

Free radical copolymerization of *N,N*-dimethylaminoethyl methacrylate with styrene and methyl methacrylate: monomer reactivity ratios and glass transition temperatures

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Abstract

BACKGROUND: The properties of copolymers depend strongly on their composition; therefore in order to tailor some for specific applications, it is necessary to control their synthesis, and, in particular, to know the reactivity ratios of their constituent monomers. Free radical copolymerizations of *N,N*-dimethylaminoethyl methacrylate (DMAEM) with styrene (ST) and methyl methacrylate (MMA) in toluene solution using 1-di(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane as initiator at 70 °C were investigated. Monomer reactivity ratios were determined for low conversions using both linear and nonlinear methods.

RESULTS: For the DMAEM/ST system the average values are $r_1 = 0.43$ and $r_2 = 1.74$; for the DMAEM/MMA system the average values are $r_1 = 0.85$ and $r_2 = 0.86$. The initial copolymerization rate, R_p , for DMAEM/ST sharply decreases as the content of ST in the monomer mixture increases up to 30 mol% and then attains a steady value. For the DMAEM/MMA copolymerization system the composition of the feed does not have a significant influence on R_p . The glass transition temperatures (T_g) of the copolymers were determined calorimetrically and calculated using Johnston's sequence length method. A linear dependence of T_g on copolymer composition for both systems is observed: T_g increases with increasing ST or MMA content.

CONCLUSION: Copolymerization reactivity ratios enable the design of high-conversion processes for the production of copolymers of well-defined properties for particular applications, such as the improvement of rheological properties of lubricating mineral oils.

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Keywords: *N,N*-dimethylaminoethyl methacrylate; free radical copolymerization; reactivity ratio; glass transition temperature

INTRODUCTION

The practical application of sophisticated copolymerizations has undergone significant progress, since even a small fraction of a particular functional monomer may have a significant impact on the value of a desired property.^{1,2} In these systems, copolymerization reactivity ratios are important quantitative parameters in the prediction of copolymer composition from any starting feed in batch, semi-batch or continuous reactors. They are also crucial in understanding the kinetic and mechanistic aspects of copolymerization.³ Recently, polymerization and copolymerization reactions of nitrogen-containing monomers have attracted the attention of researchers as a way of obtaining water-soluble polymer materials with a wide range of physicochemical and biological properties.⁴ Aminoalkyl (meth)acrylates and their salts take a prominent position among these monomers.^{5,6} The interest in polymers based on aminoalkyl esters of methacrylic acid (and their salts) is related to both the accessibility and high reactivity of the starting monomers as well as to the properties of the products.⁷ Thus, *N,N*-dimethylaminoethyl methacrylate (DMAEM) can be polymerized with other monomers to form copolymers of

interest in a variety of applications. Such copolymers may be used as flocculants, as adhesives, as gloss improvers in latex paints, in automotive coatings or as detergent and sludge dispersants in lubricating oils, as well as retention aids for papermaking, etc.^{8–10}

Many studies concerning the wide application possibilities of DMAEM copolymers have been undertaken; however, information related to polymerization kinetics and copolymerization reactivity is very scarce in the literature. In several studies the monomer reactivity ratios for copolymerization of DMAEM with methyl methacrylate (MMA) in bulk as well as in dioxane and chloroform solutions were reported.^{11–13} Copolymerizations with a few other methacrylates were also investigated, namely 2-hydroxyethyl methacrylate, ethyl- α -hydroxymethyl acrylate, (2,2-dimethyl-1,3-dioxolan-4-yl)methyl methacrylate and *tert*-butyl methacrylate.^{12,14,15} Furthermore, the effect of the polarity

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of different solvents on the reactivity ratio values in the free radical copolymerization of DMAEM with *N*-vinylcarbazole has been described.¹⁶ However, no reports have focused on an analysis of the monomer reactivity ratios and copolymer properties in the copolymerization system of DMAEM with styrene (ST).

In the work reported here, copolymerization kinetics and reactivity in binary monomer systems of DMAEM with ST and MMA in toluene were investigated. Based on the Mayo–Lewis model^{17,18} for binary radical copolymerization, and the examined interdependences between copolymer and monomer mixture compositions, the copolymerization reactivity ratios were determined using linear and nonlinear methods. The variations of glass transition temperature, T_g , with copolymer composition were established and analysed.

EXPERIMENTAL

Materials

ST, MMA and DMAEM (polymerization grade; RohMax Chemical Co.) were passed through a column of activated basic aluminium oxide (Aldrich) and purged with high-purity nitrogen prior to use. The initiator 1,1-di(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane (Trigonox 29, 90 wt% solution; Akzo Chemie) was used as received, as were the reagent-grade solvents toluene, petroleum ether and methanol.

Copolymerization

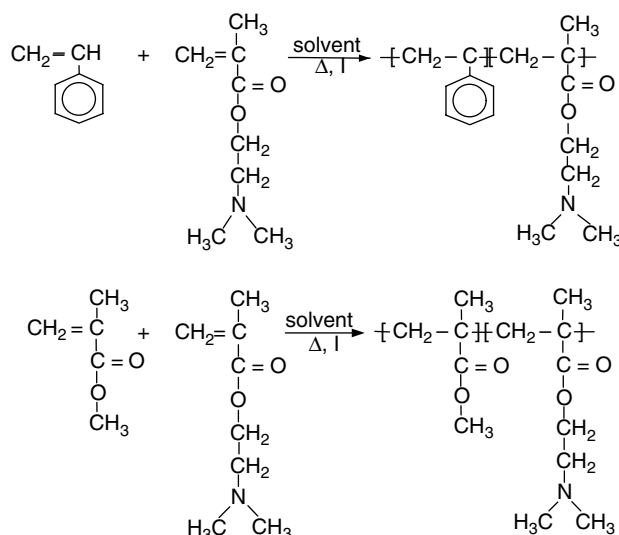
Low-conversion (<10 wt%) copolymerization kinetics of the DMAEM/ST and DMAEM/MMA systems were studied under stationary reaction conditions using the dilatometric and gravimetric methods. Reactions were carried out at 70 °C in 1 mol dm⁻³ toluene solutions, using a constant concentration (0.01 mol dm⁻³) of the initiator. Monomer mixture compositions were varied by 10 mol%. Dilatometers of about 20 cm³ were filled with the reaction mixtures and then placed in a thermostatically controlled bath; volume contractions were recorded as a function of time. The reactions were terminated by vacuum suction of the dilatometer contents followed by precipitation in excess petroleum ether or methanol. Final conversions were determined gravimetrically. The corresponding reactions are shown in Scheme 1.

