Polymerization of poly(dimethylsiloxane) macromers: 1. Copolymerization with styrene

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The synthesis and characterization of methacrylate-ended macromers ($\bar{M}_n$ 500 to 10000) and their copolymerization with styrene (M_2) is described. The experimental errors in the values of the reactivity ratios r_1 render them meaningless. Values of r_2 can be determined with more precision and increase from 1.06 to 1.55 as the molecular weight of the macromer increases. This behaviour is due to steric effects, not diffusion-controlled propagation. It is shown that the assumptions that $1 > r_1[M_1]/[M_2]$ and $r_2 > [M_1]/[M_2]$ are only valid for macromers of $\bar{M}_n > ca.$ 10000.

(Keywords: poly(dimethyl siloxane) macromers; synthesis; characterization; copolymerization; reactivity ratios)

INTRODUCTION

The preparation of graft copolymers by copolymerizing polymers carrying polymerizable terminal double bonds with a second, small monomer was first demonstrated by Bamford and coworkers in 1958[1,2]. Renewed interest in this technique came in 1974 when Milkovich[3] patented his functional macromolecular monomers under the trade name MACROMERS. Since then macromers have received much attention from synthetic polymer chemists and many new types have been prepared, mainly, though not exclusively, with polymerizable olefin or vinyl groups. The copolymerization of such macromers with small monomers provides a convenient and versatile route to well-defined graft copolymers.

Although many copolymers of macromers have been prepared, comparatively little has been published on the subject of macromer reactivity and how it is affected by the length of the macromer chain. In the particular case of radical polymerization of vinylic macromers, measurement of copolymerization reactivity ratios is the simplest method of studying reactivity and this approach has been adopted in a few investigations[4-7]. We report here the synthesis of poly(dimethylsiloxane) macromers—3-methacryloyloxypropylpoly(dimethylsiloxane) (PDMS–MA)—of varying chain length and their radical copolymerization with styrene. The reactivity ratios reveal how the reactivity of the macromer towards the styryl radical is influenced by the length of the PDMS chain.

The PDMS–MA macromers were prepared by the route shown in *Scheme 1*.

EXPERIMENTAL

Materials

Allyl methacrylate and styrene were dried over CaH_2 and distilled under vacuum. Dimethylchlorosilane was distilled under a nitrogen atmosphere.
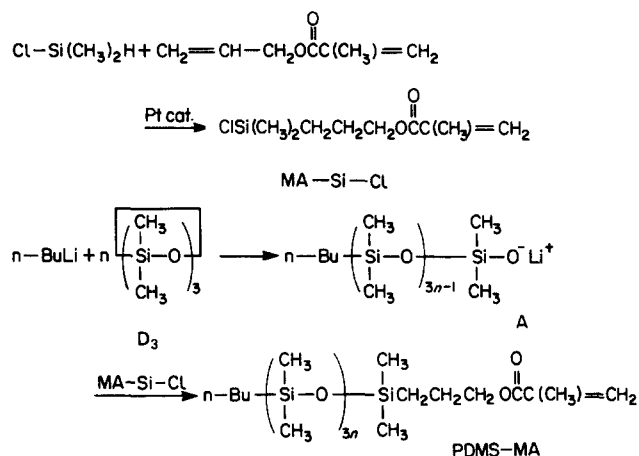
Scheme 1 Preparation of PDMS–MA macromers

Hexamethylcyclotrisiloxane (D_3) (Ventron) was sublimed under vacuum, dissolved in THF and dried over CaH_2.

n-Butyl lithium initiator in n-hexane was prepared *in vacuo* from the reaction of n-butyl chloride and metallic lithium. The precipitated lithium chloride was filtered off and the reagent solution was subdivided into sealed ampoules.

Benzoyl peroxide was purified by dissolving in chloroform and precipitating in an equal volume of methanol.

The platinum catalyst, dichloro-(bis-diethylsulphide) platinum II (BESP) was kindly donated by ICI, Organics Division and was used as supplied. All solvents were dried and distilled before use.

