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COPOLYMERISATION OF 2-HYDROXYETHYL METHACRYLATE WITH SILOXANYL MONOMERS

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Abstract—Acryloxymethylpentamethyldisiloxane (AMS) and methacryloxymethylpentamethyldisiloxane (MMS) have been prepared and purified chromatographically. Some physicochemical properties have been measured for these monomers as well as for highly purified 2-hydroxyethyl methacrylate (HEMA). Hydroxyl group analysis on copolymers of AMS with HEMA and of MMS with HEMA, obtained by free radical copolymerisation to low conversion, enabled monomer reactivity ratios to be determined by several procedures. The average values were $r_{HEMA} = 0.86$, $r_{AMS} = 0.55$ and $r_{HEMA} = 0.97$, $r_{MMS} = 0.33$. These values have been invoked in computing integral curves for the instantaneous copolymer composition throughout the whole range of conversion.

INTRODUCTION

The monomer 2-hydroxyethyl methacrylate (HEMA) is the basis for a wide variety of biomedical applications. Thus polymerisation to low conversion in ethanol yields a soluble, linear, homopolymer (PHEMA) suitable for dip coating applications [1] or as a useful matrix for drug release into an aqueous environment [2, 3]. More commonly, PHEMA is made in a crosslinked form either alone or in the presence of a co-monomer to yield hydrogels [1]. Among the more interesting co-monomers are simple and complex siloxanyl acrylates and methacrylates [4–7] capable of enhancing oxygen permeability.

Monomer reactivity ratios are an important requirement for predicting copolymer composition, especially when attempting to prepare copolymers of minimal compositional heterogeneity (azeotropes). The siloxanyl monomers considered here are acryloxymethylpentamethyldisiloxane (AMS) and methacryloxymethylpentamethyldisiloxane (MMS); the evaluation of the reactivity ratios in the systems HEMA–AMS and HEMA–MMS forms the main basis for the present communication. Particular attention is paid to the purification of the three monomers and some physicochemical properties over a range of temperature are reported.

In addition to those already quoted, the following abbreviations are also adopted: BCTS—1,3-bis(chloromethyl)tetramethyldisiloxane; DMF—*N*,*N*-dimethylformamide; EDMA—ethyleneglycol dimethacrylate; HMS—hexamethyldisiloxane.

EXPERIMENTAL

Materials

Purification of HEMA. Preliminary assessment of the purity of commercial HEMA (BP Chemicals International Ltd) was made via TLC using *n*-hexane–diethyl ether (1:1, v/v) as solvent and silica gel as absorbent. The presence of EDMA, methacrylic acid and ethylene glycol was confirmed by comparison with published [8] R_f values. Using *n*-hexane as the counter-current solvent, EDMA was removed by liquid–liquid continuous extraction [9] on an aqueous solution of HEMA (water–HEMA = 1:4, v/v) containing 0.3% w/v *t*-butyl catechol as inhibitor. A small amount of thermal polymerisation was, however, noted during prolonged extractions. This was overcome by circulating cold water round the extraction vessel. Extraction for *ca* 14–15 hr sufficed generally to remove EDMA, as evidenced by monitoring with TLC.

The HEMA was recovered from aqueous solution by salting out with NaCl, after which the separated HEMA was diluted again with ten times its own volume of water and the salting out repeated. This ensured the maximum possible extraction of ethylene glycol. Methacrylic acid was removed by dissolving the HEMA in aqueous $NaHCO_3$ followed after 1.5 hr by a salting out procedure. The HEMA was dried over anhydrous $MgSO_4$ and vacuum distilled in the presence of CuCl as inhibitor [10] (b.p. 62.5–63.5 at 0.5–0.7 mmHg, cf. 64° at 0.5 mm reported elsewhere [11]).

A further purification was made by column chromatography, using silica gel (60–120 mesh) as absorbent. The method was similar to that adopted by Macret and Hild [11] except for the use here of diethyl ether as eluant. After establishment of a constant flow rate, the eluate was collected in fractions of 7–10 ml. Only those fractions verified by TLC to contain pure HEMA were recombined, the diethyl ether being removed finally in a rotary evaporator.