Characterization

Copolymer composition

Compositional analysis of the copolymers with respect to the mole fraction of ST and MMA in the copolymers was performed using NMR with a Bruker Avance instrument. The ¹H NMR spectra were recorded at 300 MHz with deuterated chloroform (CDCl₃) as a solvent. The proton solvent signal was used as the chemical shift marker. The relative signal intensities of the spectra were measured from the integrated peak area (I_p) and calculated using an electronic integrator. Examples of ¹H NMR spectra of DMAEM/ST and DMAEM/MMA copolymers and their assignments are shown in Figs 1 and 2, respectively.

Thus, the mole fraction of monomer incorporated in the copolymer was calculated based on the intensities of the signals that appear at 4.1 ppm, corresponding to the two oxymethylene protons in the DMAEM units, at 3.6 ppm, corresponding to the –O–CH₃ protons in the MMA units, and at 6.57–7.48 ppm, corresponding to the –C₆H₅ protons in the ST units.^{19–21} The



Scheme 1. Copolymerizations of DMAEM with ST and MMA.

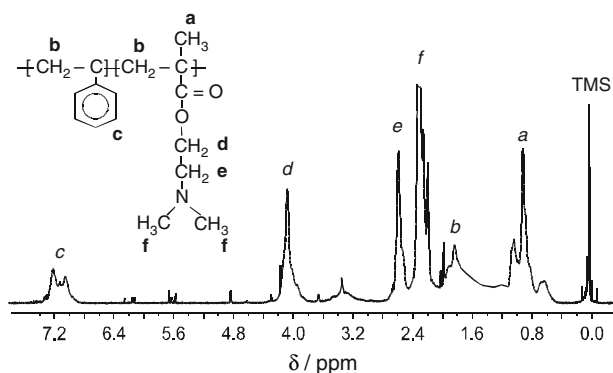


Figure 1. Characteristic ¹H NMR spectrum of poly(DMAEM-co-ST).

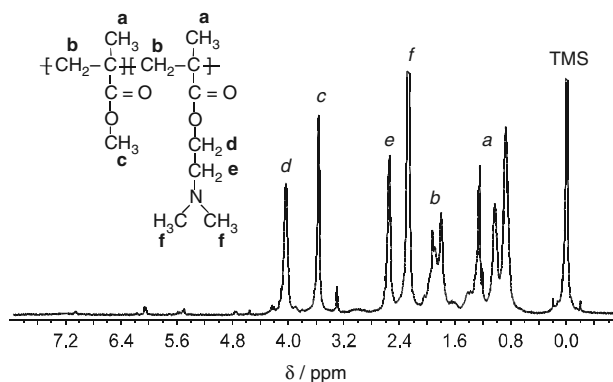


Figure 2. Characteristic ¹H NMR spectrum of poly(DMAEM-co-MMA).

corresponding equations are

$$F_{ST} = \frac{I_p(-C_6H_5)/5}{I_p(-C_6H_5)/5 + I_p(-O-CH_2-)/2} \quad (1)$$

and

$$F_{MMA} = \frac{I_p(-O-CH_3)/3}{I_p(-O-CH_3)/3 + I_p(-O-CH_2-)/2} \quad (2)$$

Glass transition temperatures

The glass transition temperatures were measured using a Mettler Toledo DSC1 differential scanning calorimeter. The temperature scale was calibrated according to the melting points of high-purity chemicals (lauric and stearic acids and indium). The samples (ca 10 mg) were scanned at $10.0\text{ }^{\circ}\text{C min}^{-1}$ under dry nitrogen ($20\text{ cm}^3\text{ min}^{-1}$). Then they were cooled from room temperature to $-50\text{ }^{\circ}\text{C}$ and maintained at this temperature for 1 min. They were then heated to $150\text{ }^{\circ}\text{C}$ and then quenched to $-50\text{ }^{\circ}\text{C}$. This procedure was repeated twice. The actual value of T_g was estimated as the temperature at the midpoint of the line drawn between the temperature of the intersection of the initial tangent with the tangent drawn through the point of inflection with the final tangent.

RESULTS AND DISCUSSION

Copolymerization and monomer reactivity ratios

Free radical homopolymerization and copolymerization reactions of DMAEM/ST and DMAEM/MMA binary systems were carried out in toluene solution using a peroxide initiator. Overall monomer conversions were kept less than 10 wt% in order to satisfy the differential copolymerization equation due to monomer reactivity calculations. The examined data for copolymer compositions as well as some reaction data for both copolymerization systems are collected in Table 1. Plots of the mole fractions of DMAEM in the feed (f) versus that in the copolymer (F) are shown in Figs 3 and 4. It is clear that the share of DMAEM in the copolymer with ST is always lower than that in the feed. In the DMAEM/MMA system, copolymer compositions are equal to the corresponding monomer mixtures.

The monomer reactivity ratios for the copolymerization of DMAEM with ST or MMA were calculated from the monomer feed ratios and previously determined copolymer compositions using linear least-squares (LLS) and nonlinear least-squares (NLLS) methods.

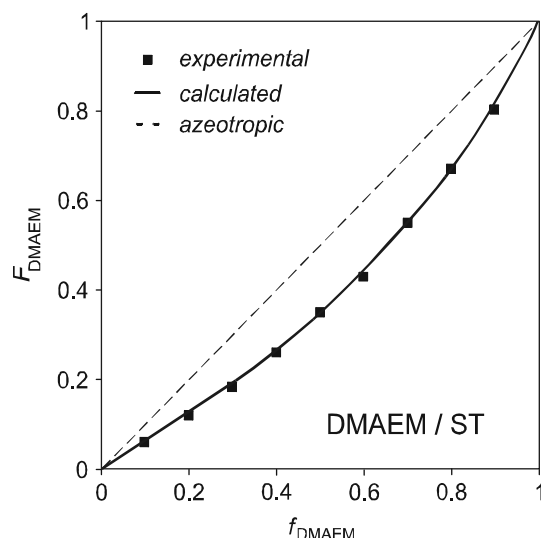


Figure 3. Copolymer (F) versus monomer feed (f) composition for copolymerization of DMAEM with ST in toluene solution, at $70\text{ }^{\circ}\text{C}$, using the peroxide initiator.

