Research Article

iMedPub Journals
http://www.imedpub.com

DOI: 10.21767/2472-1123.100006

Journal of Organic & Inorganic Chemistry
ISSN 2472-1123

2015
Vol. 1 No. 1: 6

Statistical Copolymers of Benzyl Methacrylate and Diethylaminoethyl Methacrylate: Monomer Reactivity Ratios and Thermal Properties

Kanellou A, Spilioti A, Theodosopoulos GV, Choinopoulos I and Marinos Pitsikalis

Industrial Chemistry Laboratory, Department of Chemistry, University of Athens, Panepistimiopolis Zografou, 15771 Athens, Greece

Corresponding author: Marinos Pitsikalis

pitsikalis@chem.uoa.gr

Industrial Chemistry Laboratory, Department of Chemistry, University of Athens, Panepistimiopolis Zografou, 15771 Athens, Greece.

Tel: 302107274768

Citation: Kanellou A, Spilioti A, Theodosopoulos GV, et al. Statistical Copolymers of Benzyl Methacrylate and Diethylaminoethyl Methacrylate: Monomer Reactivity Ratios and Thermal Properties. J Org Inorg Chem. 2015, 1:1.

Abstract

Statistical copolymers of benzyl methacrylate (BzMA) and diethylaminoethyl methacrylate (DEAEMA) were prepared by free radical polymerization. The reactivity ratios were estimated using the Finemann-Ross, inverted Finemann-Ross, and Kelen-Tüdos graphical methods, along with the computer program COPOINT. Structural parameters of the copolymers were obtained by calculating the dyad monomer sequence fractions and the mean sequence length. The glass-transition temperature (T_g) values of the copolymers were measured and examined by means of several theoretical equations, allowing the prediction of these T_g values. The kinetics of thermal degradation behavior of the copolymers was also studied by thermogravimetric analysis and compared with the respective homopolymers.

Keywords: Statistical copolymers; Reactivity ratios; Benzyl methacrylate; Diethylaminoethyl methacrylate; Thermal analysis; Free radical polymerization

Received: November 26, 2015; **Accepted:** December 22, 2015; **Published:** December 29, 2015

Introduction

Since the rise of the polymer era; copolymerization, simultaneously emerged as a successful method to engage and enhance the properties and application range of derived polymers. The incorporation of two different monomers, with diverse chemical and/or physical properties, on the same structure, can lead to materials with tailor-made properties [1,2]. Numerous monomers have been involved in these copolymerization studies [3-9]. Among them nitrogen containing monomers such as diethylaminoethyl methacrylate (DEAEMA) are of great interest due to their versatile nature. Specifically they can undergo post-polymerization reactions, they have excellent adhesion properties and due to the amine group offers a pH and temperature stimuli responsive character as well as water solubility by quaternization to ammonium salts [10,11]. pH-Responsive polymeric systems provide the possibility of fabricating tailorable "smart" functional materials, which may find numerous potential commercial applications, such as controlled drug delivery, personal care, oil exploration, industrial coatings, viscosity modifier, biological and membrane science, colloidal stabilization, water remedation [12-14], reversible gelation, CO_2 sensitive micellization [15,16] etc. Thermosensitivity was reported for PDEAEMA exhibiting lower critical solution temperature, LCST, meaning that the polymer precipitates from water at elevated temperatures [17,18]. Block copolymers containing PDEAEMA blocks are widely used in the literature as pH - and temperature responsive materials in aqueous solutions, as a consequence of the increase in hydrophobicity upon deprotonation [19,20]. On the other hand benzyl methacrylate (BzMA) is a very interesting monomer, which can be used as a substitute in the methacrylate family of monomers of the very commonly used styrene (St) in copolymerization studies [21]. PBzMA is also hydrophobic and amorphous as PSt but with a much lower glass transition, Tg, value [$(Tg)_{PBzMA}$=54°C instead of $(Tg)_{PSt}$=100°C] [22], leading to the formation of more flexible and easily processable copolymeric structures. BzMA has been polymerized by polymerization-induced self-assembly (PISA) [23,24] using controlled radical polymerization techniques, such as reversible addition-fragmentation chain transfer (RAFT) polymerization [25,26].

Potential applications of these structures involve drug delivery, coatings, contact lenses, sterilizable gels and emulsifiers [27,28]. It was found recently that PBzMA exhibits LCST in ionic liquids, i.e., a sharp decrease in solubility upon heating the sample above a critical temperature [29]. In the present study, the synthesis of poly(benzyl methacrylate) (PBzMA) and poly(diethylaminoethyl methacrylate) (PDEAEMA) statistical copolymers via free radical polymerization, is described. The objective of this study was to measure the monomer reactivity ratios and the structural parameters of the copolymers. The thermal properties of the copolymers were also studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

Experimental Methods

Materials

All polymerizations were conducted using high-vacuum techniques described elsewhere [30]. BzMA and DEAEMA were purchased from Aldrich and were vacuum-distilled from calcium hydride via the high vacuum line. 2,2′-Azobisisobutyronitrile, AIBN (Aldrich) was recrystallized twice from methanol, filtered and dried under vacuum. Benzene (Aldrich) was vacuum distilled from CaH_2 into a flask containing n-BuLi and finally distilled over the vacuum line.

Copolymerization studies

For the purpose of inquiring/studying the reactivity ratios of these two monomers; a set of five copolymers of BzMA and DEAEMA were prepared. Different feed ratios were involved in each copolymerization (monomer molar ratios: 80/20, 60/40, 50/50, 40/60 and 20/80). Copolymerization reactions were quenched at rather low yields (~ 10% yields). The copolymerization procedure was monitored by size exclusion chromatography, NMR, and UV spectroscopy. The experimental results were processed on the basis of the Fineman-Ross (FR), inverted Fineman-Ross (IFR) and Kelen-Tüdos (KT) equations. The computer program COPOINT was employed as well [31].

Copolymerization of BzMA with DEAEMA

The copolymerization reactions were performed in glass reactors, in benzene solutions. AIBN was employed as initiator at the concentration of 0.1% wt. As an example for sample 20/80 3.06 g (17.586 × 10^{-3} moles) BzMA, 12.77 g (69.027 × 10^{-3} moles) DEAEMA, 0.016 g AIBN and 150 ml of benzene were added in the reactor. Prior to polymerization, the mixtures were degassed under high vacuum using three freeze-thaw cycles and the reactors were flame-sealed. The copolymerizations were conducted at 60°C for 3 hours. The polymers were precipitated in methanol, the supernatant was decanted and dried. The same procedure was repeated as many times as necessary in order to remove any remaining unreacted monomers. Finally, the copolymer was dried overnight in a vacuum oven.

