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Radical copolymerization of styrene and alkyl methacrylates: monomer reactivity ratios and thermal properties

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Abstract

Copolymers containing styrene and alkyl methacrylate (*n*-butyl-, *n*-hexyl-, or stearyl methacrylate) at different compositions have been prepared by radical copolymerization. The monomer reactivity ratios were estimated using the Finemann–Ross, the inverted FR and the Kelen–Tüdos graphical methods. Structural parameters of the copolymers were obtained calculating the dyad monomer sequence fractions. The effect of the size of the alkyl methacrylate on the copolymer structure is discussed. The glass transition temperature, T_g of the copolymers with butyl and hexyl methacrylate was examined in the frame of several theoretical equations allowing the prediction of these T_g values. The best fit was obtained using methods that take into account the monomer sequence distribution of the copolymers. The copolymers of styrene with stearyl methacrylate exhibited the characteristic melting endotherm, due to the crystallinity of the methacrylate sequences and the polystyrene glass transition temperature.

1. Introduction

Copolymerization is the most successful and powerful method for effecting systematic changes in polymer properties [1]. The incorporation of two different monomers, having diverse physical and/or chemical properties, in the same polymer molecule in varying proportions leads to the formation of new materials with great scientific and commercial importance [2]. Copolymerization modulates both the intramolecular and intermolecular forces excersized between like and unlike polymer segments and consequently properties such as glass transition temperature, melting point, solubility, crystallinity, permeability, dyeability, adhesion, elasticity and chemical reactivity may be varied within wide limits. The utility of copolymerization is exemplified on the one hand by the fundamental investigations of structure-property relations [3] and on the other hand by the wide range of commercial applications [4].

The importance of copolymerization has been very soon realized in polymer science leading to an enormous amount of work both experimental and theoretical [1]. The elucidation of copolymer structure (copolymer composition, monomer sequence distribution) and kinetics (propagation rate coefficients) are the major concerns for the prediction of copolymer properties and the correlation between structure and properties. Among the various copolymerization reactions radical copolymerization is the most important since it does not demand rigorous experimental conditions and can be applied to a large variety of monomers, leading to the formation of new materials.

This study is focused on the radical copolymerization of styrene, St and alkyl methacrylates (*n*-butyl methacrylate, BMA, *n*-hexyl methacrylate, HMA, and stearyl methacrylate, SMA). A great deal of data has been accumulated in the literature for the system poly(S-*stat*-MMA) [5], but no systematic work has appeared with similar systems utilizing methacrylate monomers with

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large alkyl ester groups. In this work the monomer reactivity ratios were determined by several linear methods and predictions concerning the monomer sequence distribution are provided. The glass transition temperature of the copolymers is determined and compared with several theoretical equations. Consequently the influence of the size of the alkyl group of the methacrylate monomer on the copolymer structure and properties is discussed.

2. Experimental section

2.1. Materials

The monomers St (Merck), BMA and HMA (Polysciences) and the solvent benzene were purified over CaH_2 overnight and were vacuum distilled. SMA (Polysciences) was recrystallized three times from hexane at −20 °C. 2,2′-Azobisisobutyronitrile, AIBN (Aldrich) was recrystallized twice from methanol and dried in vacuum.

2.2. Copolymerization reaction

The copolymerization was performed in glass reactors using benzene solutions with a total monomer concentration 10 wt.%. AIBN in a concentration of 0.1 wt.% was the initiator. The solutions were degassed under high vacuum using three freeze–thaw cycles and the reactors were flame-sealed. The polymerizations were conducted at 50 °C for a few hours. The polymers were precipitated in methanol, redissolved in toluene and reprecipitated in methanol to remove the excess monomers and were dried in a vacuum oven. The following notation is used for the samples: SBMA, SHMA and SSMA for the poly(S-*stat*-BMA), poly(S-*stat*-HMA) and poly(S-*stat*-SMA) copolymers respectively.