Table 1. Summary of copolymerization and copolymer properties data^a

	f_{DMAEM}	F_{DMAEM}	X (%)	t_p (s)	R_p ($\text{mol dm}^{-3}\text{ s}^{-1}$)	T_g ($^{\circ}\text{C}$)
DMAEM/ST	1.0	1.000	6.9	2 433	2.82×10^{-5}	16.60
	0.9	0.789	7.0	6 083	1.20×10^{-5}	18.92
	0.8	0.666	5.8	8 958	6.83×10^{-6}	27.95
	0.7	0.553	4.8	11 948	4.24×10^{-6}	35.14
	0.6	0.430	5.4	14 640	3.92×10^{-6}	38.03
	0.5	0.352	4.2	15 418	2.92×10^{-6}	39.10
	0.4	0.257	5.8	15 395	3.77×10^{-6}	40.20
	0.3	0.184	7.5	25 024	3.18×10^{-6}	49.05
	0.2	0.120	5.2	25 460	2.72×10^{-6}	53.47
	0.1	0.062	6.5	26 170	2.55×10^{-6}	65.74
DMAEM/MMA	0.0	0.000	9.8	27 111	3.62×10^{-6}	68.41
	1.0	1.000	6.9	2 433	2.82×10^{-5}	16.60
	0.9	0.879	5.8	2 911	2.01×10^{-5}	18.84
	0.8	0.793	6.7	3 147	2.15×10^{-5}	22.63
	0.7	0.699	7.7	3 350	2.29×10^{-5}	29.70
	0.6	0.618	7.2	3 315	2.14×10^{-5}	44.00
	0.5	0.496	6.9	3 080	2.23×10^{-5}	49.84
	0.4	0.404	7.9	3 993	2.00×10^{-5}	56.17
	0.3	0.298	7.5	3 845	1.95×10^{-5}	57.41
	0.2	0.214	8.1	4 237	1.90×10^{-5}	61.67
	0.1	0.125	8.9	5 122	1.73×10^{-5}	67.90
	0.0	0.000	5.1	3 849	1.31×10^{-5}	71.35

^a f , molar fraction of monomer in the feed; F , molar fraction of monomer in copolymer; X , total monomer conversion; t_p , polymerization time; R_p , initial polymerization rate; T_g , copolymer glass transition temperature.

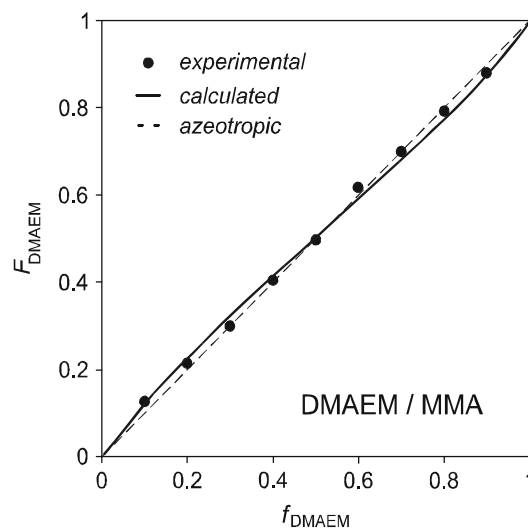


Figure 4. Copolymer (F) versus monomer feed (f) composition for copolymerization of DMAEM with MMA in toluene solution, at $70\text{ }^{\circ}\text{C}$, using the peroxide initiator.

Determination of reactivity ratios using LLS methods

The Finemann–Ross (FR), inverted Finemann–Ross (IFR), Kelen–Tüdös (KT) and extended Kelen–Tüdös (EKT) LLS methods were used to determine the reactivity ratios in the copolymerization systems investigated. The FR equation represents one of the earliest attempts to linearize the copolymer composition

equation:²²

$$G = r_1 H - r_2 \quad (3)$$

where $G = X(Y - 1)/Y$ and $H = X^2/Y$ ($X = f_1/f_2$; $Y = F_1/F_2$). The IFR equation gives r_1 as the intercept and r_2 as the slope:²³

$$\frac{G}{H} = -r_2 \frac{1}{H} + r_1 \quad (4)$$

The FR and IFR plots for the DMAEM/MMA copolymerization system are shown in Figs 5 and 6.

The KT method introduces new parameters into the linearized copolymerization equation:²⁴

$$\eta = \left(r_1 + \frac{r_2}{\alpha}\right) \xi - \frac{r_2}{\alpha} \quad (5)$$

where $\eta = G/(\alpha + H)$, $\xi = H/(\alpha + H)$ and $\alpha = (H_{\max}H_{\min})^{1/2}$. The intercept at $\xi = 0$ and $\xi = 1$ of the η versus ξ plot gives $-r_2/\alpha$ and r_1 , respectively. $H_{\max}$ and $H_{\min}$ are the highest and lowest values of H . The effect of conversion is considered in the EKT equation.²⁵ The partial molar conversion of monomer 2 is defined as

$$\xi = W \left(\frac{\mu + X}{\mu + Y} \right) \quad (6)$$

where W is the weight conversion of polymerization and μ is the ratio of the molecular mass of monomer 2 to that of monomer 1.

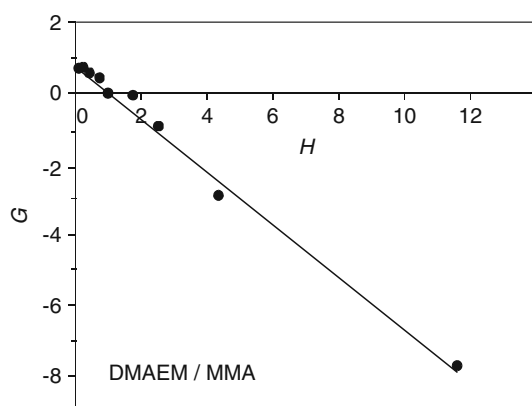


Figure 5. FR plot for the DMAEM/MMA copolymerization system.