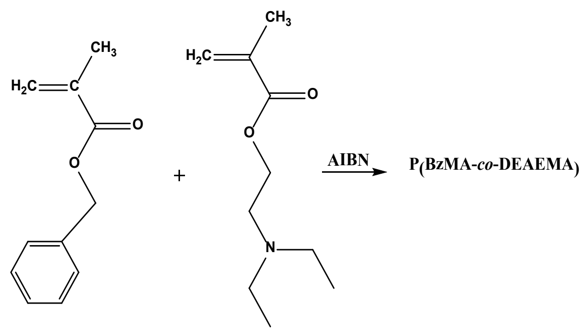
Characterization techniques

Size Exclusion Chromatography (SEC) experiments were carried out at 40°C using a modular instrument consisting of a Waters model 510 pump, U6K sample injector, 401 refractometer, 486 UV spectrophotometer, and a set of 5 μ-Styragel columns with a continuous porosity range from 500 to 10^6 Å. The columns were housed in an oven thermostatted at 40°C. THF was the carrier solvent at a flow rate of 1 mL/min. The system was calibrated with nine PS standards having molecular weights in the range of 970–600,000. The glass-transition temperatures were obtained by differential scanning calorimetry (DSC) using a 2910 modulated DSC model from TA instruments. The samples were heated or cooled at a rate of 5°C/min. The second heating results were obtained in all cases. The thermal stability of the copolymers was studied by thermogravimetric analysis (TGA) employing a Q50 TGA model from TA instruments. The samples were heated at a rate of 10°C/min under nitrogen atmosphere. The composition of the copolymers was also determined from ^{1}H-NMR spectra, which were recorded in chloroform-d at 30°C with a Varian Unity Plus 300/54 NMR spectrometer.

Results and Discussion

Statistical copolymers of BzMA with DEAEMA

The free radical copolymerization of BzMA with DEAEMA was conducted in benzene solutions using AIBN as the initiator at 60°C **(Scheme 1)**. In all cases the conversion was kept at low values, to satisfy the differential copolymerization equation. The copolymers were purified by repeated precipitations in methanol, where both monomers are soluble. The molecular characteristics of the samples are given in **Table 1**. The samples have typical high molecular weights and molecular weight distributions in the range expected for conventional radical polymerization. Compared with statistical copolymers of BzMA prepared by radical polymerization in bulk [32] or PBzMA and statistical copolymers, prepared by atom transfer radical polymerization (ATRP) [33] it is obvious that in the present study the solution copolymerization

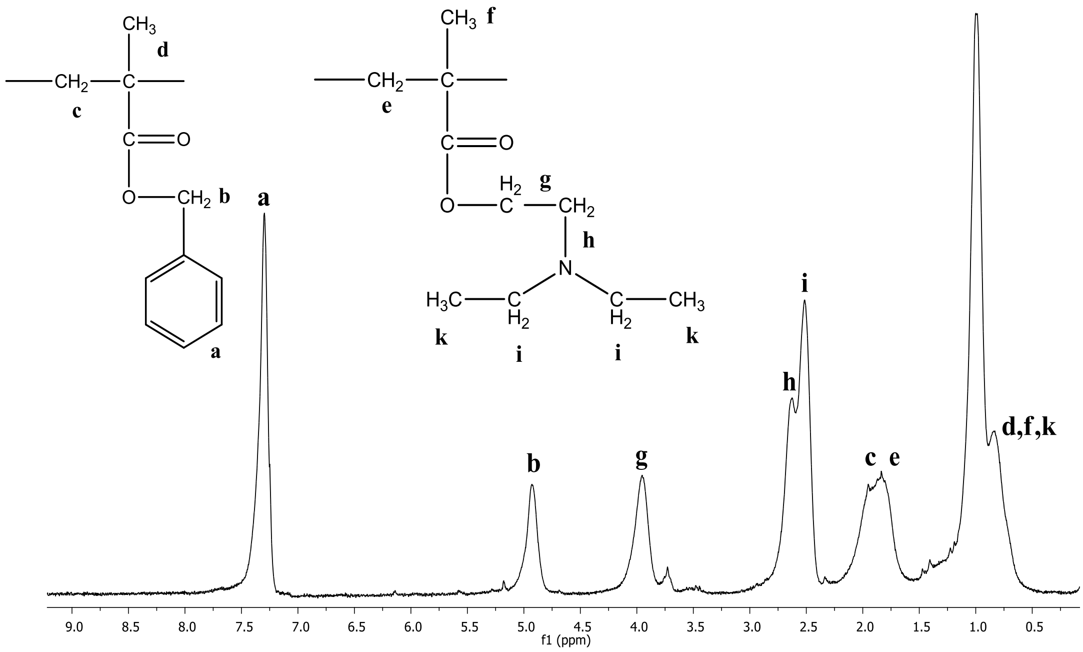


Scheme 1 Synthesis of the statistical copolymers.

Table 1 Molecular characteristics of the copolymers[a].

Sample	M_w	$I=M_w/M_n$
20-80	93800	1.53
40-60	98400	1.60
50-50	194900	1.60
60-40	150600	1.49
80-20	157300	1.61

[a]by SEC in THF at 40°C



Scheme 2 ^{1}H NMR spectrum of sample 40-60 in $CDCl_3$.

leads to rather narrow distributions. Different copolymers are symbolized by the various feed molar ratios of the monomers, e.g., sample 20/80 indicates the copolymer for the synthesis of which 20% BzMA and 80% DEAEMA were employed as the molar feed composition. The molecular weights were measured by SEC using a calibration curve constructed by polystyrene standards. NMR spectroscopy was employed to measure the composition of the copolymers. The analysis was based on the signals at 4.70 and 3.80 ppm which are attributed to the $-CH_2-$ groups adjacent to the carboxylate groups of BzMA and DEAEMA monomer units respectively. A characteristic example is given in **Scheme 2.**

Monomer reactivity ratios and statistical analysis of the copolymers

The monomer reactivity ratios were determined using the Fineman-Ross (FR) [34], inverted Fineman-Ross (IFR) [34] and Kelen-Tüdos (KT) [35] graphical methods. A computer program, called COPOINT, was also employed [36-38]. According to the Fineman-Ross method, the monomer reactivity ratios can be obtained by the equation:

$$G=Hr_{BzMA}-r_{DEAEMA} \quad (1)$$

where the reactivity ratios, r_{BzMA} and r_{DEAEMA} correspond to the BzMA and DEAEMA monomers, respectively. The parameters G and H are defined as follows:

$$G=X(Y-1)/Y \text{ and } H=X^2/Y \quad (2)$$

$$\text{with } X=M_{BzMA}/M_{DEAEMA} \text{ and } Y=dM_{BZMA}/dM_{DEAEMA} \quad (3)$$

M_{BzMA} and M_{DEAEMA} are the monomer molar compositions in feed and dM_{BzMA} and dM_{DEAEMA} the copolymer molar compositions.

The inverted Fineman-Ross method is based on the equation:

$$G/H=r_{BzMA}-(1/H)_{DEAEMA} \quad (4)$$

The plots of the G versus H values and the G/H versus 1/H values yield the reactivity ratios r_{BzMA} and r_{DEAEMA} from the intercept and the slope of the graphs.