2.3. Characterization techniques

The copolymers were characterized by size exclusion chromatography, SEC at 40 °C using a modular instrument consisting of a Waters Model 510 pump, a Waters Model U6K sample injector, a Waters Model 401 differential refractometer, a Waters Model 486 UV spectrophotometer and a set of four μ-Styragel columns with a continuous porosity range from 10^3 to 10^6 Å housed in an oven. The flow rate was 1 ml/min and tetrahydrofuran, THF the carrier solvent. The copolymer compositions were determined by UV-SEC analysis at 260 nm, where only the styrene units absorb.

The glass transition and melting temperatures were measured using a TA Model 29100. The samples were heated or cooled at a rate of 10 °C/min. The second heating results were obtained in all cases.

3. Results and discussion

The free radical copolymerization of St with BMA, HMA or SMA was conducted in benzene solutions at 50 °C for a few hours. In all cases the conversion was lower than 10% to satisfy the differential copolymerization equation. The molecular characteristics of the samples are given in Table 1. The molecular weights were measured by SEC using a calibration curve constructed by polystyrene standards. UV-SEC analysis at 260 nm was employed to measure the composition of the copolymers.

The monomer reactivity ratios were determined using the Finemann–Ross (FR) [6], the inverted Finemann–Ross (IFR) [6] and the Kelen–Tüdos (KT) [7] graphical methods. According to the FR method the monomer reactivity ratios can be obtained by the equation:

$$G = Hr_S - r_M \quad (1)$$

where the reactivity ratios, r_S and r_M correspond to the styrene and the alkyl methacrylate monomers respectively. The parameters G and H are defined as follows:

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

with

$$X = M_S/M_M \text{ and } Y = \mathrm{d}M_S/\mathrm{d}M_M \quad (3)$$

Table 1
Molecular characteristics of the copolymers

Sample	$^{a}M_n \times 10^3$	$^{a}I = M_w/M_n$	Conversion (%)
SBMA 1	22.9	1.44	0.6
SBMA 2	33.2	1.25	0.2
SBMA 3	28.2	1.28	0.8
SBMA 4	21.8	1.45	2.3
SBMA 5	25.2	1.44	2.6
SHMA 1	37.9	1.37	3.2
SHMA 2	25.0	1.41	2.4
SHMA 3	28.7	1.40	2.1
SHMA 4	27.8	1.37	1.9
SHMA 5	24.6	1.41	1.7
SSMA 1	32.6	1.31	5.3
SSMA 2	30.3	1.24	1.6
SSMA 3	24.7	1.60	2.6
SSMA 4	23.2	1.50	2.3
SSMA 5	39.1	1.23	1.8

[a] By size exclusion chromatography in THF at 40 °C. The molecular weights are polystyrene equivalent molecular weights.

M_S and M_M are the monomer molar compositions in feed and dM_S and dM_M the copolymer molar compositions.

The inverted FR method is based on the equation:

$$G/H = r_S - (1/H)r_M \tag{4}$$

The plots of the G vs H values and the G/H vs $1/H$ values yield the reactivity ratios r_S and r_M from the intercept and the slope of the graphs.

Alternatively the reactivity ratios can be obtained using the KT method which is based on the equation:

$$\eta = (r_S + r_M/\alpha)\xi - r_M/\alpha \tag{5}$$

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

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

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 $\xi = 0$ and $\eta = 1$ are used to calculate the reactivity ratios according to the equations:

$$\xi = 0 \Rightarrow \eta = -r_M/\alpha \quad \text{and} \quad \xi = 1 \Rightarrow \eta = r_S \tag{7}$$

The copolymerization data for all systems are provided in Table 2. The graphical plots concerning the methods previously reported are given in Figs. 1–3, whereas the reactivity ratios are summarized in Table 3.