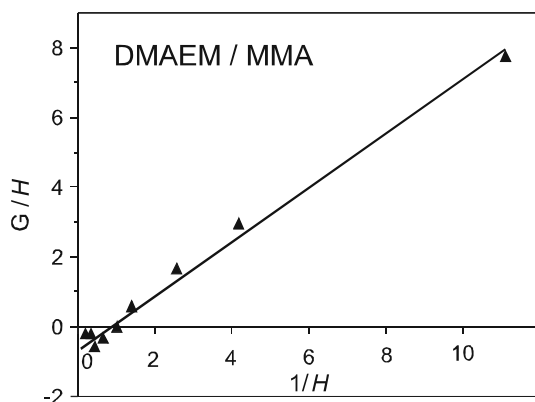


Figure 6. IFR plot for the DMAEM/MMA copolymerization system.

The partial molar conversion of monomer 1 is

$$\xi_1 = \xi_2 \left(\frac{Y}{X} \right) \quad (7)$$

Then

$$Z = \frac{\log(1 - \xi_1)}{\log(1 - \xi_2)} \quad (8)$$

where $H = Y/Z^2$, $G = (Y - 1)/Z$, $\mu = G/(\alpha + H)$ and $\xi = H/(\alpha + H)$. The KT and EKT plots for low-conversion data for the DMAEM/ST copolymerization system are shown in Figs 7 and 8. The values of reactivity ratios calculated using the LLS methods presented are summarized in Table 2.

Determination of reactivity ratios using NLLS method

The NLLS procedure of Tidwell and Mortimer²⁶ (TM) is considered to be one of the most accurate procedures for determination of monomer reactivity ratio values. The computation procedure is basically a Gauss–Newton NLLS method, which was modified by Box to ensure rapid convergence to a pair of values.²⁷ A brief description of the method consists of initial estimates of r_1 and r_2 , commonly from the linear methods, most often using the KT method. A set of computations was performed (MATLAB[®]) yielding the sum of the squares of the differences between the observed and computed polymer composition. The summation is

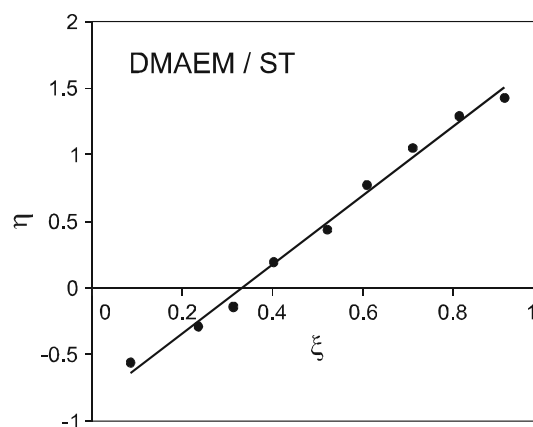


Figure 7. KT plot for the DMAEM/ST copolymerization system.

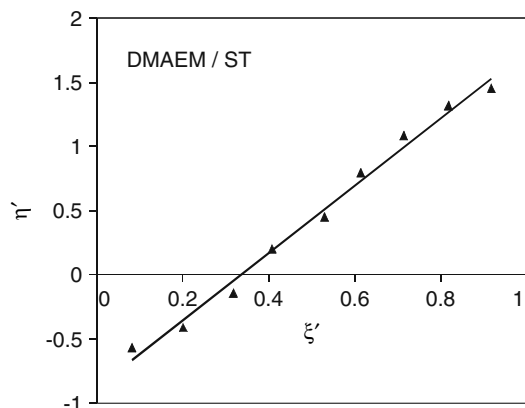


Figure 8. EKT plot for the DMAEM/ST copolymerization system.

Table 2. A summary of the copolymerization reactivity ratios calculated for the free radical copolymerizations of DMAEM with MMA and ST using various methods

Monomer	Method	r_1	r_2	$r_1 \times r_2$
DMAEM/ST	FR	0.45 ± 0.01	1.80 ± 0.05	0.81
	IFR	0.47 ± 0.03	1.78 ± 0.03	0.84
	KT	0.43 ± 0.01	1.72 ± 0.03	0.74
	EKT	0.42 ± 0.02	1.75 ± 0.00	0.74
	TM	0.44 ± 0.00	1.74 ± 0.01	0.77
	Average ^a	0.43	1.74	0.75
DMAEM/MMA	FR	0.72 ± 0.07	0.74 ± 0.09	0.53
	IFR	0.71 ± 0.08	0.78 ± 0.05	0.55
	KT	0.82 ± 0.03	0.85 ± 0.02	0.70
	EKT	0.84 ± 0.01	0.81 ± 0.02	0.68
	TM	0.89 ± 0.10	0.92 ± 0.09	0.82
	Average ^a	0.85	0.86	0.73

^a Average values are calculated from the KT, EKT and TM method results.

then minimized by iteration, yielding reactivity ratios.²⁶ The values obtained for both copolymerization systems are given in Table 2.

The numerical values of the reactivity ratios obtained using the various methods are very close, especially for the DMAEM/ST copolymerization system, indicating a high reliability of the examined values. In the copolymerization system of DMAEM with MMA, the addition tendencies of the growing radicals with both monomer ends to the comonomers are approximately equal to one another, $r_1 = 0.85$ and $r_2 = 0.86$, indicating an almost ideal copolymerization system. This means that copolymer compositions are almost equal to the feed composition (Fig. 4), with a random placement of two monomeric units along the copolymer chain (Table 2). In the copolymerization system of DMAEM with ST, a different behaviour is observed. Growing radicals with ST ends are added to the ST monomer at a higher rate than to DMAEM monomer. Moreover, the radical with DMAEM exhibits affinity towards the ST monomer. Therefore, the copolymer is rich in ST units and probably has some ST

blocks along the copolymer chain (Fig. 3). The tendency to form an alternating structure of copolymers in the DMAEM/ST system is rather small due to the insufficient differences in reactivity ratio values, where $r_1 = 0.43$ and $r_2 = 1.74$. Theoretical curves representing the molar fraction of DMAEM in the feed (f) and the molar fraction in the copolymer (F) for both copolymerization systems, calculated from the reactivity ratios obtained, are shown in Figs 3 and 4. A very good agreement between experimental and calculated data is found. In Table 3 the literature data for reactivity ratio values for copolymerization of DMAEM with other monomers are given. There are no available data for the copolymerization of DMAEM with ST, unlike the copolymerization of DMAEM with MMA. The reactivity ratios calculated for the copolymerization of DMAEM with MMA fit well with literature data. Small differences in the values obtained, besides the polymerization type, probably originate from the solvents used due to the changes in interactions between the monomer (radical) and solvent molecules.¹⁶

Copolymerization reaction rate

Dilatometry is a well-known method for determination of polymerization rates.²⁸ The necessary condition is a volume change during the polymerization, and a correlation between shrinkage and conversion (X) yields the equation

$$X = \frac{1}{K} \frac{\Delta V}{V} \times 100 \quad (9)$$

where V is the initial volume, ΔV the decrease in the volume and K the so-called conversion factor.²⁸ In all the experiments performed, a linear dependence of total monomer mass conversion on polymerization time was found ($r^2 > 0.95$); typical results are shown in Figs 9 and 10. It is evident that an increase of ST or MMA content in the monomer mixture produces a decrease in the total monomer conversion for equal polymerization times. When comparing the two systems studied, DMAEM/ST and DMAEM/MMA, the observed decrease is more pronounced for the DMAEM/ST system. This is probably due to the resonance stabilization of styrene-terminated growing macroradicals, which in turn leads to lower propagation rates for those radicals.