Preparation of 3-methacryloyloxypropyl(dimethyl chlorosilane) MA-Si-Cl)

The addition of hydridosilanes to various allyl acrylates is the subject of several patents[8-11] and the procedure

quoted in these is the basis of our preparation of MA-Si-Cl (see *Scheme 1*). Dimethylchlorosilane (24 g, 0.25 mol) was added over 30 min to a mixture of allyl methacrylate (25.2 g, 0.20 mol), 2,6-ditert-butyl-*p*-cresol (0.71 g) and BESP (0.0198 g) in toluene (5 ml) prewarmed to 40°C and under a nitrogen atmosphere. The reaction mixture was heated to 60°C for 45 min then cooled and the product, MA-Si-Cl, distilled under vacuum (B.P. 64°C–68°C at 0.05 mm Hg, yield 22 g, 50%). Portions of the terminating agent were separated into break-seal ampoules and sealed under vacuum.

Preparation of 3-methacryloyloxypropylpoly(dimethylsiloxane) (PDMS–MA) macromers

The PDMS–MA macromers were prepared from the anionic polymerization of D_3 using standard high vacuum techniques[12] with initiator, monomer and terminating agent contained in separate ampoules fitted with glass break-seals. The n-BuLi in n-hexane was admitted to a reaction flask containing 40–50 ml of THF cooled to 0°C. A 50% solution of D_3 in THF was slowly added with stirring over a period of 5 min and the polymerization was continued at 0°C tor 12–20 h, until almost 100% conversion was reached. After cooling to −78°C, the polymerization was terminated by the addition of MA-Si-Cl (10% excess). The THF was removed under vacuum and the LiCl precipitate was removed by filtration. The PDMS–MA macromer was then purified by reprecipitation from THF into a methanol/water mixture.

The molecular weights of the macromers were obtained directly by gel permeation chromatography (g.p.c.) and by vapour pressure osmometry (v.p.o.). The g.p.c. was a Waters Associates 200 instrument equipped with μ-Styragel columns of pore sizes 10^5, 10^4, 10^3, 500 and 100 Å; the solvent was chloroform at ambient temperature and polystyrene standards were used for calibration. The v.p.o. was a Hitachi–Perkin Elmer model 115; readings were taken with four or five different concentrations of macromer in chloroform at 35°C and $\bar{M}_n$ was calculated from the extrapolated value in the usual way. Molecular weights (M_n) were also estimated by u.v. and ^{1}H n.m.r. (220 MHz) spectroscopy. In the former it was assumed that each macromer chain was terminated by a methacrylate group; these end groups were counted by spectrophotometery of n-hexane solutions taking the extinction coefficient at 215 nm as $7670 \, l \, mol^{-1} \, cm^{-1}$, the value derived from n-hexane solutions of n-butyl methacrylate. The functionality is given by the ratio $\bar{M}_n$ (v.p.o.)/$\bar{M}_n$ (u.v.). The value of $\bar{M}_n$ from ^{1}H n.m.r. spectros-
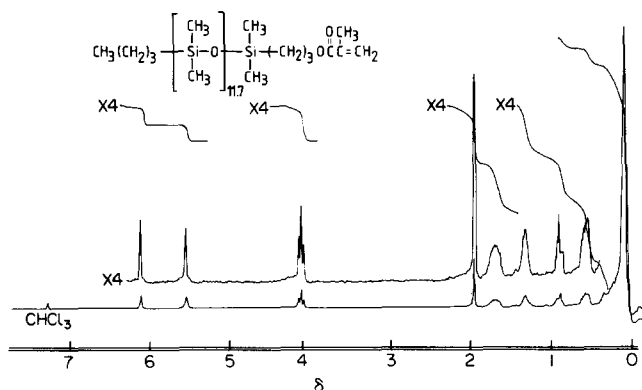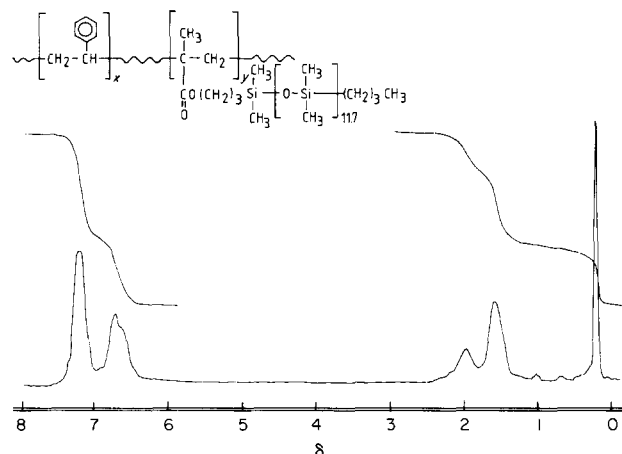