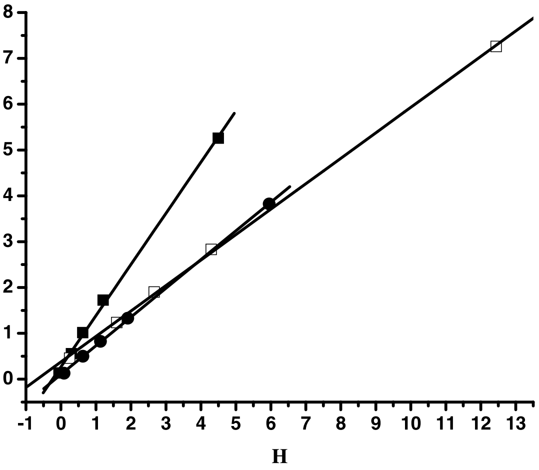

Fig. 1. FR plots for the SBMA (□), SHMA (●) and SSMA (■) copolymers.

Good agreement was obtained with data previously reported in the literature for the system poly(S-*stat*-BMA) [8]. In all cases and for all graphical methods the plots were linear indicating that these copolymerizations follow the conventional copolymerization kinetics and that the reactivity of a polymer radical is determined only by the terminal monomer unit.

For all systems the r_S values are higher than the r_M values. The difference is increased by increasing the size of the ester group of the methacrylate. This result shows

Table 2
Copolymerization data for the copolymers SBMA, SHMA and SSMA

Sample	M_S	dM_S	X	Y	G	H	$1/H$	G/H	η	ξ
SBMA 1	0.2545	0.4636	0.3413	0.8642	−0.0536	0.1348	7.4189	−0.3979	−0.0549	0.1380
SBMA 2	0.4765	0.5987	0.9102	1.4916	0.3000	0.5554	1.8004	0.5401	0.2147	0.3975
SBMA 3	0.5772	0.6477	1.3654	1.8382	0.6226	1.0142	0.9860	0.6139	0.3354	0.5464
SBMA 4	0.6719	0.7088	2.0481	2.4337	1.2065	1.7236	0.5802	0.7000	0.4703	0.6718
SBMA 5	0.8452	0.8502	5.4615	5.6736	4.4989	5.2574	0.1902	0.8557	0.7376	0.8620
α	0.8418									
SHMA 1	0.2901	0.5635	0.4085	1.2911	0.0921	0.1292	7.7373	0.7127	0.2468	0.3463
SHMA 2	0.5215	0.7038	1.0897	2.3758	0.6310	0.4998	2.0007	1.2625	0.8484	0.6720
SHMA 3	0.6204	0.7645	1.6346	3.2463	1.1311	0.8231	1.2150	1.3742	1.0600	0.7714
SHMA 4	0.7103	0.8189	2.4519	4.5221	1.9097	1.3294	0.7522	1.4365	1.2137	0.8449
SHMA 5	0.8674	0.9179	6.5385	11.1862	5.9540	3.8218	0.2616	1.5579	1.4644	0.9400
α	0.2440									
SSMA 1	0.4483	0.5908	0.8125	1.4438	0.2498	0.4572	2.1871	0.5462	0.1096	0.2006
SSMA 2	0.6842	0.7917	2.1667	3.8014	1.5967	1.2350	0.8097	1.2929	0.5224	0.4040
SSMA 3	0.7647	0.8475	3.2500	5.5576	2.6652	1.9006	0.5262	1.4023	0.7160	0.5106
SSMA 4	0.8298	0.8936	4.8750	8.3946	4.2943	2.8311	0.3532	1.5168	0.9229	0.6085
SSMA 5	0.9286	0.9588	13.0000	23.2836	12.4417	7.2583	0.1378	1.7141	1.3702	0.7994
α	1.2174									

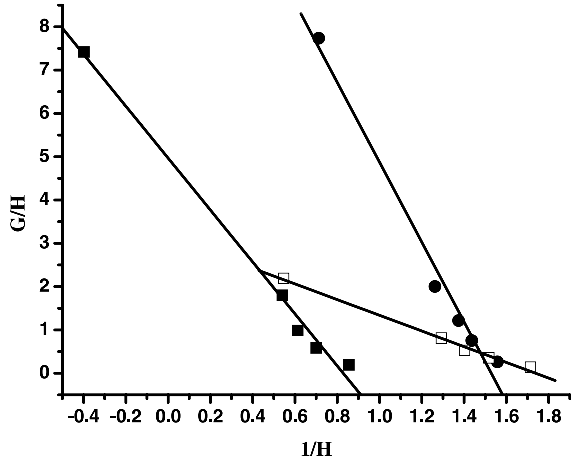

Fig. 2. Inverted FR plots for the SBMA (■), SHMA (●) and SSMA (□) copolymers.