Alternatively, the reactivity ratios can be obtained using the Kelen-Tüdos method which is based on the equation:

$$\eta=(r_{BzMA}+r_{DEAEMA}/\alpha)\xi-r_{DEAEMA}/\alpha \quad (5)$$

where η and ξ are functions of the parameters G and H:

$$\eta=G/(\alpha+H) \text{ and } \xi=H/(\alpha+H) \quad (6)$$

and α a constant which is equal to $(H_{max}H_{min})^{1/2}$, H_{max}, H_{min} being the maximum and the minimum H values, respectively from the series of measurements. From the linear plot of η as a function of ξ, the values of η for ξ=0 and ξ=1 are used to calculate the reactivity ratios according to the equations:

$$\xi=0 \Rightarrow \eta=-r_{DEAEMA}/\alpha \text{ and } \xi=1 \Rightarrow \eta=r_{BzMA} \quad (7)$$

The detailed copolymerization data for all systems are provided in **Table 2**. The graphical plots concerning the methods previously reported are given in **Figures 1-3**, whereas the reactivity ratios are summarized in **Table 3**. The computer program COPOINT evaluates the copolymerization parameters using comonomer/copolymer composition data as obtained from copolymerization experiments with finite monomer conversion. Although the mathematical treatment can be applied up to full monomer conversion, it is recommended not to exceed 20-30 mol%. COPOINT numerically integrates a given copolymerization equation in its differential from. The copolymerization parameters can be obtained

Table 2 Copolymerization data for the statistical copolymers.

Sample	M (VP)	dM (VP)	M (PEG)	dM (PEG)	X	Y	Gm	Hm	1/Hm	Gm/Hm
20-80	0.2030	0.3013	0.7970	0.6987	0.254705	0.431229	-0.335940	0.150441	6.647111	-2.233050
40-60	0.4035	0.4648	0.5965	0.5352	0.676446	0.868460	-0.102460	0.526885	1.897946	-0.194460
50-50	0.5003	0.5363	0.4997	0.4637	1.001201	1.156567	0.135535	0.866706	1.153794	0.156379
60-40	0.6006	0.6051	0.3994	0.3949	1.503756	1.532287	0.522376	1.475756	0.677619	0.353972
80-20	0.8010	0.7537	0.1990	0.2463	4.025126	3.060089	2.709763	5.294498	0.188875	0.511807
α=0.892475										

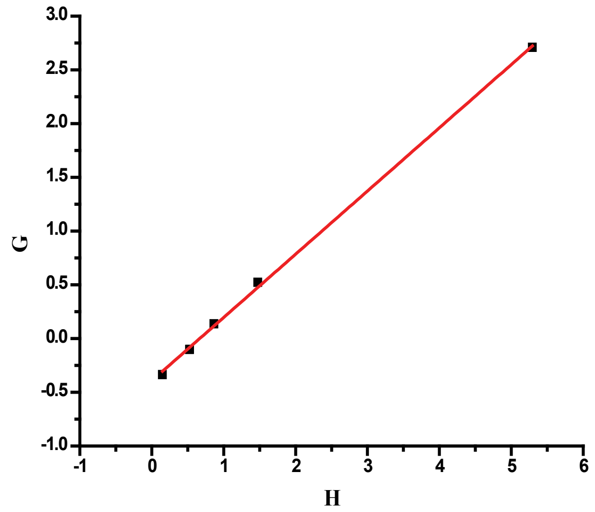


Figure 1 Fineman-Ross plot for the statistical copolymers.

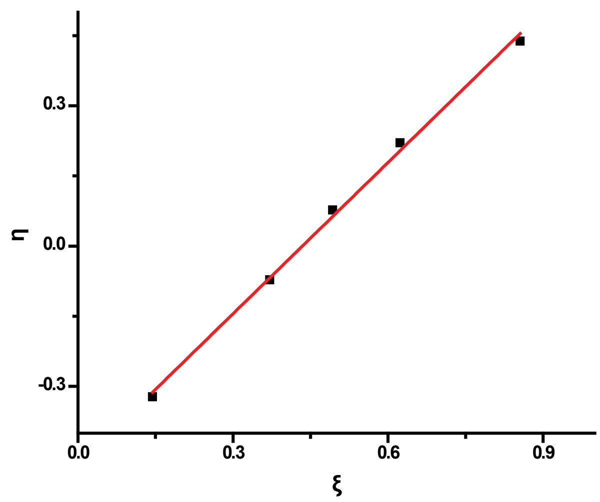


Figure 3 Kelen-Tüdos plot for the statistical copolymers.

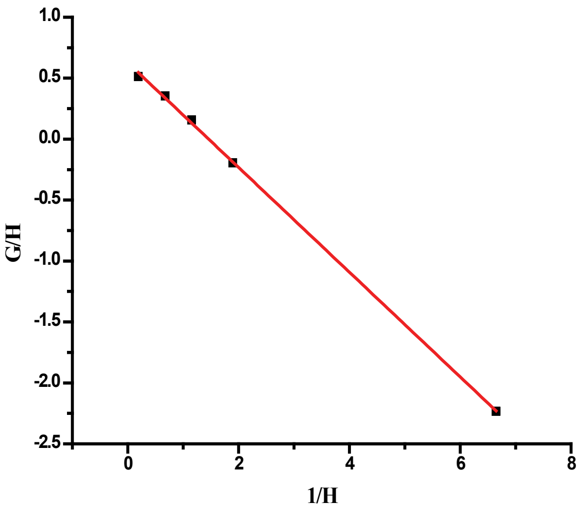


Figure 2 Inverted Fineman-Ross plot for the statistical copolymers.

by minimizing the sum of square differences between measured and calculated polymer compositions. Errors of the fitted parameters are estimated from the statistical error of the sum of square differences, as well as from a quadratic approximation of this sum in the vicinity of the optimized values of the copolymerization parameters. The plots were linear in all cases and for all graphical methods, thus indicating that these copolymerizations follow conventional copolymerization kinetics and that the reactivity of all polymer radicals is determined only by the terminal monomer

Table 3 Reactivity ratios measured by different methods.

Method	r_{BzMA}	r_{DEAEMA}
FR	0.588	0.393
iRF	0.627	0.430
KT	0.610	0.418
COPOINT	0.600	0.398

unit. It is obvious that all methods provide similar data concerning the reactivity ratios for both monomers. According to the data obtained by COPOINT r_{BzMA}=0.600 and r_{DEAEMA}=0.398. This result implies that the homopolymerization of the two monomers is not favored, or in other words that there is a tendency for the production of an alternating copolymer. However, the probability for the incorporation of BzMA units is slightly greater than for the incorporation of DEAEMA units ($r_{BzMA}>r_{DEAEMA}$). This kind of copolymerization is characterized as nonideal azeotropic [39]. The statistical distribution of the dyad monomer sequences M_{BzMA}-M_{BzMA}, M_{DEAEMA}-M_{DEAEMA} and M_{BzMA}-M_{DEAEMA} were calculated using the method proposed by Igarashi [40]:

$$X=\phi_{BzMA}-\frac{2\phi_{BzMA}(1-\phi_{BzMA})}{1+\left[(2\phi_{BzMA}-1)^2+4r_{BzMA}r_{DEAEMA}\phi_{BzMA}(1-\phi_{BzMA})\right]^{1/2}} \quad (8)$$

$$Y=(1-\varphi_{BzMA})-\frac{2\varphi_{BzMA}(1-\varphi_{BzMA})}{1+\left[(2\varphi_{BzMA}-1)^2+4r_{BzMA}r_{DEAEMA}\varphi_{BzMA}(1-\varphi_{BzMA})\right]^{1/2}} \quad (9)$$

$$Z=\frac{4\varphi_{BzMA}(1-\varphi_{BzMA})}{1+\left[(2\varphi_{BzMA}-1)^2+4r_{BzMA}r_{DEAEMA}\varphi_{BzMA}(1-\varphi_{BzMA})\right]^{1/2}} \quad (10)$$