Figure 2 ^{1}H n.m.r. spectrum of a copolymer of styrene and macromer PDMS–MA2; 22 wt% macromer

copy was calculated from the ratio of the integral of the n-butyl protons (δ ppm, 0.30–1.30) to that of the dimethyl-siloxy protons (δ ppm, 0.08) (*Figure 1*). For macromers of $M_n > ca.$ 5000 this method is insensitive. The functionality of the macromers was also determined by ^{1}H n.m.r. by comparing the n-butyl proton integrals with a set of methacrylatge proton integrals: $CH_2 = C(CH_3)$– (δ ppm, 6.09, 5.53); $CH_2 = C(CH_3)$– (δ ppm, 1.92); $-CO_2CH_2$– (δ ppm, 4.10). The data from this characterization work on three macromers PDMS–MA1, –MA2 and –MA3 of different $\bar{M}_n$ values are summarized in *Table 1*.

The data in *Table 1* show satisfactory agreement among the values of $\bar{M}_n$ evaluated by the various techniques; these values are also reasonably close to the value of $\bar{M}_n$ calculated from the molar ratio of initiator to D_3 assuming 100% conversion and no destruction of n-BuLi. The functionality is also close to unity, indicating that *Scheme 1* operates effectively. Our results are in close agreement with those of Kawakami *et al.*[15] who prepared PDMS macromers by a very similar method. It is worth recording here that we have also prepared PDMS–MA macromers by an alternative route in which a PDMS oligomer terminated by an $-Si(Me)_2H$ function was synthesized by terminating the living silanolate ion (A in *Scheme 1*) with $ClSi(Me)_2H$. The macromer was then produced by the catalysed $\equiv$ Si–H addition of the functionalized oligomer to allyl methacrylate. The methacrylate functionality of the product macromers, however, was always less than unity and in our experience the route described in *Scheme 1* is more satisfactory.

Copolymerization of PDMS–MA macromers with styrene

PDMS–MA macromers were copolymerized with styrene in benzene solution (total monomer concentration 40% w/v) with 1.0 mol% benzoyl peroxide initiator at 60°C. Polymerizations were conducted under vacuum in glass dilatometers to not greater than 5% conversion. For each pair of monomers five copolymers of varying compositions were prepared, the mole fraction of styrene M_2 in the monomer feed being varied as widely as practicable to optimise accuracy in the calculation of reactivity ratios. For the macromer of lowest $\bar{M}_n$ PDMS–MA1, the mole fraction of M_2 varied from 0.85 to 0.98, but for the macromer of highest M_n, PDMS–MA3, M_2 had to be confined to the much narrower range 0.997 to 0.999. After precipitating the copolymers in methanol, unreacted macromer was removed by extracting with pet-

Figure 1 ^{1}H n.m.r. spectrum of macromer PDMS–MA2 $(\bar{M}_n \sim 1110)$
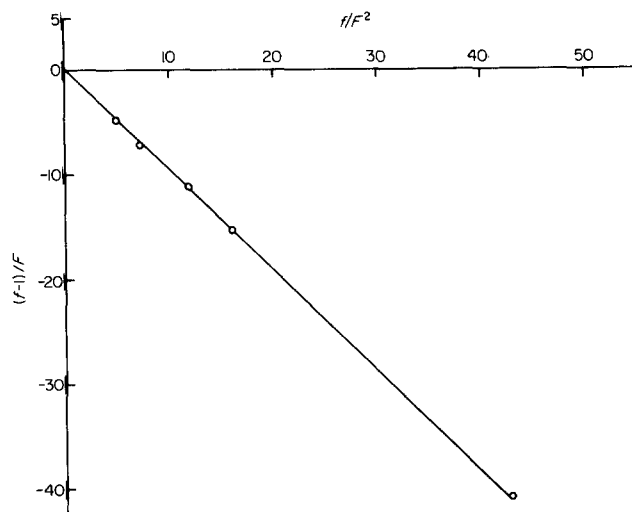
Figure 3 Fineman–Ross plot $((f\text{-}1)/F$ vs. $f/F^2)$ for copolymers of styrene and PDMS–MA1. F = mole ratio of monomers in feed; f = mole ratio of monomers in copolymer
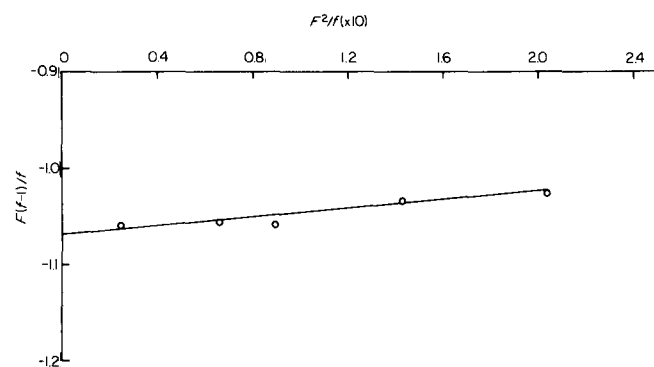
Figure 4 Fineman–Ross plot $(F(f-1)/f$ vs. $F^2/f)$ for copolymers of styrene and PDMS–MA1. F = mole ratio of monomers in feed; f = mole ratio of monomers in copolymer