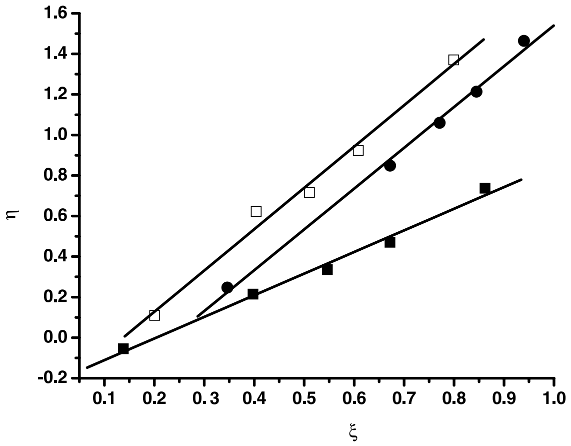

Fig. 3. KT plots for the SBMA (■), SHMA (●) and SSMA (□) copolymers.

Table 3
Reactivity ratios for the copolymers SBMA, SHMA and SSMA

	r_S	r_M	$r_S \cdot r_M$
SBMA			
FR	0.895	0.239	0.214
IFR	0.826	0.165	0.136
KT	0.850	0.183	0.156
SHMA			
FR	1.596	0.164	0.262
IFR	1.524	0.107	0.163
KT	1.541	0.115	0.177
SSMA			
FR	1.799	0.674	1.212
IFR	1.734	0.548	0.950
KT	1.758	0.510	0.896

that the incorporation of styrene units in the copolymer structure is kinetically favored by increasing the size of the alkyl group of the methacrylate monomer. The single parameter that can best describe the copolymer structure is the product of the reactivity ratios $r_S \cdot r_M$. Fig. 4 shows the dependence of this product on the number of carbon atoms of the alkyl ester groups for the systems poly(S-*stat*-alkyl methacrylate). The KT results obtained from this study plus literature data [8] for the systems poly(S-*stat*-MMA), poly(S-*stat*-ethyl methacrylate) and poly(S-*stat*-octyl methacrylate) were used to construct this plot. Initially low $r_S \cdot r_M$ values are obtained with both reactivity ratios being lower than unity. This is an indication that these systems have a tendency towards alternation. Increasing the size of the alkyl ester group of the methacrylate monomer leads to higher $r_S \cdot r_M$ values showing, in connection with the increased r_S values that longer styrene sequences are formed.

The statistical distribution of the dyad monomer sequences M_S–M_S, M_M–M_M and M_S–M_M were calculated using the method proposed by Igarashi [9]:

$$X = \phi_1 - \frac{2\phi_S(1-\phi_S)}{1+\left[(2\phi_S-1)^2+4r_Sr_M\phi_S(1-\phi_S)\right]^{1/2}} \tag{8}$$

$$Y = (1-\phi_S) - \frac{2\phi_S(1-\phi_S)}{1+\left[(2\phi_S-1)^2+4r_Sr_M\phi_S(1-\phi_S)\right]^{1/2}} \tag{9}$$

$$Z = \frac{4\phi_S(1-\phi_S)}{1+\left[(2\phi_S-1)^2+4r_Sr_M\phi_S(1-\phi_S)\right]^{1/2}} \tag{10}$$

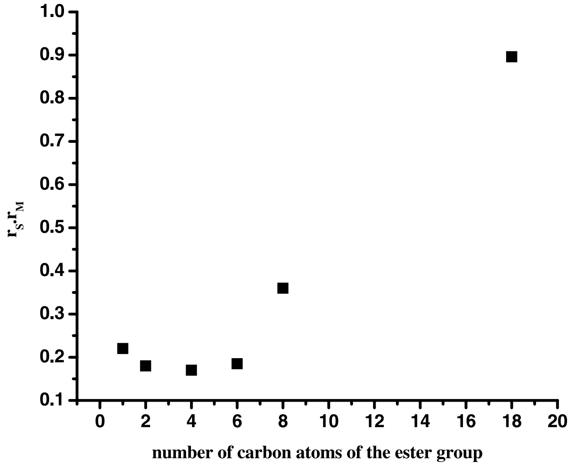

Fig. 4. Dependence of the reactivity ratios product $r_S \cdot r_M$ on the number of carbon atoms of the alkyl ester groups for the systems poly(S-*stat*-alkyl methacrylate).