Synthesis of AMS and MMS. In the preparation of AMS and MMS, sodium acrylate and potassium methacrylate respectively are required. These were prepared according to the method of Morawetz and Rubin [12]. Freshly distilled acrylic (or methacrylic) acid was added slowly with stirring to a methanolic solution of sodium (or potassium) hydroxide, the temperature being maintained below 20°. Dropwise addition of the resultant solution to a large excess of acetone yielded a white precipitate, which was filtered, washed with acetone and dried *in vacuo* at room temperature. These salts were used in the preparation of the required monomers according to methods similar to those already published [4, 5], but differing in certain aspects, which we have found to optimise convenience, safety (e.g. omission of benzene), yield and purity. Accordingly, full details are presented of the recommended procedures for the preparation and purification.

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The synthesis is a two-stage process; the first yields a di-acrylate (or di-methacrylate) which is converted in the second stage to AMS (or MMS).

Stage 1

$$ClH_2CSi(CH_3)_2OSi(CH_3)_2CH_2Cl + 2H_2C = C(R)COOM \rightarrow$$
$$2MCl + H_2C = C(R)COOCH_2Si(CH_3)_2OSi(CH_3)_2CH_2OCOC(R) = CH_2$$

Stage 2

$$H_2C = C(R)COOCH_2Si(CH_3)_2OSi(CH_3)_2CH_2OCOC(R) = CH_2 + Si(CH_3)_3OSi(CH_3)_3 \rightarrow$$
$$H_2C = C(R)COOCH_2Si(CH_3)_2OSi(CH_3)_3$$

Here, M = Na and R = H for the preparation of AMS and M = K and R = CH_3 for the preparation of MMS. The compositions of reactants, catalysts etc. for both stages are specified in Table 1, where the product from stage 1 means the di-acrylate (or di-methacrylate).

In stage 1 the reactants were all mixed simultaneously and heated at reflux temperature for 2 hr with periodic agitation. (Note: we have found it inadvisable to adopt the reported procedure [4, 5] of gradually adding the alkali metal acrylate or methacrylate down the condenser, since this led to some premature polymerisation of them.) The alkali metal chloride produced was filtered off and the excess of acrylic (or methacrylic) acid and the DMF were removed by washing with dilute aqueous $NaHCO_3$ and water. Separation of the siloxanyl and aqueous phases was assisted by adding NaCl to the aqueous phase, and several hours were allowed for separation to occur. The siloxanyl product was dried over anhydrous $MgSO_4$ and then used directly in the next stage of the synthesis.

In stage 2 the siloxanyl product from stage 1 was added to the reactants indicated in Table 1. The mixture was left at room temperature for 36 hr prior to being washed with water, separated and dried over anhydrous $MgSO_4$. The monomer was then isolated by vacuum distillation in the presence of hydroquinone as inhibitor (b.p. 48° at 1.5 mm Hg for AMS and 73–74° at 4 mm Hg for MMS). The purities of the monomers were examined by TLC, using silica gel plates, *n*-hexane–diethyl ether (1:1, v/v) as solvent and 0.2% v/v potassium permanganate in acetone as spraying medium to reveal the spots. For AMS, only a single spot was revealed ($R_f = 0.76$). For MMS, the R_f value was 0.79 but additional spots due to minute traces of hydroquinone and of one unidentified species were revealed.

Further purification by column chromatography was conducted, therefore, only on MMS, using silica gel as absorbent and *n*-hexane–diethyl ether (1:1, v/v) as eluant. Prior to the purification the absorbent was fully wetted and swollen with the eluant. MMS (*ca* 1 ml) was deposited dropwise on the column, covered with more silica gel to which more eluant was then added. A steady flow rate (1 drop per 4–5 sec) was established by maintaining a constant level of the eluant above the silica gel. The initial fraction comprised only eluant and the next fraction contained pure MMS (as evidenced by TLC). Traces of impurity were detected in later fractions. Repetition of this procedure enabled a total of *ca* 25 ml purified MMS to be obtained. The eluant from this was removed in a rotary evaporator at room temperature.