Where X, Y and Z are the mole fractions of the M_{BzMA}-M_{BzMA}, M_{DEAEMA}-M_{DEAEMA} and M_{BzMA}-M_{DEAEMA} dyads in the copolymer respectively and $\varphi_{\mu BzMA}$ the BzMA mole fraction in the copolymer. Mean sequence lengths $_{BzMA}$ and μ_{DEAEMA} were also calculated using the following equations [41]:

$$\mu_{BzMA} = 1 + r_{BzMA}\frac{[M_{BzMA}]}{[M_{DEAEMA}]} \quad (11)$$

$$\mu_{DEAEMA} = 1 + r_{DEAEMA}\frac{[M_{DEAEMA}]}{[M_{BzMA}]} \quad (12)$$

The data are summarized in **Table 4**, and the variation of the dyad fractions with the BzMA mole fraction in the copolymers is displayed in **Figure 4**. The results confirm the conclusions drawn by the reactivity ratios and show the high content of BzMA-DEAEMA heterodyads in the copolymer structure.

Glass transition temperature of the statistical copolymers

The thermal properties of the copolymers are influenced by their chemical structure and composition and the monomer sequence distributions. Several relationships have been employed to describe the effect of these parameters on the glass transition temperature of the copolymers [42]. The simplest equation describing the effect of composition on Tg is the Gibbs-Di Marzio equation [43]:

$$Tg=\varphi_{BzMA}Tg_{MMA} + \varphi_{DEAEMA}Tg_{DEAEMA} \quad (13)$$

Where, φ_{BzMA}, φ_{DEAEMA} are the mole fractions of BzMA and DEAEMA, respectively, in the copolymer and Tg_{BzMA}, Tg_{DEAEMA} the glass transition temperatures of the two homopolymers, respectively. Tg_{DEAEMA} was found to be equal to 293 K, whereas Tg_{PBzMA} is equal to 327 K.

A similar relationship was introduced by Fox [44]:

$$\frac{1}{Tg} = \frac{w_{BzMA}}{Tg_{BzMA}} + \frac{w_{DEAEMA}}{Tg_{DEAEMA}} \quad (14)$$

Where w_{BzMA} and w_{DEAEMA} are the weight fractions of BzMA and DEAEMA in the copolymer.

Based on the free volume concept, Johnston proposed the following equation [45]:

$$\frac{1}{Tg} = \frac{w_{MMA}P_{BzMA-BzMA}}{Tg_{BzMA-BzMA}} + \frac{w_{DEAEMA}P_{DEAEMA-DEAEMA}}{Tg_{DEAEMA-DEAEMA}} + \frac{w_{BzMA}P_{BzMA-DEAEMA} + w_{DEAEMA}P_{DEAEMA-BzMA}}{Tg_{BzMA-DEAEMA}} \quad (15)$$

it is assumed that the BzMA-BzMA, DEAEMA-DEAEMA and DEAEMA-BzMA or BzMA-DEAEMA dyads have their own glass transition temperatures, $Tg_{BzMA-BzMA}$, $Tg_{DEAEMA-DEAEMA}$ and $Tg_{BzMA-DEAEMA}$, respectively. $Tg_{BzMA-BzMA}$ and $Tg_{DEAEMA-DEAEMA}$ can be considered as the glass transition temperatures for the respective homopolymers, whereas $Tg_{BzMA-DEAEMA}$ is the glass transition temperature of the alternating copolymer P(BzMA-alt-DEAEMA). W_i is the weight fraction of the i component and $P_{BzMA-BzMA}$, $P_{DEAEMA-DEAEMA}$, $P_{BzMA-DEAEMA}$ and $P_{DEAEMA-BzMA}$ are the probabilities of having various linkages. These probabilities can be calculated using the monomer reactivity ratios [46]:

$$P_{BzMA-BzMA} = \frac{r_{BzMA}}{r_{BzMA} + \frac{[M_{DEAEMA}]}{[M_{BzMA}]}} \quad (16)$$

$$P_{BzMA-DEAEMA} = \frac{[M_{DEAEMA}]}{r_{BzMA}[M_{BzMA}]+[M_{DEAEMA}]} \quad (17)$$

$$P_{DEAEMA-BzMA} = \frac{[M_{BzMA}]}{r_{DEAEMA}[M_{DEAEMA}]+[M_{BzMA}]} \quad (18)$$

$$P_{DEAEMA-DEAEMA} = \frac{r_{DEAEMA}[M_{DEAEMA}]}{r_{DEAEMA}[M_{DEAEMA}]+[M_{BzMA}]} \quad (19)$$

Barton suggested the following equation [27]:

$$Tg=XTg_{BzMA-BzMA}+YTg_{DEAEMA-DEAEMA}+ZTg_{BzMA-DEAEMA} \quad (20)$$

Where X, Y, Z are the monomer dyad fractions (Equations 11-13).

To apply these theories it is necessary to know the glass transition temperature of the respective alternating copolymers. However, these data are not provided in the literature. Therefore, the linearized forms of the Johnston and Barton equations are used to obtain the $Tg_{BzMA-DEAEMA}$ values. The plots, given in **Figures 5 and 6**, are straight lines passing through the origin. This is an indication that these theoretical methods can better predict the Tg values of statistical copolymers or, in other words, that the monomer sequence distribution is an important parameter defining the Tg of a statistical copolymer. The $Tg_{BzMA-DEAEMA}$ values, calculated by the Johnston and Barton equations, are 312.8 and 311.6 K, respectively. It is obvious that the results obtained by the two methods are not identical but in very close agreement. For the statistical copolymers one transition was observed, meaning that the samples are not phase separated, and the Tg values increase upon increasing the BzMA content. The experimental results concerning the Tg of the statistical copolymers along with the predictions of all models are given in **Table 5**. It is evident that the predicted values from the Gibbs-DiMarzio and Fox equations are in better agreement with the experimental results. It is obvious that the Johnston and Barton equations overestimate

Table 4 Structural data of the copolymers.

Sample	X	Y	Z	μ (B)	μ (D)
20-80	0.06264	0.46004	0.23865	1.66	3.09
40-60	0.23018	0.30058	0.23462	2.34	2.04
50-50	0.31657	0.24397	0.21973	2.78	1.78
60-40	0.40544	0.19524	0.19966	3.36	1.59
80-20	0.61359	0.10619	0.14011	5.70	1.29

the $Tg_{BzMA\text{-}DEAEMA}$ values. Since the copolymers are characterized by high heterodyad contents it is reasonable to expect positive deviations of the predictions made by these methods, compared to the experimental results. However, even the Johnston and Barton methods can efficiently be applied for the prediction of the Tg values of the copolymers. This result can be attributed to the random placement of the comonomer units along the copolymeric chains and to the relatively similar Tg values of the respected homopolymers.