Table 4
Structural data for the copolymers SBMA, SHMA and SSMA

Sample	M_S–M_S	M_M–M_M	M_S–M_M	μ_S	μ_M
SBMA 1	0.1085	0.1813	0.7102	1.29	1.54
SBMA 2	0.2637	0.0664	0.6699	1.77	1.20
SBMA 3	0.3391	0.0438	0.6171	2.16	1.13
SBMA 4	0.4425	0.0250	0.5325	2.74	1.09
SBMA 5	0.7050	0.0047	0.2904	5.64	1.03
SHMA 1	0.2210	0.0940	0.6850	1.63	1.28
SHMA 2	0.4365	0.0290	0.5345	2.68	1.10
SHMA 3	0.5447	0.0157	0.4396	3.52	1.07
SHMA 4	0.6460	0.0082	0.3458	4.78	1.05
SHMA 5	0.8372	0.0014	0.1614	11.08	1.02
SSMA 1	0.3426	0.1610	0.4963	2.43	1.63
SSMA 2	0.6239	0.0404	0.3356	4.81	1.24
SSMA 3	0.7118	0.0168	0.2620	6.71	1.16
SSMA 4	0.7975	0.0104	0.1921	9.57	1.10
SSMA 5	0.9192	0.0015	0.0793	23.85	1.04

where X, Y and Z are the mole fractions of the M_S–M_S, M_M–M_M and M_S–M_M dyads in the copolymer respectively and φ_s the styrene mole fraction in the copolymer. Mean sequence lengths μ_S and μ_M were also calculated using the following equations [10]:

$$\mu_S = 1 + r_S \frac{[M_S]}{[M_M]} \tag{11}$$

$$\mu_M = 1 + r_M \frac{[M_M]}{[M_S]} \tag{12}$$

The data are summarized in Table 4, whereas Figs. 5–7 display the variation of the dyad fractions with the styrene mole fraction in the copolymers.

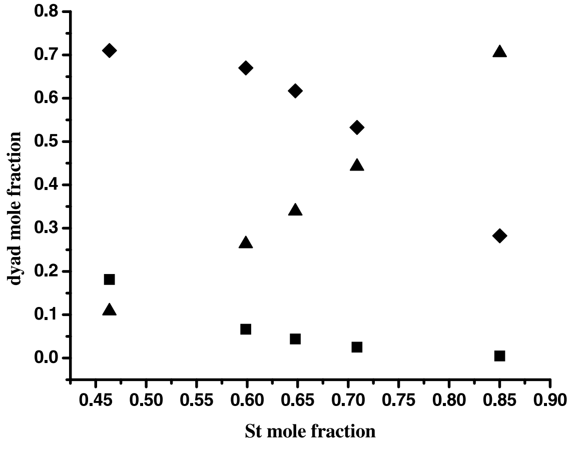

Fig. 5. Dyad monomer sequence fractions vs the styrene mole fraction for the SBMA copolymers: M_S–M_S (▲), M_M–M_M (■) and M_S–M_M (◆) dyads.