Table 1. Composition of reactants for preparation of AMS and MMS (quantities expressed as parts by weight)

	AMS	MMS
Stage 1		
Sodium acrylate	1.00	—
Potassium methacrylate	—	0.68
Acrylic acid	1.25	—
Methacrylic acid	—	1.00
BCTD	1.00	1.00
DMF	1.25	1.25
Hydroquinone	0.10	0.10
Product	1.03	1.27
Stage 2		
Product from stage 1	1.03	1.27
HMS	3.84	1.87
Trifluoroacetic acid	0.10	0.10
Conc. sulphuric acid	0.10	0.10
Hydroquinone	0.10	0.10
Final product	0.60	0.90

Refractive index and density. The refractive indices n_D of all three purified monomers were measured on an Abbe refractometer fitted with an external recirculatory thermostat. Values were obtained at several temperatures within the range 10–50°. The densities of purified AMS and MMS were measured at several temperatures within the range 5–46°, using a previously calibrated dilatometer.

Copolymerisation. Copolymerisations were effected in outgassed, sealed, ampoules at 60° using 4,4′-azobis-4-cyanopentanoic acid at an overall concentration of 1×10^{-3} mol/l as initiator and ethanol as solvent. The ratio of monomers to solvent was 1:7 (v/v). Nine different feed compositions were used, the initial mole fractions of HEMA lying within the range 0.083–0.635 for the system HEMA–AMS and within the range 0.090–0.882 for the system HEMA–MMS. Conversions of 13% were attained in 2.5–3 hr in the former system, but rather more quickly (1.5–2 hr) in the latter. Copolymers were precipitated in an excess of petroleum ether (b.p. 60–80°), washed with precipitant and dried to constant weight *in vacuo* at 40°. The copolymer compositions were determined by analysing for the hydroxyl content (specific to the HEMA portion only) via acetylation and titration [13]. The accuracy of the procedure was checked by analysing a sample of pure PHEMA.

RESULTS AND DISCUSSION

Properties of monomers

The boiling points of the monomers at low pressure have been quoted in the Experimental section. The densities ρ(g cm^{-3}) of AMS and MMS varied linearly with temperature T(°C) as follows:

$$\text{AMS: } \rho = 0.9067 + 9.90 \times 10^{-4}(T\text{-}25)$$

$$\text{MMS: } \rho = 0.9056 + 9.53 \times 10^{-4}(T\text{-}25)$$

The observed linear dependences of refractive index n_D on T(°C) are

$$\text{AMS: } n_D = 1.4154 - 4.71 \times 10^{-4}(T\text{-}25)$$

$$\text{MMS: } n_D = 1.4193 - 3.79 \times 10^{-4}(T\text{-}25)$$

$$\text{HEMA: } n_D = 1.4507 - 4.00 \times 10^{-4}(T\text{-}25)$$

Reactivity ratios

Four graphical procedures involving the compositions of feed and copolymer have been invoked in evaluating the reactivity ratios r_1 and r_2 (where subscript 1 denotes HEMA and subscript 2 signifies either AMS or MMS). Details of the plots involved are not reproduced here, but are available from the appropriate references indicated in Table 2. The quoted average values and the uncertainties in them

Table 2. Reactivity ratios at 60° for the copolymerisations HEMA (1)–AMS (2) and HEMA (1)–MMS (2)

	HEMA–AMS		HEMA–MMS	
Procedure	r_1	r_2	r_1	r_2
Fineman–Ross [14]	0.88	0.57	0.97	0.34
Kelen–Tüdös [15]	0.86	0.52	0.97	0.33
Mayo–Lewis [16]	0.83	0.58	0.98	0.34
Curve fitting [17]	0.86	0.52	0.97	0.34
Average values	0.86 (±0.04)	0.55 (±0.04)	0.97 (±0.02)	0.33 (±0.01)

have been obtained on the basis of the unlisted uncertainties in the individual procedures.

Since r_1 and r_2 are both less than unity in each system, an azeotropic feed composition $(f_1)_c$ exists and is given by

$$(f_1)_c = (1 - r_2)/(2 - r_1 - r_2)$$

where f is expressed as a mole fraction. The values of $(f_1)_c$ in the systems HEMA–AMS and HEMA–MMS are thus 0.763 and 0.957 respectively. The instantaneous copolymer composition F_1, expressed as a mole fraction, can be calculated readily from the copolymer-composition equation [16–18]. For the present systems, calculation showed that $F_1 > f_1$ when $(f_1)_c > f_1 > 0$.