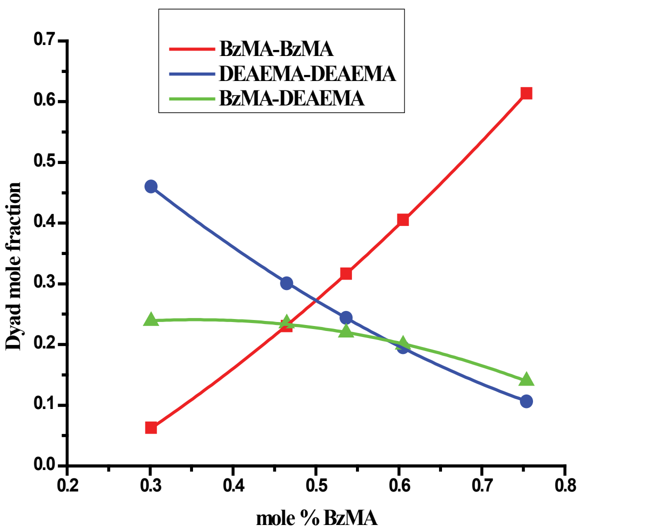


Figure 4 Distribution of dyad sequences of the statistical copolymers.

Kinetics of the thermal decomposition of the statistical copolymers

TGA measurements were employed to study the kinetics of the thermal decomposition of the statistical copolymers. The activation energy, Ea, of mass loss upon heating was calculated using the isoconversional Ozawa-Flynn-Wall (OFW) [47-49] and Kissinger methods [50]. The OFW approach is a "model free" method, which assumes that the conversion function F(α), where α is the conversion, does not change with the alteration of the heating rate, β, for all values of α. The OFW method involves the measuring of the temperatures corresponding to fixed values of α from experiments at different heating rates β. Therefore, plotting lnβ vs. 1/T in the form of

$$\ln \beta = \ln \frac{AE}{R} - \ln F(\alpha) - \frac{E}{RT} \qquad (21)$$

should give straight lines with slope directly proportional to the activation energy, where T is the absolute temperature, A is the pre-exponential factor (min^{-1}) and R is the gas constant (8.314 J/K.mol). If the determined activation energy is the same for the various values of α, then the existence of a single-step

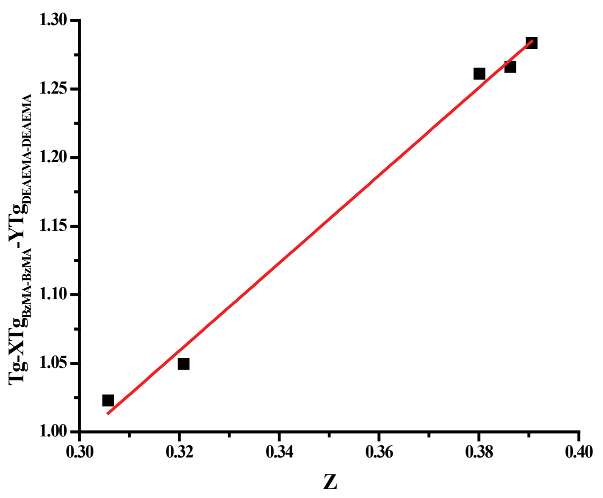


Figure 5 Plot of the linearized form of the Barton equation.

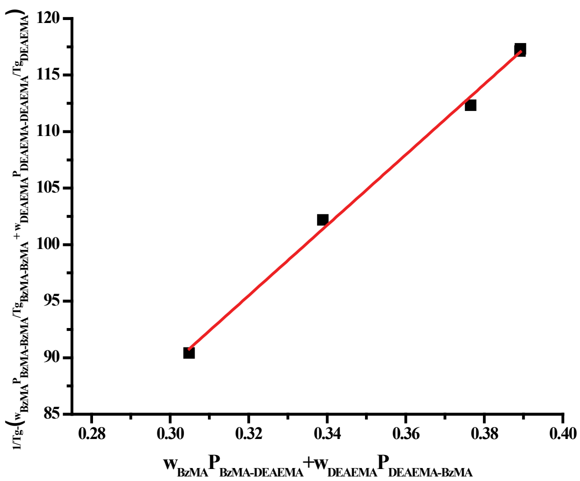


Figure 6 Plot of the linearized form of the Johnston equation.

Table 5 Glass transition temperatures of the homo- and copolymers.

Sample	Tg	$Tg_{Gibbs\text{-}Di\ Marzio}$	Tg_{Fox}	$Tg_{Johnston}$	Tg_{Barton}
PBzMA	327				
80-20	314.6	318.8	317.7	323.6	324.0
60-40	309.3	313.7	312.3	319.0	320.1
50-50	307.8	311.4	309.9	316.5	318.0
40-60	305.6	309.0	307.5	313.7	315.6
80-20	300.5	303.4	302.2	306.8	309.2
PDEAEMA	293				

degradation reaction can be concluded with certainty. The OFW method is the most useful method for the kinetic interpretation of thermogravimetric data, obtained from complex processes like the thermal degradation of polymers. It can be applied without knowing the reaction order. The linearity of the OFW diagrams in a broad range of conversions proves that it is an efficient method for the analysis of the thermal decomposition of the copolymers. A characteristic example is given in **Figure 7**. However, deviations from the linearity were observed in very low or very high conversions, since these results refer to the decomposition of parts of the macromolecules that are not representative of the overall copolymeric chains, due to the statistical character of the distribution of the different monomer units.

The activation energy E was also calculated from plots of the logarithm of the heating rate versus the inverse of the temperature at the maximum reaction rate in constant heating experiments, according to the Kissinger method. Using the equation:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\frac{AR}{E} + \ln\left[n(1-\alpha_p)^{n-1}\right] - \frac{E}{RT_p} \qquad (22)$$

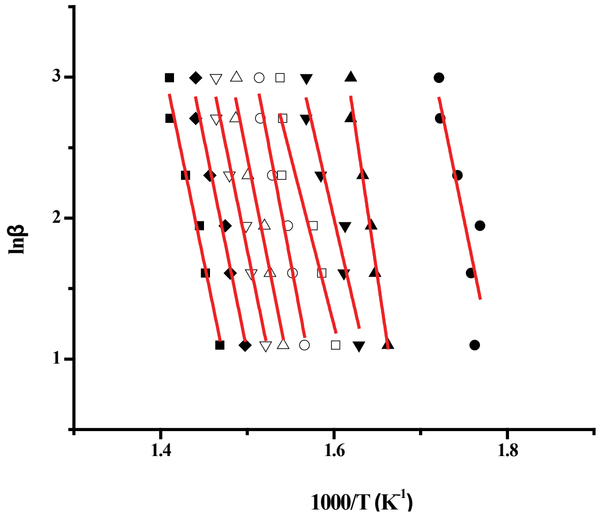


Figure 7 OFW plots lnβ vs 1000 /T for the copolymer 60-40 (●:α=0.1, ▲:α=0.2, ▼:α=0.3, ◷:α=0.4, o:α=0.5, △:α=0.6, ▽:α=0.7, ♦:α=0.8, ■:α=0.9).