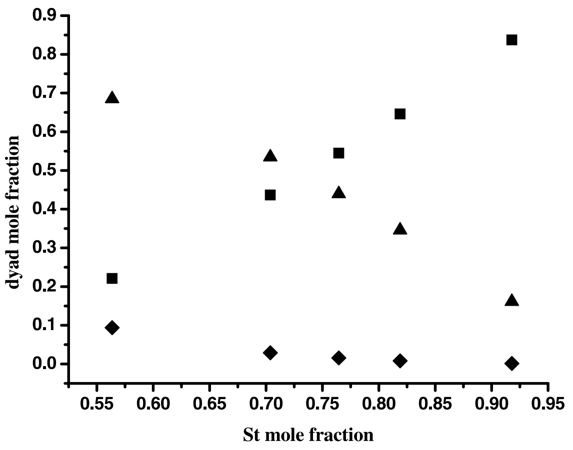

Fig. 6. Dyad monomer sequence fractions vs the styrene mole fraction for the SHMA copolymers: M_S–M_S (■), M_M–M_M (◆) and M_S–M_M (▲) dyads.

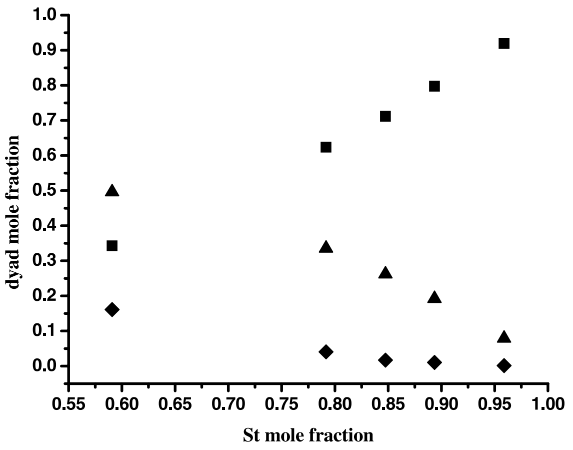

Fig. 7. Dyad monomer sequence fractions vs the styrene mole fraction for the SSMA copolymers: M_S–M_S (■), M_M–M_M (◆) and M_S–M_M (▲) dyads.

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 [11]. The simplest equation describing the effect of composition on T_g is the Gibbs–Di Marzio equation [12]:

$$T_g = \varphi_S T_{gS} + \varphi_M T_{gM} \tag{13}$$

where φ_S, φ_M are the mole fractions of styrene and methacrylate monomers respectively in the copolymer and T_{gS}, T_{gM} the glass transition temperatures of the two homopolymers respectively.

Table 5
Glass transition temperatures for the copolymers SBMA and SHMA

Sample	PS (wt.%)	[a]$(T_g)_{exp}$ (K)	[b]$(T_g)_{GM}$ (K)	[c]$(T_g)_F$ (K)
SBMA 1	38.78	315.6	330.1	319.7
SBMA 2	52.21	324.4	340.9	330.0
SBMA 3	57.38	325.6	344.8	334.1
SBMA 4	64.06	326.4	349.7	339.7
SBMA 5	80.60	343.3	361.0	354.2
SHMA 1	44.13	281.6	327.2	306.0
SHMA 2	59.24	301.6	341.9	321.6
SHMA 3	66.51	310.5	348.3	329.7
SHMA 4	73.45	320.9	354.0	337.8
SHMA 5	87.25	340.3	364.4	355.2

[a] Experimental result by DSC measurements.

[b] Theoretical prediction using the Gibbs–Di Marzio equation (Eq. (13)).

[c] Theoretical prediction using the Fox equation (Eq. (14)).

A similar relationship was introduced by Fox [13]:

$$\frac{1}{T_g} = \frac{w_S}{T_{gS}} + \frac{w_M}{T_{gM}} \tag{14}$$

where w_S and w_M are the weight fractions of styrene and methacrylate monomers in the copolymer.

The experimental results concerning the T_g of the SBMA and SHMA copolymers along with the predictions of the Gibbs–Di Marzio and Fox equations are given in Table 5. It is obvious that large positive deviations are obtained by these two methods due to the fact that they are based only on thermodynamic and free volume theories of the glass transition and they do not take into consideration the monomer sequence distribution and the effect of their compatibility on steric and energetic interactions. Therefore several models have been proposed that take into account these considerations.