The observed linear conversion *versus* time relationship is evidence that the experiments were performed under stationary

Table 3. Literature data for reactivity ratio values for copolymerization of DMAEM (monomer 1) with various monomers

Monomer 2 ^a	r_1, r_2	Reaction conditions ^b	Reference
MMA	$r_1 = 1.01; r_2 = 0.42$	Dioxane, $T = 65^\circ\text{C}$, $c(\text{AIBN}) = 5 \times 10^{-3} \text{ mol dm}^{-3}$	11
MMA	$r_1 = 1.30; r_2 = 0.74$	Bulk, 50, 60, 80°C , $c(\text{AIBN}) = 5 \times 10^{-3} \text{ mol dm}^{-3}$	12
MMA	$r_1 = 0.89; r_2 = 1.12$	CHCl_3 , 60°C , $c(\text{AIBN}) = 5 \times 10^{-3} \text{ mol dm}^{-3}$	13
HEMA	$r_1 = 0.446; r_2 = 1.626$	Bulk, $T = 50^\circ\text{C}$, $c(\text{AIBN}) = 10^{-2} \text{ mol dm}^{-3}$	14
EHMA	$r_1 = 0.664; r_2 = 3.755$	Bulk, $T = 50^\circ\text{C}$, $c(\text{AIBN}) = 10^{-2} \text{ mol dm}^{-3}$	14
tBMA	$r_1 = 0.97; r_2 = 1.26$	CDCl_3 , $T = 50^\circ\text{C}$, $c(\text{AIBN}) = 5 \times 10^{-3} \text{ mol dm}^{-3}$	15
SMA	$r_1 = 1.40; r_2 = 0.65$	CDCl_3 , 50°C , $c(\text{AIBN}) = 5 \times 10^{-3} \text{ mol dm}^{-3}$	15
NVC	$r_1 = 1.34; r_2 = 0.33$	Dioxane, $T = 60^\circ\text{C}$, $c(\text{AIBN}) = 5 \times 10^{-3} \text{ mol dm}^{-3}$	16
NVC	$r_1 = 1.10; r_2 = 0.15$	MEK, $T = 60^\circ\text{C}$, $c(\text{AIBN}) = 5 \times 10^{-3} \text{ mol dm}^{-3}$	16
NVC	$r_1 = 0.88; r_2 = 0.10$	DMF, $T = 60^\circ\text{C}$, $c(\text{AIBN}) = 5 \times 10^{-3} \text{ mol dm}^{-3}$	16
NVC	$r_1 = 1.63; r_2 = 0.44$	Toluene, $T = 60^\circ\text{C}$, $c(\text{AIBN}) = 5 \times 10^{-3} \text{ mol dm}^{-3}$	16
MMA	$r_1 = 1.13; r_2 = 1.07$	CDCl_3 , $T = 60^\circ\text{C}$, Pd(II)-based complex	29

^a NVC, *N*-vinylcarbazole; HEMA, 2-hydroxyethyl methacrylate; EHMA, ethyl- α -hydroxymethyl acrylate; tBMA, *tert*-butyl methacrylate; SMA, solketal methacrylate ((2,2-dimethyl-1,3-dioxolan-4-yl)methyl methacrylate).

^b MEK, methylethyl ketone; DMF, *N,N*-dimethylformamide.

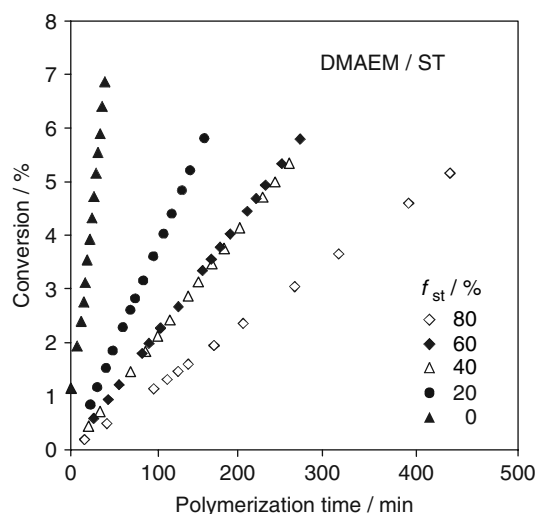


Figure 9. Total monomer conversion versus polymerization time for copolymerization of DMAEM and ST in toluene solution at 70 °C using the peroxide initiator.

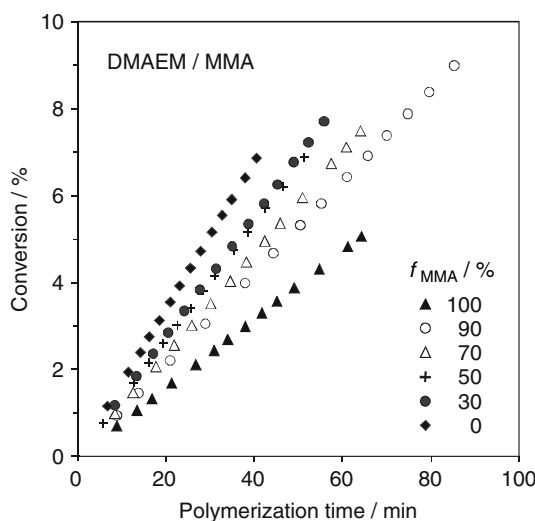


Figure 10. Total monomer conversion versus polymerization time for copolymerization of DMAEM and MMA in toluene solution at 70 °C using the peroxide initiator.