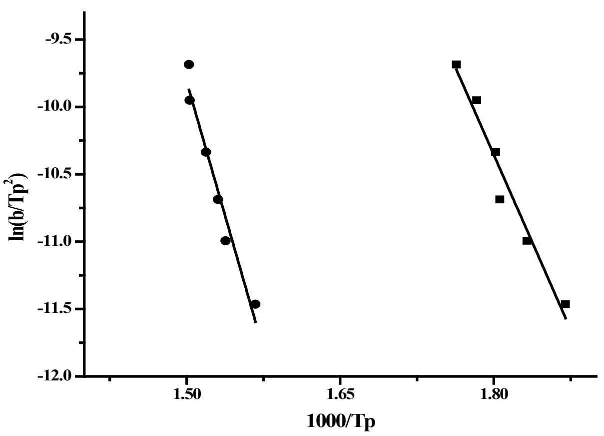


Figure 8 Kissinger plot ln(β/Tp^2) vs 1000/Tp for sample 80-20.

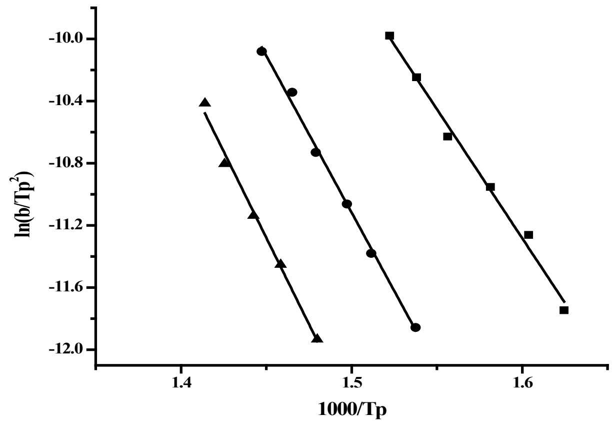


Figure 9 Kissinger plot ln(β/Tp^2) vs 1000/Tp for sample 50-50.

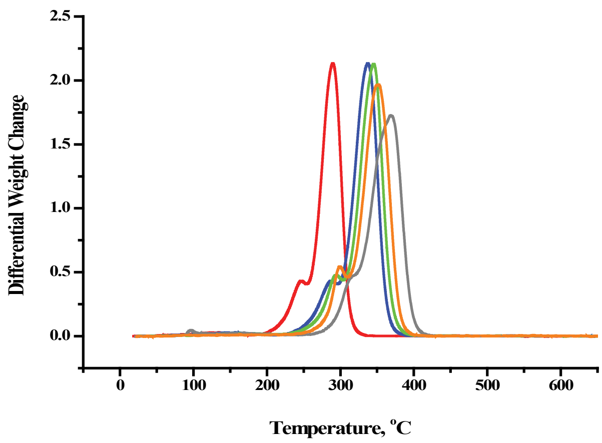


Figure 10 Derivative weight loss with temperature for PBzMA under different heating rates (from left to right 3 to 20°C/min).

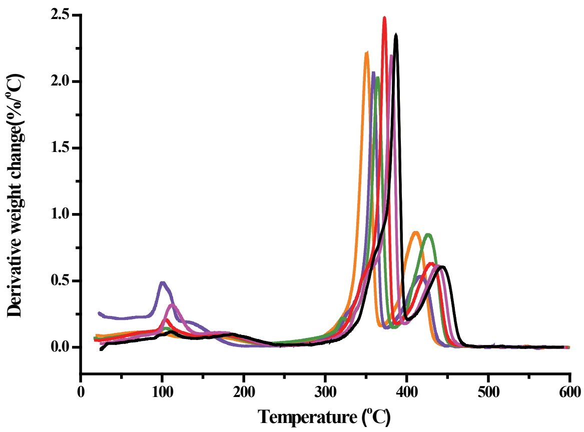


Figure 11 Derivative weight loss with temperature for PDEAEMA under different heating rates (from left to right 3 to 20°C/min).

where T_p and α_p are the absolute temperature and the conversion at the maximum weight-loss and n is the reaction order. The E values can be calculated from the slope of the plots of $\ln(\beta/T_p^{2})$ versus $1/T_p$. Characteristic examples are given in **Figures 8 and 9**. The statistical copolymers were thermally degraded at different heating rates. Examples of the derivative thermogravimetry measurements under different heating rates are displayed in **Figures 10-13**. The two homopolymers present similar range of decomposition temperatures, showing two maxima of their thermal decomposition. The main decomposition peak is similar for both homopolymers, observed between 330 and 370°C. The second decomposition peak is observed at lower temperatures for PBzMA (285-315°C) compared to PDEAEMA (410-440°C). These results indicate that the decomposition mechanism is rather complex for both monomers. The main decomposition event is probably attributed to the decomposition of the main chain, which is chemically similar for both homopolymers. The second decomposition peak is probably related with the decomposition of the side groups. It seems that the diethylaminoethyl- groups offer greater thermal stability compared to the benzyl groups. In other words, the thermolysis of the side groups of PBzMA is favored. This result is verified by literature reports showing that the general mechanism of the thermal degradation of the polymethacrylates involves the loss of the ester side group to form methacrylic acid followed by cross-linking [51]. In the case of the copolymers the temperature range of the decomposition is much broader covering the ranges of both homopolymers. The samples 80-20 and 20-80 show two decomposition maxima at temperatures close to PBzMA and PDEAEMA respectively, obviously due to the much higher content in BzMA and DEAEMA units. The other samples show three decomposition maxima, combining the thermal degradation behavior of both homopolymers [51]. The activation energies measured by the Kissinger method **(Table 6)** have lower values than that measured by the OFW method **(Table 7)**, something which is rather common in the literature and reflects the different theoretical background on which the two methods are based. The activation energies from the OFW method change considerably upon changing the decomposition

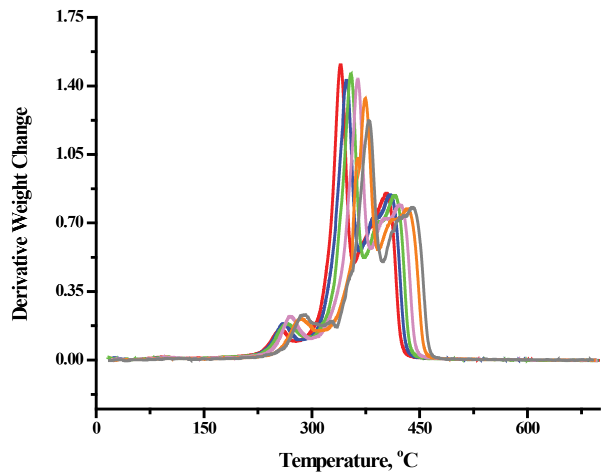


Figure 12 Derivative weight loss with temperature for sample 40/60 under different heating rates (from left to right 3 to 20°C/min).