Based on the free volume concept Johnston proposed the following equation [14]:

$$\frac{1}{T_g} = \frac{w_S P_{SS}}{T_{gSS}} + \frac{w_M P_{MM}}{T_{gMM}} + \frac{w_S P_{SM} + w_M P_{MS}}{T_{gSM}} \tag{15}$$

It is assumed that SS, MM and MS or SM dyads have their own glass transition, T_{gSS}, T_{gMM} and T_{gSM} respectively. T_{gSS} and T_{gMM} can be considered as the glass transition temperatures for the respective homopolymers, where T_{gSM} is the glass transition temperature of the alternating copolymer PS-*alt*-PM. W_i is the weight fraction of the *i* component and P_{SS}, P_{MM}, P_{SM} and P_{MS} are the probabilities of having various linkages. These probabilities can be calculated using the monomer reactivity ratios [10]:

$$P_{SS} = \frac{r_S}{r_S + \frac{[M_M]}{[M_S]}} \tag{16}$$

$$P_{SM} = \frac{[M_M]}{r_S[M_S] + [M_M]} \tag{17}$$

$$P_{MS} = \frac{[M_S]}{r_M[M_M] + [M_S]} \tag{18}$$

$$P_{MM} = \frac{r_M[M_M]}{r_M[M_M] + [M_S]} \tag{19}$$

Barton suggested the following equation [15]:

$$T_g = XT_{gSS} + YT_{gMM} + ZT_{gSM} \tag{20}$$

where X, Y, Z are the monomer dyad fractions (Eqs. (8)–(10)).

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 T_{gSM} values. The plots, given in Figs. 8 and 9 are straight lines passing through the origin. For the SBMA copolymers the T_{gSM} values calculated by the Johnston and Barton equations are 358.4 and 354.2 K respectively, whereas the corresponding values for the SHMA copolymers are 275.5 and 279.6 K. It is obvious that similar results are obtained by the two methods for both type of copolymers. This is an indication that these theoretical methods can better predict the T_g values of statistical copolymers or in other words that the monomer sequence distribution is an important parameter defining the T_g of a statistical copolymer.

A different situation exists with the SSMA copolymers, since it is well known that polymethacrylates with

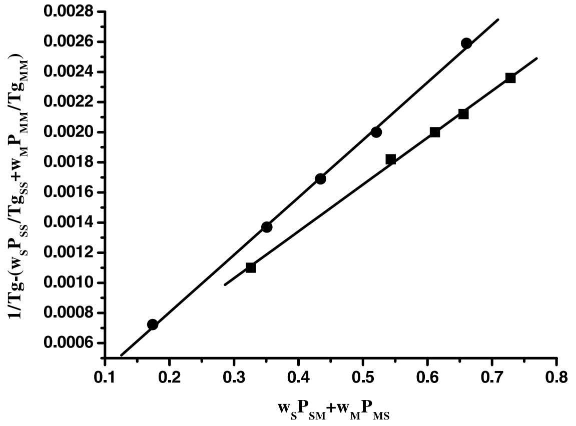

Fig. 8. Linearized form of the Jhonston equation for the SBMA (■) and SHMA (●) copolymers.

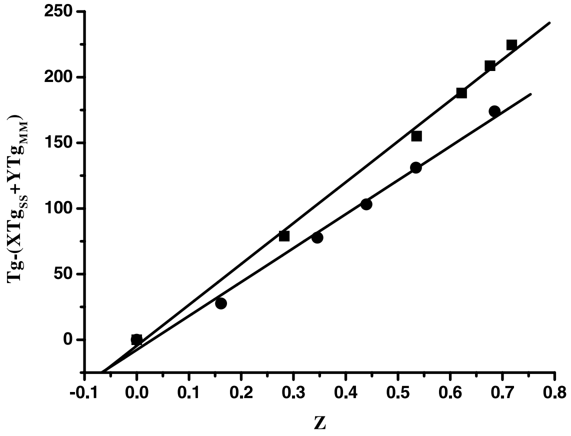

Fig. 9. Linearized form of the Barton equation for the SBMA (■) and SHMA (●) copolymers.

long alkyl side groups form crystal domains [16]. Recent results concerning the conformational and crystallization behavior of PSMA homopolymers have been reported [17]. The experimental results from the SSMA copolymers are given in Table 6. In all cases the characteristic melting endotherm corresponding to the melting of the SMA crystallites and the glass transition of the styrene segments are obvious.