conditions. Thus, the results may be used to calculate the initial polymerization rates, R_p , for both systems investigated using the equation³⁰

$$R_p = \frac{m}{V M_R} \frac{\Delta X}{\Delta t} \quad (10)$$

where m is the total monomer mass, X is the total monomer mass conversion, V is the volume of the dilatometer and t is the reaction time. M_R is the average monomer molar mass:

$$M_R = \sum_{i=1}^n F_{R,i} M_i \quad (11)$$

where M_i and $F_{R,i}$ are the molar masses and average molar fractions, respectively, of particular monomers in the copolymer, previously established from NMR measurements. The calculated rate values are given in Table 1 and shown in Figs 11 and 12 for the DMAEM/ST

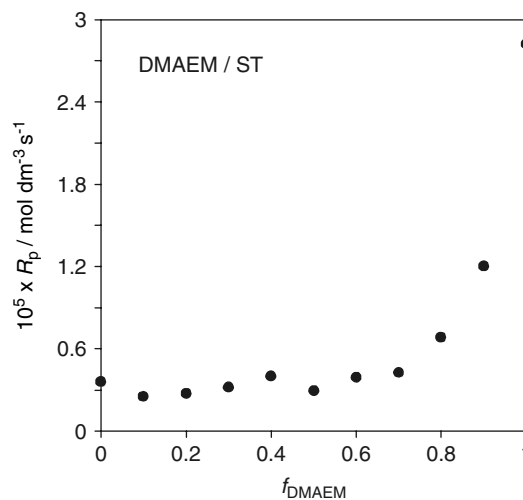


Figure 11. Initial polymerization rate, R_p , versus DMAEM molar fraction in feed, f_{DMAEM} , for the copolymerization of DMAEM and ST in toluene solution at 70 °C using the peroxide initiator.

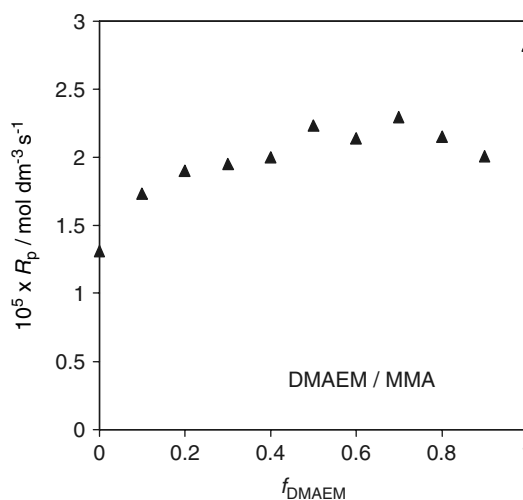


Figure 12. Initial polymerization rate, R_p , versus DMAEM molar fraction in feed, f_{DMAEM} , for the copolymerization of DMAEM and MMA in toluene solution at 70 °C using the peroxide initiator.

and DMAEM/MMA systems, respectively. Copolymerization rates are found to lie between the corresponding homopolymerization rate values for all the systems investigated. The initial reaction rate R_p for the homopolymerization reactions decreases in the order DMAEM > MMA > ST, which is in accordance with literature findings.³¹ For the DMAEM/ST system, R_p sharply decreases as the content of ST in the monomer mixture increases. With 10 mol% of ST in the feed, the rate of polymerization of DMAEM decreases by a factor of about 2.3. After the initial large decrease, the rate of copolymerization decreases rather slowly with an additional increase in ST concentration in the feed. However, the composition of the monomer feed no longer exerts an influence on the overall reaction rate of the DMAEM/MMA copolymerization system; as the MMA fraction in the feed increases, the average polymerization rate only slightly decreases. The observed polymerization rates are significantly larger for the MMA-containing system, due to the already mentioned resonance stabilization of ST-terminated growing macroradicals. The small deviations from this tendency in

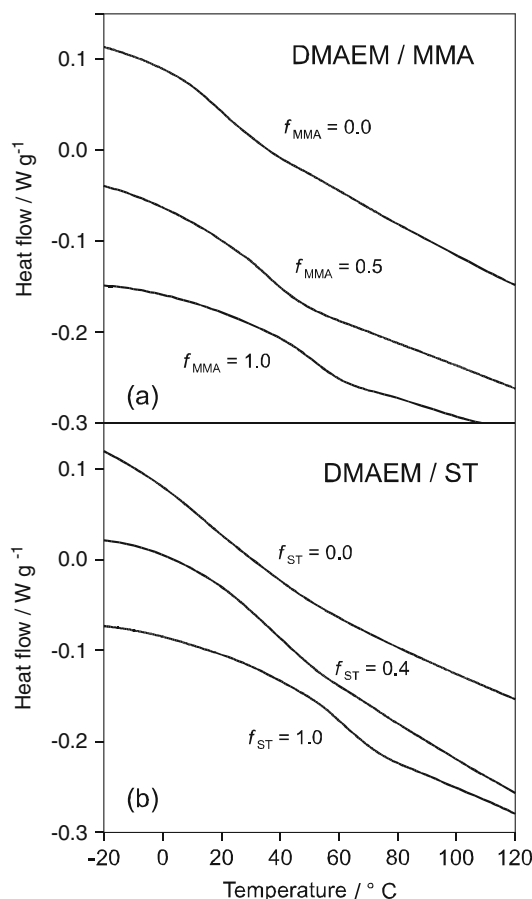


Figure 13. DSC curves of homopolymers and copolymers: (a) DMAEM/MMA system; (b) DMAEM/ST system.

plots representing polymerization rate *versus* monomer mixture composition may be related to possible experimental errors and to concentration change due to differences in the molar masses of monomers. Therefore, the initiator efficiency and termination kinetics may be affected, and consequently polymer conversion and initial polymerization rate.³²

Glass transition temperature of copolymers

The glass transition temperatures of both types of copolymers were determined using DSC in a nitrogen atmosphere over a wide range of copolymer compositions. The DSC curves obtained (Fig. 13) show a single, relatively long relaxation period with weakly indicated glass transition temperatures. The copolymer T_g values range between 16.6 and 68.4 °C, and 16.6 and 71.4 °C for the DMAEM/ST and DMAEM/MMA copolymers, respectively. Also, it can be seen that an increase of the MMA or ST content in the copolymers results in an increase of the glass transition temperature. The T_g values of the prepared copolymers are given in Table 1. The variation of T_g with the composition of the copolymers is shown in Fig. 14.

