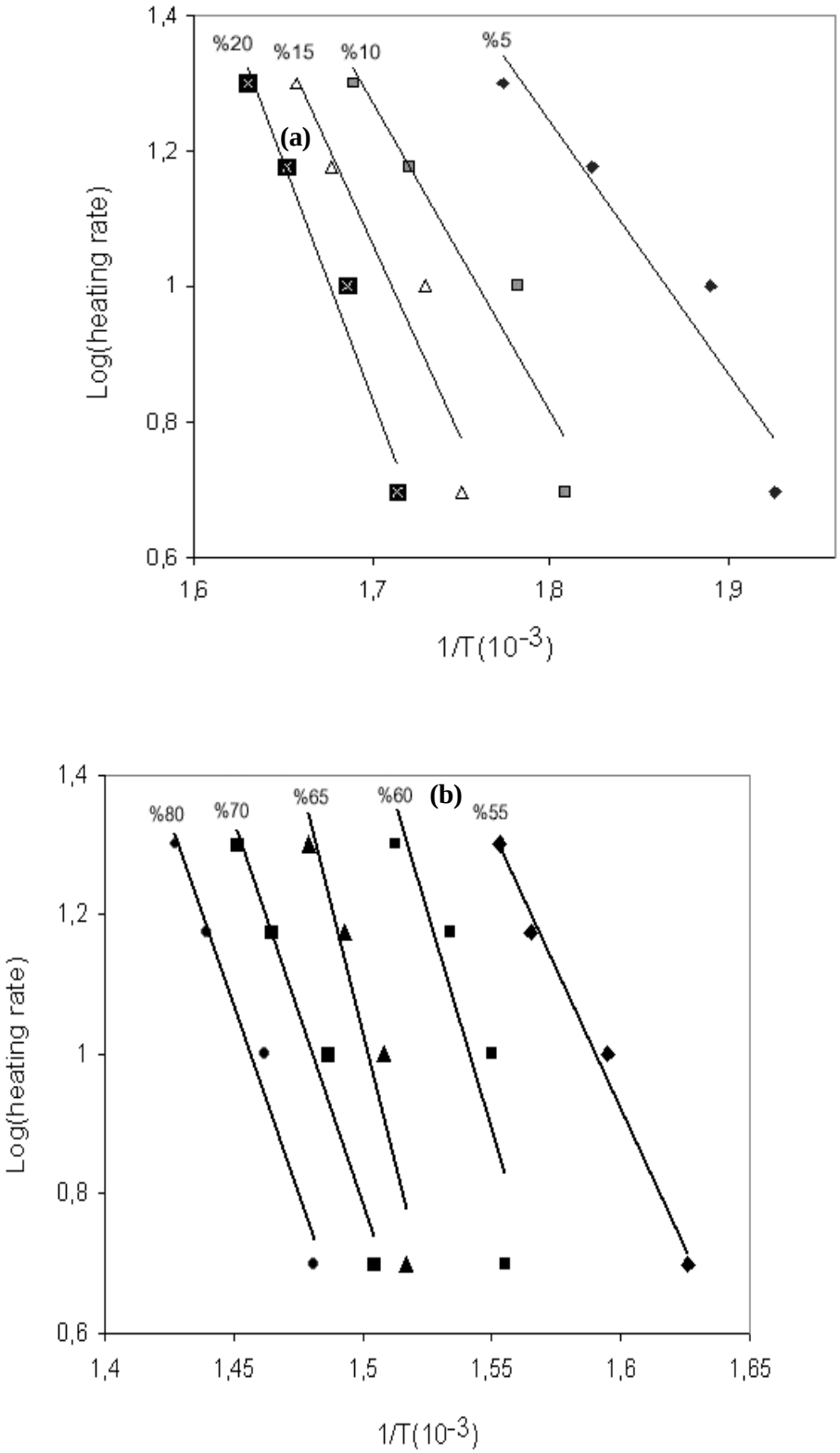


Figure 11 MHRK plots of a) the first stage and b) the second stage at degradation of poly(DEAEMA)

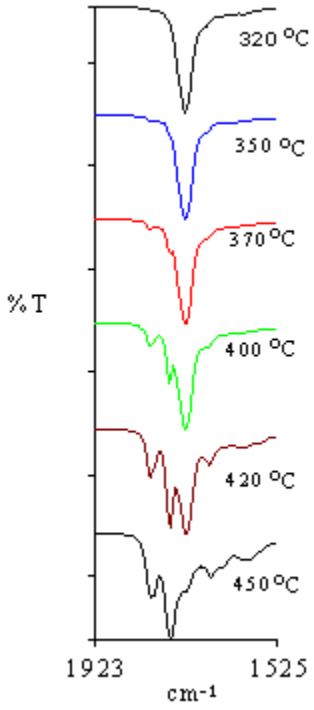


Figure 12 FT-IR spectra monitoring C=O stretch of partially degraded poly(DEAEMA)