The PS T_g values are very close to what is expected for the corresponding homopolymer. This is very well correlated with the result obtained from the structural analysis and the reactivity ratios for this system. It was concluded, by the high μ_S and r_S values that long styrene monomeric sequences were formed during the copolymerization. Consequently the glass transition, which is due to segmental motions, is expected to occur at high temperatures, close to those observed for PS homopolymers. Only for sample SSMA 1 with the smallest PS content a lower T_g value was observed.

The melting temperature and the enthalpy of melting for the PSMA homopolymer are 34 °C and 75.9 J/g [17]. Flory has predicted a decrease of the melting temperature for copolymers comprised of amorphous and crystallizable segments [18]. The melting point depression is influenced by the length of the crystallizable segment and the thermodynamic interactions between the two components. This behavior was already reported in the case of polyS-*block*-polySMA diblock copolymers [19] and is much more intense in the case of statistical copolymers, according to the results included in Table 6. This behavior is reasonable, due to the small SMA sequence length for these samples. The change of the normalized enthalpy of melting for the polyS-*block*-polySMA diblock copolymers [19] and the statistical copolymers with the PS content is plotted in Fig. 10. It is obvious that much lower ΔH values are observed for the statistical copolymers in agreement with the previous discussion.

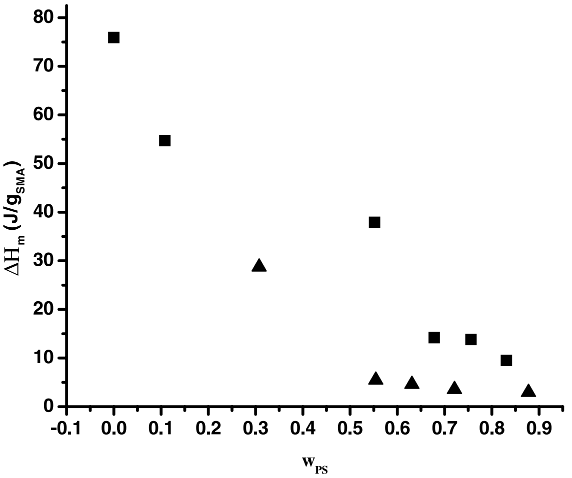

Fig. 10. Normalized enthalpy of melting vs the weight fraction of PS for the polyS-*block*-polySMA (■) and the poly(S-*stat*-SMA) (▲) copolymers.

Table 6
DSC results of the SSMA copolymers

Sample	w_{PS} (%)	$(T_g)_{PS}$ (°C)	$(T_m)_{PSMA}$ (°C)	$(\Delta H)_m$ (J/g_{SMA})
SSMA 1	30.76	85.8	20.1	28.73
SSMA 2	55.44	90.2	13.8	5.46
SSMA 3	63.10	99.5	10.1	4.61
SSMA 4	72.09	92.5	10.5	3.55
SSMA 5	87.75	92.8	9.7	2.96

4. Conclusions

Copolymers of styrene and alkyl methacrylates (*n*-butyl-, *n*-hexyl- or stearyl methacrylate) have been prepared by free radical polymerization in benzene at 50 °C. The reactivity ratios of the copolymers were estimated using linear graphical methods. The r_S values were higher than the corresponding r_M values in all cases, meaning that a kinetic preference exists for the incorporation of styrene in the copolymer structure. When the size of the methacrylate ester group is small there is a tendency towards alternation. This result was confirmed by the calculation of the monomer dyad sequences fractions. The glass transition temperatures of the SBMA and SHMA copolymers were obtained and compared with the predictions provided by several theoretical models. Among these models the Johnston and the Barton equations offer the best fit to the experimental data, because they take into consideration the effect of the monomer sequence distribution to the glass transition temperature. The SSMA copolymers show the characteristic melting endotherms, due to the crystallization of the methacrylate alkyl ester chains and the glass transition of the polystyrene segments.

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