roleum ether (B.P. 40°C–60°C). The composition of the copolymers was determined from the ^{1}H n.m.r. spectra by measuring the integrals of the aromatic styryl protons (δ ppm, 6.58, 7.05) and the dimethylsiloxy protons (see *Figure 2*). Each set of copolymerization data was subjected to analysis by the Fineman–Ross[13] and Kelen–Tudos[14] methods for determining reactivity ratios. *Figures 3–5* show the Fineman–Ross and Kelen–Tudos plots for the PDMS–MA1/styrene system. The copolymerization parameters summarized in *Table 2* were determined from each graph by a linear least squares method.

RESULTS AND DISCUSSION

The composition of a copolymer from a macromer M_1 and small monomer M_2 copolymerization is governed by the propagation steps, as in a conventional radical copolymerization, according to the following well-established set of equations:

$$\sim M_1{}^\bullet + M_1 \xrightarrow{k_{11}} \sim M_1{}^\bullet \tag{1}$$

$$\sim M_1{}^\bullet + M_2 \xrightarrow{k_{12}} \sim M_2{}^\bullet \tag{2}$$

$$\sim M_2{}^\bullet + M_1 \xrightarrow{k_{21}} \sim M_1{}^\bullet \tag{3}$$

$$\sim M_2{}^\bullet + M_2 \xrightarrow{k_{22}} \sim M_2{}^\bullet \tag{4}$$

Table 1 PDMS–MA macromer characterization data

Macromer	n-BuLi (moles × 10²)	D_3 (g)	$\bar{M}_n$ (calc'd)[a]	$\bar{M}_n$ (v.p.o.)	$\bar{M}_n$ (^{1}H n.m.r.)	$\bar{M}_n$ (u.v.)[b]	$\bar{M}_n$ (g.p.c.)[c]	$\bar{M}_w$ (g.p.c.)[c]	$\bar{M}_w/\bar{M}_n$ (g.p.c.)[c]	Functionality (v.p.o./u.v.)[d]	Functionality (n.m.r.)[e]
PSMS-MA1	3.15	10.01	560	500	590	460	—	—	—	1.08	1.03
PDMS-MA2	1.55	12.02	1020	1160	1110	1060	1360	1770	1.30	1.10	1.10
PDMS-MA3	0.120	10.01	8640	9750	—	10400	8540	10240	1.20	0.94	—

[a] Calculated from the equation: $\bar{M}_{n(\text{calc'd})} = \dfrac{D_3(g)}{\text{n-BuLi (moles)}} + 57$ (MW of $CH_3(CH_2)_3{}^-$) $+ 185$ (MW of $-Si(CH_3)_2(CH_2)_3OCOC(CH_3) = CH_2$)

[b] Determined by u.v. spectroscopy — ϵ for each macromer is assumed to be the same as that for n-butyl methacrylate ($\epsilon = 7670$ 1 mol^{-1} cm^{-1} at 215 nm in n-hexane)

[c] Determined by g.p.c. calibrated with polystyrene standards

[d] Macromer functionality calculated from the ratio $\bar{M}_{n(v.p.o)}/\bar{M}_{n(u.v.)}$

[e] Macromer functionality determined by ^{1}H n.m.r. spectroscopy

The reactivities of the propagating species in this scheme are assumed to be affected only by the electronic and steric nature of the chain ends and not by the nature of the penultimate or other unit. This kinetic scheme yields the well-known copolymer composition equation