One can see that the experimental T_g values for the copolymers do not agree with the theoretical values predicted by the Fox equation,³³ which assumes that T_g of a copolymer depends only on the relative amounts of each monomer and T_g of the respective pure homopolymers, according to the expression

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (12)$$

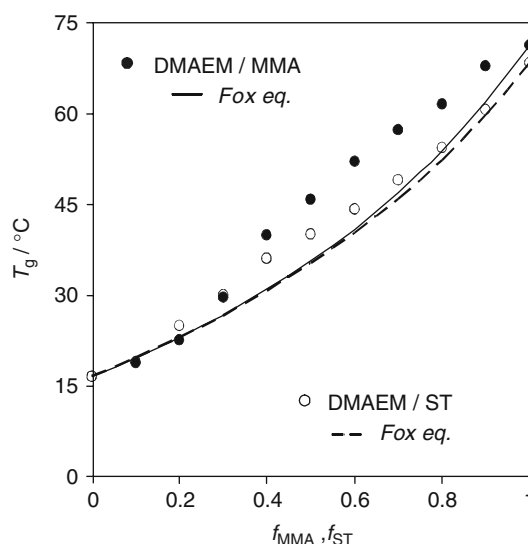


Figure 14. Experimental copolymer T_g values and those predicted by the Fox equation *versus* molar fractions of MMA (f_{MMA}) and ST (f_{ST}) in copolymer with DMAEM.

where T_g is the glass transition temperature of a copolymer composed of two monomer units M_1 and M_2 with mass fractions w_1 and w_2 , while T_{g1} and T_{g2} are the glass transition temperatures of the homopolymers, respectively. Johnston³⁴ proposed a new equation that can be considered as an extension of the earlier work of Fox and which predicts T_g in terms of monomer unit sequences (dyad sequences) in a copolymer. He assumes that M_1M_1 , M_1M_2 or M_2M_1 and M_2M_2 dyads have their own glass transition temperature, with the overall T_g of a copolymer described by the following expression:

$$\frac{1}{T_g} = \frac{w_1 P_{11}}{T_{g11}} + \frac{w_2 P_{22}}{T_{g22}} + \frac{w_1 P_{12} + w_2 P_{21}}{T_{g12}} \quad (13)$$

where w_1 and w_2 are the mass fractions of the two monomer units M_1 and M_2 , respectively. T_{g11} , T_{g22} and T_{g12} denote the T_g contribution of the M_1M_1 , M_2M_2 and M_1M_2 or M_2M_1 dyads in the copolymer, and can be substituted by T_g of M_1 homopolymer, M_2 homopolymer and the expected T_g for the alternating M_1M_2 copolymer, respectively. P_{11} , P_{22} and P_{12} or P_{21} indicate the probabilities of the M_1M_1 , M_2M_2 and M_1M_2 or M_2M_1 dyads in the copolymer chain, respectively, and can be calculated using monomer feed compositions and monomer reactivity ratios.³⁵ In Fig. 15 are represented the calculated dyad molar fractions for both systems investigated. The literature value for T_g of polymerized DMAEM is reported to be 19 °C,³⁶ which is in good agreement with the value obtained in this work. However, commonly reported values for T_g of polystyrene and poly(methyl methacrylate) are 105 and 100 °C,³⁵ respectively, which are higher than those estimated in our measurements. The lower values are the consequence of the variation in the molar mass of polymers, as was shown for polystyrene by Sperling and Hernandez-Sanchez,^{37,38} or due to the DSC instrument. Considering the copolymer T_g values of both systems and using a linearized form of Johnston's equation, we estimated T_{g12} . Those values are 46.85 and 44.0 °C for DMAEM/ST and DMAEM/MMA copolymer systems. Application of Johnston's equation to the experimental values of T_g obtained for both copolymer systems shows very good agreement, as shown in Figs 16 and 17. In comparison to the Fox relationship, Johnston's

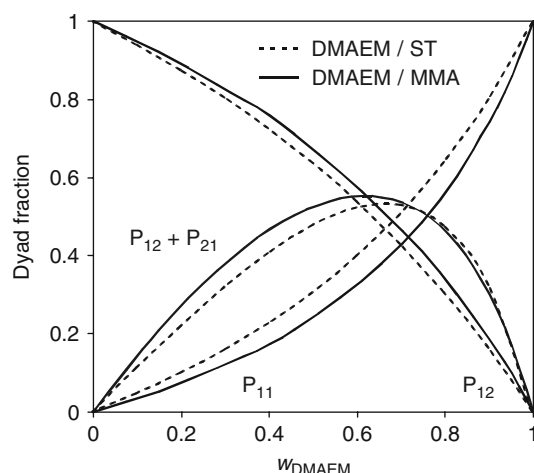


Figure 15. Dyad molar fraction versus DMAEM weight fraction in the copolymer chain for DMAEM/ST and DMAEM/MMA copolymers.

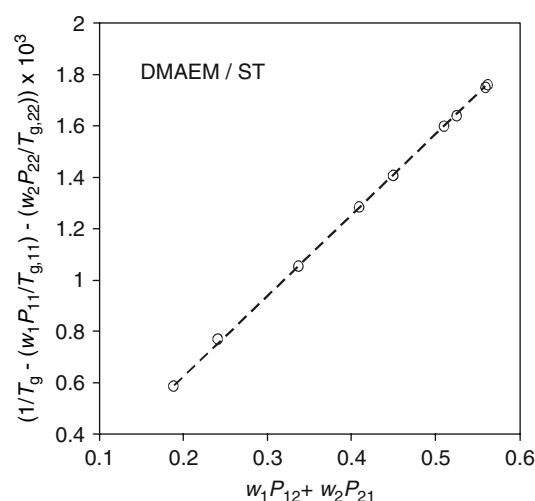


Figure 16. Application of the linearized expression of Johnston's equation to the DMAEM/ST copolymer system.

equation describes T_g of both investigated copolymer systems very accurately because it recognizes the sequence distribution and copolymer microstructure, as a consequence of the monomer reactivity ratios.

CONCLUSIONS

Copolymerization of DMAEM and ST or MMA proceeds readily in toluene solution in the presence of a free radical initiator. The copolymerization reactivity ratios for the DMAEM/ST system show a tendency towards an alternating copolymerization reaction, whereas for the DMAEM/MMA system an ideal copolymerization reaction takes place. The initial reaction rate, R_p , for the homopolymerization reactions decreases in the order DMAEM > MMA $\gg$ ST. In the DMAEM/ST system, R_p sharply decreases as the content of ST in the monomer mixture increases up to 30 mol%.