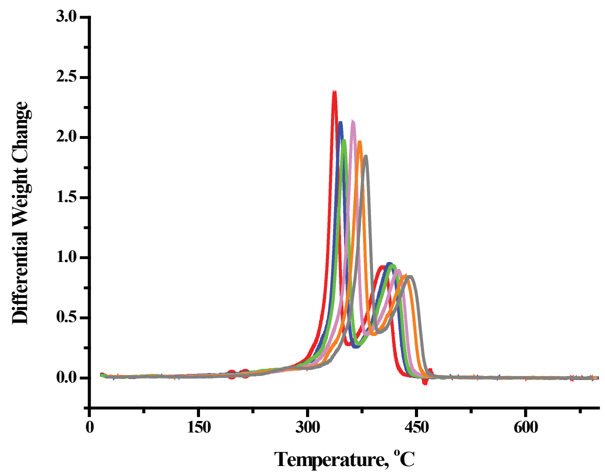


Figure 13 Derivative weight loss with temperature for sample 20/80 under different heating rates (from left to right 3 to 20°C/min).

Table 6 Activation Energies, J, by the Kissinger Method.

Sample	Ea_1	Ea_2	Ea_3
20-80	131.02	187.25	-
40-60	125.15	142.43	184.83
50-50	138.06	167.69	184.78
60-40	162.14	152.21	199.72
80-20	143.71	220.40	-
PBzMA	147.85	146.16	-
PDEAEMA	166.45	220.68	-

Table 7 Activation Energies, J, by the OFW Method.

Conversion	20-80	40-60	50- 50	60-40	80-20	BzMA	DEAEMA
0.1	154.18	204.50	278.17	249.43	166.19	147.45	-
0.2	166.65	219.28	217.08	343.96	307.56	170.86	-
0.3	154.89	183.23	182.53	221.46	367.05	173.98	204.84
0.4	149.87	172.94	178.03	199.48	336.63	172.21	231.40
0.5	151.77	189.42	211.96	272.95	310.19	168.96	208.97
0.6	221.72	207.44	214.69	257.62	286.34	165.95	190.72
0.7	230.62	211.75	217.04	248.63	281.38	160.56	176.64
0.8	221.23	215.64	225.72	251.68	274.50	162.78	378.76
0.9	219.85	217.38	220.59	247.55	293.53	160.98	246.44

conversion, indicating that the decomposition mechanism is complex during the thermal decomposition for both the homo- and the copolymers. PBzMA shows lower Ea values compared to PDEAEMA reflecting its lower thermal stability. It is rather surprising that the copolymers reveal higher Ea values than both homopolymers. This behavior can be attributed to the fact that at temperatures below 300°C the thermolysis of the side groups of BzMA units takes place leading to the formation of moieties that may react with the diethylamine groups of the DEAEMA monomer units leading to temporal crosslinking and therefore to transient networks, which are thermally very stable. Upon increasing the BzMA content of the copolymers the Ea values gradually increase. The thermolysis of the side groups of BzMA facilitates the formation of the transient networks leading to increased thermal stability of the structures, in agreement with literature results.

Conclusion

Free radical polymerization techniques were employed for the synthesis of statistical copolymers of benzyl methacrylate (BzMA) and diethylaminoethyl methacrylate (DEAEMA). The reactivity ratios were measured in the frame of several graphical and non-graphical methods. The computer program COPOINT revealed that r_{BzMA}=0.600 and r_{DEAEMA}=0.398, implying that a nonideal azeotropic copolymerization is effective. The homopolymerization of the two monomers is not favored, since both reactivity ratios are lower than unity. Therefore, a tendency for the production of an alternating copolymer prevails with slightly greater probability for the incorporation of BzMA than DEAEMA units ($r_{BzMA}>r_{DEAEMA}$). The dyad monomer distributions and the mean sequence lengths were also measured. The Tg values of the copolymers were measured and were compared with the predictions of several theoretical models. It was found that Fox and Gibbs-Di Marzio equations fit better the experimental data. The kinetics of thermal decomposition of the copolymers was also studied and the results were compared with those of the respective homopolymers. In all cases the mechanism of thermal decomposition is complex. In the case of PBzMA the process involves initially the decomposition of the side groups. The copolymers revealed higher activation energies of thermal decomposition, Ea, values than both homopolymers. This behavior can be attributed to the thermolysis of the side groups of BzMA units leading to the formation of moieties that may react with the diethylamine groups of the DEAEMA monomer units leading to temporal crosslinking and therefore to transient networks, which are thermally very stable.

References

1 Tirrell DA (1985) In: Encyclopedia of Polymer Sciences and Engineering. 2nd edn. Mark H, Bikales NM, Overberger CG, Menges G (eds), John Wiley & Sons, New York 4: 192.

2 Zutty NL, Faucher JA (1962) The stiffness of ethylene copolymers J Polym Sci 60: S36-S37.

3 Stergiou G, Dousikos P, Pitsikalis M (2002) Radical copolymerization of styrene and alkyl methacrylates: Monomer reactivity ratios and thermal properties. Eur Polym J 38: 1963-1970.

4 Makrikosta G, Georgas D, Siakali-Kioulafa E, Pitsikalis M (2005) Statistical copolymers of styrene and 2-vinylpyridine with trimethylsilyl methacrylate and trimethylsilyloxyethyl methacrylate. Eur Polym J 41: 47-54.

5 Kostakis K, Mourmouris S, Kotakis K, Nikogeorgos N, Pitsikalis M, et al. (2005) Influence of the cocatalyst structure on the statistical copolymerization of methyl methacrylate with bulky methacrylates using the zirconocene complex Cp_2ZrMe_2. J Polym Sci Polym Chem Ed 43: 3305-3314.

6 Kotzabasakis V, Petzetakis N, Pitsikalis M, Hadjichristidis N, Lohse DJ (2009) Copolymerization of tetradecene-1 and octene-1 with silyl-protected 10-undecen-1-ol using a C_s-symmetry hafnium metallocene catalyst. A route to functionalized poly(α-olefins). J Polym Sci Polym Chem Ed 47: 876-886.

7 Driva P, Bexis P, Pitsikalis M (2011) Radical Copolymerization of 2-Vinyl Pyridine and Oligo(Ethylene Glycol) Methyl Ether Methacrylates: Monomer Reactivity Ratios and Thermal Properties. Eur Polym J 47: 762-771.

8 Droulia M, Anastasaki A, Rokotas A, Pitsikalis M, Paraskevopoulou P (2011) Statistical Copolymers of Methyl Methacrylate and 2-Methacryloyloxyethyl ferrocenecarboxylate: Monomer Reactivity Ratios, Thermal and Electrochemical Properties. J Polym Sci Polym Chem Ed 49: 3080-3089.

9 Floros G, Agrafioti F, Grigoropoulos A, Paraskevopoulou P, Mertis K, et al. (2013) Statistical copolymers of norbornene and 5-vinyl-2-norbornene by a ditungsten complex mediated ring opening metathesis polymerization. Synthesis, thermal properties and kinetics of thermal decomposition. J Polym Sci Part A Polym Chem 51: 4835-4844.

10 Karra E, Petrakou I, Driva P, Pitsikalis M (2013) Radical Copolymerization of 2-Vinyl Pyridine with Functional Methacrylates: Monomer Reactivity Ratios and Thermal Properties Macromolecules, An Ind J 9: 68-77.