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{1 + r_1[M_1]/[M_2]}{r_2 + [M_1]/[M_2]} \tag{5}$$

where $d[M_1]/d[M_2]$ and $[M_1]/[M_2]$ represent the molar ratios of the monomers in the copolymer and monomer feed respectively, and $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$. The Fineman–Ross and Kelen–Tudos methods, from which the reactivity ratios in *Table 2* were calculated, are
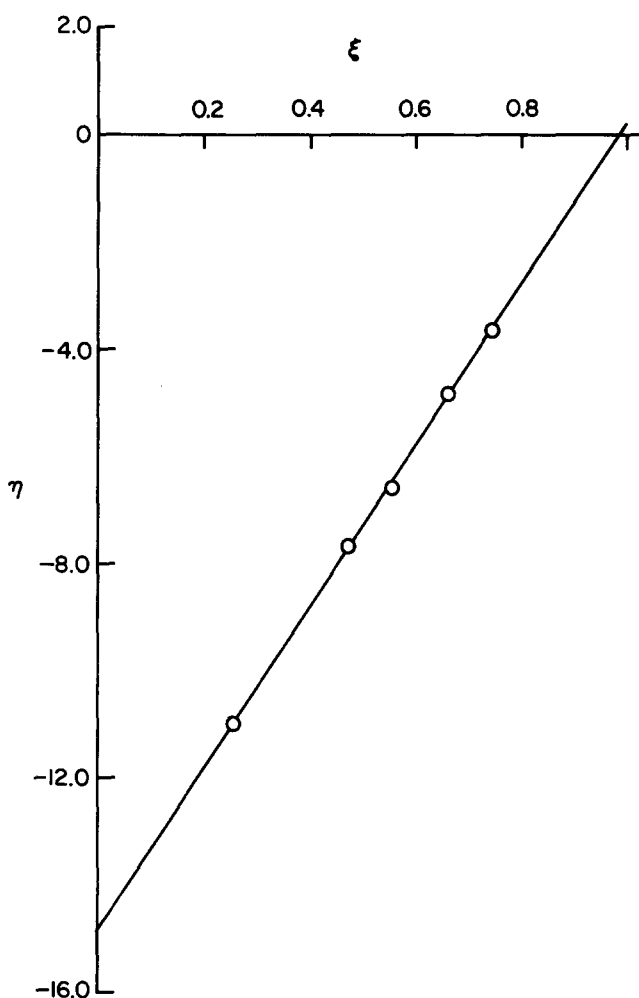
Figure 5 Kelen–Tudos plot for copolymers of styrene and PDMS–MA1. $\zeta = H(\alpha + H)$, $\eta = G(\alpha + H)$, $\alpha = \sqrt{H_{max}H_{min}}$ where $G = F(f-1)/f$, $H = F^2/f$, and F and f as in *Figures 3* and *4*

linearised versions of equation (5). In the present case both methods give similar results, the agreement in r_2 for each set of data being particularly close.

The most obvious feature in *Table 2* is the huge error in the values of the reactivity ratio r_1, particularly with the macromer of highest molecular weight. It is clear that meaningful values of r_1 cannot be obtained except when dealing with macromers of relatively low molecular weight. By contrast, values of r_2 can be determined with some degree of confidence.

The source of the large errors in the values of r_1 is the large difference between the macromer and styrene mole fractions in both the feed and copolymer (typically of the order of 1 mole macromer to 2000 moles styrene for a macromer with $\bar{M}_n \simeq 10^4$). Because of these large errors, many reports omit values of r_1 and only quote r_2 for various macromer/small monomer copolymerizations[4,5]. Ito and coworkers[7], however, have reported values of r_1 and r_2 for the copolymerization of a methacrylate-terminated polystyrene macromer ($\bar{M}_n$ 3180) with 2-hydroxyethylmethacrylate (HEMA) (M_2). These reactivity ratios were $r_1 = -0.2 \pm 9.8$ and $r_2 = 1.6 \pm 0.2$. As in the case of our data in *Table 2*, only the value of r_2 has any significance; r_1 has even less significance than our values for PDMS–MA1 and PDMS–MA2.