The values of T_g range between 16.6 and 68.4 °C, and 16.6 and 71.4 °C for the DMAEM/ST and DMAEM/MMA copolymer systems, respectively. Johnston's equation describes very well T_g of both

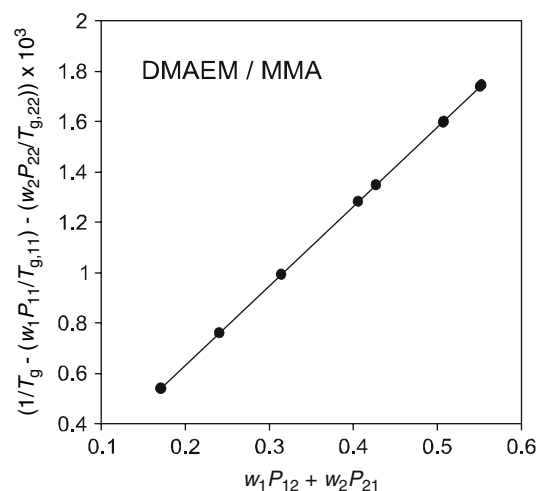


Figure 17. Application of the linearized expression of Johnston's equation to the DMAEM/MMA copolymer system.

copolymer systems investigated depending on the structure and composition.

ACKNOWLEDGEMENT

Financial support from the Ministry of Science, Education and Sport of the Republic of Croatia (125-1251963-1980) is gratefully acknowledged.

REFERENCES

- 1 Mortier RM and Orszulik ST (eds), *Chemistry and Technology of Lubricants*, 2nd edition. Chapman & Hall, London, p. 144 (1997).
- 2 Odian AG, *Principles of Polymerization*, 4th edition. Wiley, New York, pp. 198–332 (2004).
- 3 Ziaee F and Nekoomanesh M, *Polymer* **39**:203 (1998).
- 4 Khelfallah NS, Peretolchin M, Klapper M and Müllen K, *Polym Bull* **53**:295 (2005).
- 5 Askarov MA, Mukhitdinova NA and Nazarov A, *Polymerization of Aminoalkyl Acrylates*. Fan, Tashkent (1977). [in Russian].
- 6 Bune EV, Sheinker AP and Teleshov EN, *Vysokomol Soedin A* **31**:1347 (1989).
- 7 Shatalov GV, Verezhnikov VN, Plaksitskaya TV, Kuznetsov VA, Poyarkova TN and Yan'shina AV, *Polym Sci A* **48**:563 (2006).
- 8 Exxon Chemical Patents Inc., Viscosity index improver–dispersant additive useful in oil compositions. US Patent 4780228 (1988).
- 9 Gu L, Zhu S and Hrymak AN, *Colloid Polym Sci* **280**:1435 (2002).
- 10 Sideridou ID and Karabela MM, *J Appl Polym Sci* **109**:2503 (2008).
- 11 Orbay M, Laible R and Dulog L, *Macromol Chem* **183**:47 (1982).
- 12 Camail M, Essaoudi H, Margaillan A and Vernet JL, *Eur Polym J* **31**:1119 (1995).
- 13 Yuan S, Decheng W and Junlian H, *J Polym Sci A: Polym Chem* **39**:604 (2001).
- 14 Martín-Gomis L, Cuervo-Rodríguez R, Fernández-Monreal MC and Madruga EL, *J Polym Sci A: Polym Chem* **41**:2659 (2003).
- 15 Larissa NM and Warren TF, *J Polym Sci A: Polym Chem* **43**:4666 (2005).
- 16 Sideridou-Karayannidou I and Seretoudi G, *Polymer* **41**:4223 (1997).
- 17 Mayo FR and Lewis FM, *J Am Chem Soc* **66**:1594 (1944).
- 18 Alfrey T and Goldfinger GJ, *J Chem Phys* **12**:205 (1944).
- 19 Coskun M and Ilter Z, *J Polym Sci A* **40**:1184 (2002).
- 20 Vijayanand PS, Penlidis A and Nanjundan S, *J Macromol Sci A* **40**:125 (2003).
- 21 Balaji R, Sivakumar N, Vijayanand PS and Nanjundan S, *J Macromol Sci A* **38**:159 (2001).
- 22 Finemann M and Ross S, *J Polym Sci A* **2**:1687 (1964).
- 23 Mahdavian AR, Abdollahi M, Mokhtabad L and Ziaee F, *J Macromol Sci A: Pure Appl Chem* **43**:1583 (2006).
- 24 Kelen T and Tüdös F, *J Macromol Sci A* **9**:1 (1975).

- 25 Kelen T and Tüdös F, *J Macromol Sci A* **16**:1238 (1981).
- 26 Tidwell PW and Mortimer GA, *J Polym Sci A* **3**:369 (1965).
- 27 Box GEP, *Bulletin of the Institute of Internationale Statistique* **14**:215 (1958).
- 28 Dietrich B and Disselhoff G, *Polymer* **18**:963 (1977).
- 29 Pang XA, Sun HM and Shen Q, *Polymer* **45**:4029 (2004).
- 30 Jukić A, Rogošić M, Vidović E and Janović Z, *Polym Int* **56**:112 (2007).
- 31 Vidović E, Sarić K and Janović Z, *Croat Chem Acta* **75**:769 (2002).
- 32 McKenna TF, Villanueva A and Santos AM, *J Polym Sci A: Polym Chem* **37**:571 (1999).
- 33 Fox TG and Flory PJ, *J Appl Phys* **21**:581 (1950).
- 34 Johnston NW, *J Macromol Sci Rev Macromol Chem C* **14**:215 (1976).
- 35 Harwood HJ and Ritchey WM, *J Polym Sci B* **2**:601 (1964).
- 36 Brandrup J, Immergut EH and Grulke EA (eds), *Polymer Handbook*, 4th edition. John Wiley, New York (1999).
- 37 Sperling LH, *Introduction to Physical Polymer Science*, 4th edition. John Wiley, New York (2006).
- 38 Hernández-Sánchez F, Meseguer Dueñas JM and Gómez Ribelles JL, *J Thermal Anal Calorim* **72**:631 (2003).