11 Nagasaki Y, Sato Y, Kato M (1997) A novel synthesis of semitelechelic functional poly(methacrylate)s through an alcoholate initiated polymerization. Synthesis of poly[2-(N,N-diethylaminoethyl) methacrylate] macromonomer. Macromol Rapid Comm 18: 827-835.

12 Dai S, Ravi P, Tam KC (2008) pH-Responsive polymers: synthesis, properties and applications. Soft Matter 4: 435-449.

13 Schmaljohann D (2006) Thermo- and pH-responsive polymers in drug delivery. Adv Drug Delivery Rev 58: 1655-1670.

14 Kost J, Langer R (2001) Responsive polymeric delivery systems. Adv Drug Delivery Rev 46: 125-148.

15 Li Y, Tang Y, Narain R, Lewis AL, Armes SP (2005) Biomimetic stimulus-responsive star diblock gelators. Langmuir 21: 9946-9954.

16 Yan B, Han D, Boissiere O, Ayotte P, Zhao Y (2013) Manipulation of block copolymer vesicles using CO_2: Dissociation or "breathing". Soft Matter 9: 2011-2016.

17 Schmalz A, Hanisch M, Schmalz H, Müller AHE (2010) Polymer Double stimuli-responsive behavior of linear and star-shaped poly(N,N-diethylaminoethyl metyacrylate) in aqueous solutions. Polymer 51: 1213-1217.

18 Aseyev V, Tenhu H, Winnik FM (2011) Non-ionic thermoresponsive polymers in waters. Adv Polym Sci 242: 29-89.

19 Hu J, Zhang G, Ge Z, Liu S (2014) Stimuli responsive tertiary amine methacrylate-based block copolymers. Synthesis, supramolecular self-assembly and functional applications. Progr Polym Sci 39: 1096-1143.

20 Hu J, Liu S (2010) Responsive Polymers for Detection and Sensing Applications: Current Status and Future Developments. Macromolecules 43: 8315-8330.

21 Demirelli K, Bezgin F (2012) Synthesis and characterization of lactone functional macromonomers by end group deactivation and their use in miktoarm star polymer. Open J Polym Chem 2: 42-55.

22 Brandrup J, Immergut EH, Grulke EA (1999) Polymer Handbook. 4th edn. John Wiley & Sons.

23 Monteiro MJ, Cunningham MF (2012) Polymer Nanoparticles via Living Radical Polymerization in Aqueous Dispersions: Design and Applications. Macromolecules 45: 4939-4957.

24 Charleux B, Delaittre G, Rieger J, d'Agosto F (2012) Polymerization-Induced Self-Assembly: From Soluble Macromolecules to Block Copolymer Nano-Objects in One Step. Macromolecules 45: 6753-6765.

25 Perrier S, Takolpuckdee P (2005) Macromolecular design via reversible addition-fragmentation chain transfer (RAFT)/xanthates (MADIX) polymerization. J Polym Sci, Part A: Polym Chem 43: 5347-5393.

26 Moad G, Rizzardo E, Thang SH (2008) Radical addition-fragmentation chemistry in polymer synthesis. Polymer 49: 1079-1131.

27 De Brouwer H, Schellekens MAJ, Klumperman B, Monteiro MJ, German A (2000) Controlled radical polymerization of styrene and maleic anhydride and the synthesis of novel polyolefin-based block copolymers by reversible addition-fragmentation chain-transfer (RAFT) polymerization. J Polym Sci, Part A: Polym Chem 38: 3596-3603.

28 Liu J, Duong H, Whittaker MR, Davis TP, Boyer C (2012) Synthesis of functional core, star polymers via RAFT polymerization for drug delivery applications. Macromol Rapid Commun 33: 760-766.

29 Zhang C, Maric M (2014) Statistical terpolymers with thermo-responsive fluorescence response in an ionic liquid: effects of solvatophilicity on LCST phase separation and reversibility. Polym Chem 4926-4938.

30 Hadjichristidis N, Iatrou H, Pispas S, Pitsikalis M (2000) Anionic Polymerization: High Vacuum Techniques. J Polym Sci Part A: Polym Chem 38: 3211-3234.

31 Beginn U (2005) COPOINT a simple computer program to determine copolymerization parameters by numerical integration. e-Polymers 73: 1-24.

32 Ozlem-Gundogdu S, Gurel EA, Hacaloglu J (2015) Pyrolysis of poly(methyl methacrylate) copolymers. J Anal Appl Pyrol 113: 529-538.

33 Demirelli K, Coskun M, Kaya E (2004) Polymers based on benzyl methacrylate: Synthesis via atom transfer radical polymerization,

characterization and thermal stabilities. J Polym Sci Part A: Polym Chem 42: 5964-5973.

34 Fineman M, Ross S (1950) Linear method for determining monomer reactivity ratios in copolymerization. J Polym Sci 5: 259-262.

35 Kelen T, Tüdos F (1975) Analysis of the Linear Methods for Determining Copolymerization Reactivity Ratios. I. A New Improved Linear Graphic Method. J Macromol Sci A A9: 1-27.

36 Odian G (1991) Principles of Polymerization. Wiley Interscience. 3rd edn.

37 Flory PJ (1953) Principles of Polymer Chemistry. Cornell University Press, Ithaca, USA.

38 Hiemenz PC (1984) Polymer Chemistry. The Basic Concepts, Marcel Dekker Inc. New York, USA.

39 Igarashi S (1963) Representation of composition and blockiness of the copolymer by a triangular coordinate system. J Polym Sci Polym Lett Ed 1: 359-363.

40 Elias HG (1971) Macromolecules. Plenum Press: New York, NY, USA 2: 761.

41 Wood LA (1958) Glass transition temperatures of copolymers. J Polym Sci 28: 319-330.

42 Couchman PR, Karasz FR (1978) A classical thermodynamic discussion of the effect of composition on glass transition temperatures. Macromolecules 11: 117-119.

43 Gibbs JH, Di Marzio EA (1963) Molecular interpretation of glass temperature depression by plasticizers. J Polym Sci A 1: 1417-1428.

44 Fox TG, Flory PJ (1950) Second order transition temperatures and related properties of polystyrene. I. Influence of molecular weight. J Appl Phys 21: 581-591.

45 Johnston NW (1976) Sequence distribution-Glass transition effects. J Macromol Sci Rev Macromol Chem Phys C 14: 215.

46 Barton JM (1970) Relation of glass transition temperature to molecular structure of addition copolymers. J Polym Sci C 30: 573.

47 Ozawa T (1965) A New Method of Analyzing Thermogravimetric Data. Bull Chem Soc Jpn 38: 1881-1886.

48 Flynn J, Wall LA (1966) A quick, direct method for the determination of activation energy from thermogravimetric data. J Polym Sci Part B Polym Lett 4: 323-328.

49 Ozawa T (1970) Kinetic analysis of derivative curves in thermal analysis. J Therm Anal Calorim 2: 301-324.

50 Kissinger HE (1956) Variation of Peak Temperature with Heating Rate In Differential Thermal Analysis. J Res Nat Bur Stand 57: 217-221.

51 Kissinger HE (1957) Reaction kinetic in differential thermal analysis. Anal Chem 29: 1702-1712.