It has been pointed out by Bamford et al.[1] and others[4,5] that as a consequence of the great disparity in number-average molecular weight of the macromer and the small monomer, the following inequalities hold

$$1 \gg r_1[M_1]/[M_2] \quad \text{and} \quad r_2 \gg [M_1][/M_2]$$

the first of these being especially valid when the macromer is reluctant to homopolymerize (k_{11} very small). With these simplifications equation (5) reduces to

$$\frac{d[M_1]}{d[M_2]} \simeq \frac{[M_1]}{[M_2]} \cdot \frac{1}{r_2} \tag{6}$$

According to this one-parameter equation the copolymer composition is governed by r_2, i.e. by the relative rates of reactions (3) and (4) above. In the present case the monomer feed ratios $[M_1]/[M_2]$ varied as follows: PDMS–MA1, 0.023–0.173; PDMS–MA2, 0.014–0.105; PDMS–MA3, 0.0006–0.0024. Since r_2 is close to unity it is clear that the second inequality is valid only for the PDMS–MA3 copolymerizations; certainly not for the macromer-rich compositions in the other sets of copolymerizations. If r_1 is taken to lie in the range 0.2 to 0.3 the first inequality is valid for PDMS–MA3 and possibly also for the macromer-rich compositions in the other two sets. The inapplicability of equation (6) to the copolymerizations with the macromers PDMS–MA1 and PDMS–MA2 is further demonstrated in the following manner. Values of r_2 (r_{2app}) were calculated from monomer feeds

Table 2 Reactivity ratios for PDMS–MA macromer (M_1)/styrene (M_2) copolymerizations

Macromer	Graph of $(f-1)/F$ vs. f/F^2 (Figure 3)		Graph of $F(f-1)/f$ vs. F^2/f (Figure 4)		Kelen–Tudos Method (Figure 5)	
	r_1	r_2	r_1	r_2	r_1	r_2
PDMS–MA1	0.15 ± 0.15	1.06 ± 0.10	0.21 ± 0.10	1.07 ± 0.11	0.18 ± 0.10	1.07 ± 0.10
PDMS–MA2	0.44 ± 0.29	1.07 ± 0.15	0.16 ± 0.16	1.05 ± 0.15	0.27 ± 0.21	1.06 ± 0.15
PDMS–MA3	−45 ± 164	1.51 ± 0.23	−3 ± 97	1.59 ± 0.21	−22 ± 118	1.55 ± 0.21

F and f mole ratio of monomers in the feed and copolymer respectively

and copolymer compositions assuming that equation (6) was valid. These values of r_{2app}, plotted against the mole ratio of monomers in the feed $[M_1]/[M_2]$ in *Figure 6*, show a definite upward trend as $[M_1]/[M_2]$ increases. If equation (6) had been valid for these copolymerizations r_{2app} should have remained invariant with $[M_1]/[M_2]$. For the copolymers of PDMS–MA3 any such trend in r_{2app} is small and is masked by experimental errors. In this case r_{2app} varies in a random manner from 2.00 to 1.33 with an average value of 1.61 which is close to the values of r_2 quoted in *Table 2* for this system. We conclude that it is safe to calculate r_2 from equation (6) only when the number-average molecular weight of the macromer is of the order 10 000 or greater. It is interesting, however, to reexamine *Figure 6* where we note that the curves approach linearity as the ratio $[M_1]/[M_2]$ decreases and extrapolate to values of r_2 close to those for PDMS–MA1 and 2 in *Table 2*. This occurs because as $[M_1]/[M_2]$ diminishes the first of the above inequalities becomes valid before the second. Simplifying equation (5) with the approximation $1 \gg r_1[M_1]/[M_2]$ yields

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{1}{r_2 + [M_1]/[M_2]} \qquad (7)$$

Rearranging equation (7) gives

$$r_2 = \frac{d[M_2]}{d[M_1]} \cdot \frac{[M_1]}{[M_2]} - \frac{[M_1]}{[M_2]} \qquad (8)$$

The first term on the r.h. side of equation (8) is identical to r_{2app} referred to above, and hence we can recast equation (8) as

$$r_{2app} = r_2 + [M_1]/[M_2] \qquad (9)$$

In the limit of $[M_1]/[M_2] = 0$, $r_{2app} = r_2$. Equation (9) provides a convenient graphical method for evaluating r_2 when $r_1 \to 0$, or when, as in the present circumstances where the macromers can homopolymerize slowly, the first inequality becomes valid before the second.

A second feature in *Table 2* is the variation in r_2 with increasing macromer molecular weight. This is presented graphically (*Figure 7*) as a plot of r_2 versus the uncoiled length of the side-chain[16] attached to the methacrylate group. *Figure 7* also includes values of r_2 from the literature for the copolymerization of several n-alkyl esters of methacrylic acid with styrene[17]. The graph shows an initial sigmoidal increase in r_2 with side-chain length followed by a plateau where the increase in r_2 is much more gradual. Between points 7 and 8, the side chain changes from polymethylene to polysiloxane in nature, and it is not certain whether the steepness of the gradient
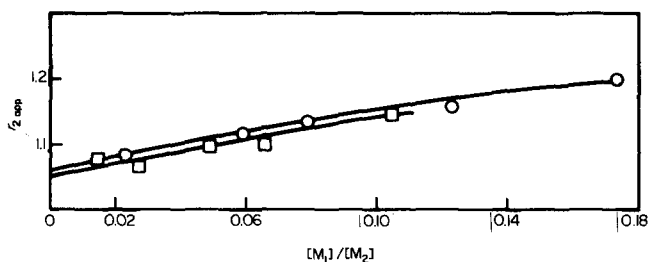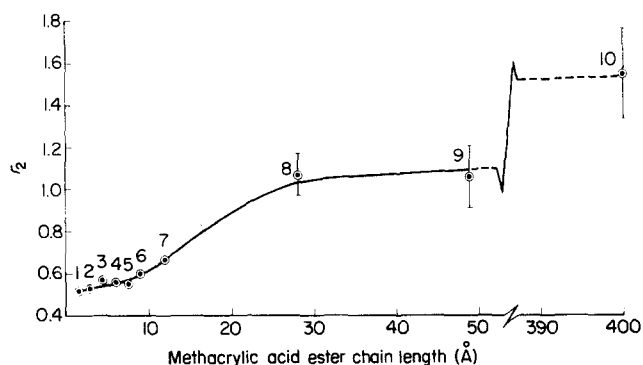

Figure 7 r_2 for styrene-n-alkyl methacrylate ester copolymerizations vs. length of extended ester side chain. For points 1–7, numbers correspond to numbers of C atoms in alkyl groups[17]. Points 8–10, from macromers PDMS–MA1, –MA2 and –MA3 respectively

in that region is due to the change in side-chain structure or side-chain length. Thus, it is possible that there is a change in reactivity, when siloxane units replace methylene groups on the side chain of monomer M_1, as a consequence of changes in polymer radical–monomer/macromer and polymer–solvent interactions. Nevertheless, it is clear from *Figure 7* that r_2 increases as the length of the side chain on M_1 increases.

Ito et al.[7] and Yamashita et al.[18] have determined r_2 values for the copolymerization of methacryloyl polystyrene macromers with HEMA (M_2). For macromers of $\bar{M}_n$ 3180, 14 000 and 23 000 the corresponding values of r_2 were 1.6, 2.0 and 2.3 respectively. With methyl methacrylate as M_1, r_2 is reported as 1.05[19]. The trend in these values of r_2 with increasing side-chain length of the methacrylate monomer M_1 is very similar to that shown in *Figure 7*. It seems probable that this behaviour is quite general and a possible explanation follows.

The reactivity ratio r_2 is equal to the ratio of the rate coefficients k_{22}/k_{21} of the propagation reactions (4) and (3) above. When the small monomer, styrene, in the present case, is M_2 it is unlikely that k_{22} is greatly affected by the length of the side chain on the macromer M_1. It therefore follows that the observed increase in r_2 is due to a decrease in k_{21} as the length of the macromer chain is increased. That is, the bulky side chain presents a steric barrier to the radical–macromer reaction (3). Kennedy and Lo have suggested that the radical–macromer reaction is diffusion-controlled like termination in radical polymerization[5]. This is a misleading analogy; the radical–macromer reaction does not conform to the accepted concept of diffusion-controlled reactions which are characterized by high rates and low energies of activation. The radical–radical termination rate coefficient is at least five orders of magnitude greater than k_{21}. The radical–macromer addition like any other radical–monomer reaction, is activation-controlled and the decrease in k_{21} with length of the macromer chain is most likely due to the decreased probability of the large radical $\sim M_2^\bullet$ 'finding' the reactive double bond on the bulky macromer during a macromer–radical encounter. It may be that as the macromer side chain increases in length the entropy of activation associated with reaction (3) becomes more strongly negative.

Figure 6 r_{2app} (from equation (6)) vs. $[M_1]/[M_2]$ for copolymers of styrene (M_2) and macromers PDMS–MA1 ○ and PDMS–M2 □

ACKNOWLEDGEMENTS

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