The compositional drift of copolymer with increasing fractional conversion (C) of unreacted total monomers may be determined from the Skeist equation [19]

$$\ln(1 - C) = \int_{f_{1i}}^{f_{1j}} \frac{df_1}{F_1 - f_1} \qquad (1)$$

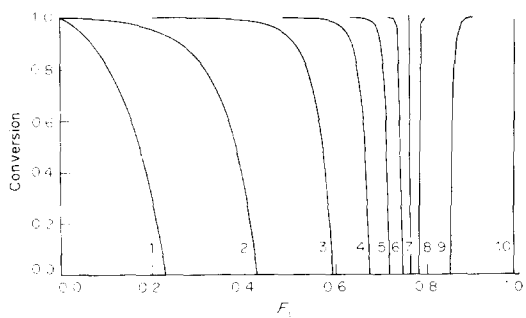

Fig. 1. Fractional conversion vs instantaneous copolymer composition (mole fraction of HEMA) for the system HEMA–AMS. Curves 1–10 relate to initial feed compositions f_1 of 0.157, 0.357, 0.557, 0.657, 0.710, 0.743, 0.763, 0.783, 0.857 and 0.990 respectively. Curve 7 is the case $f_1 = (f_1)_c$.

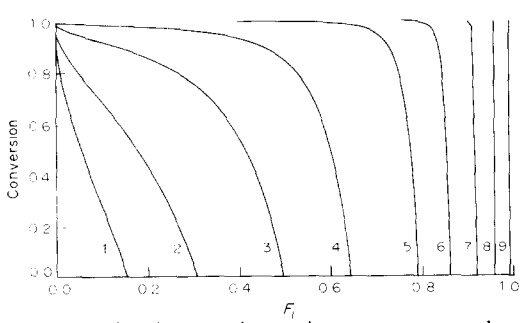

Fig. 2. Fractional conversion vs instantaneous copolymer composition (mole fraction of HEMA) for the system HEMA–MMS. Curves 1–9 relate to initial feed compositions f_1 of 0.063, 0.163, 0.363, 0.563, 0.763, 0.850, 0.917, 0.957 and 0.990 respectively. Curve 8 in the case $f_1 = (f_1)_c$.

Here one calculates C when f_1 changes during this conversion from a value f_{1i} to a value f_{1j}, the algebraic sign of $(f_{1j} - f_{1i})$ being dependent on whether r_1 is $>$ or $< r_2$ and also on whether the initial feed composition is $>$ or $< (f_1)_c$. We have found it convenient to utilise equation (2) which is an integral form of equation (1) due to Meyer and Lowry [20].

$$C = 1 - \left(\frac{f_{1j}}{f_{1i}}\right)^{\alpha}\left(\frac{1 - f_{1j}}{1 - f_{1i}}\right)^{\beta}\left(\frac{f_{1i} - \delta}{f_{1j} - \delta}\right)^{\gamma} \qquad (2)$$

where $\alpha = r_2/(1 - r_2)$; $\beta = r_1/(1 - r_1)$; $\gamma = (1 - r_1 r_2)/[(1 - r_1)(1 - r_2)]$; $\delta = (1 - r_2)/(2 - r_1 - r_2)$.

The computations were made by means of a program developed here. It was written in Fortran 77 for use on the Prime 750 and the diagrams were produced on a Calcomp 1051 plotter.

The results for the systems HEMA–AMS and HEMA–MMS are shown in Figs 1 and 2 respectively. In the former, ten initial feed compositions are considered; in the latter there are curves for nine different initial values of f_1. For each system, the plot for the case of $f_1 = (f_1)_c$ displays, of course, constancy of F_1 over the entire conversion.

Constancy of F_1 over an appreciable range of conversion is observed also for certain of the systems in which the initial f_1 is not equal to $(f_1)_c$. As a further illustration of this, we have taken arbitrarily the conditions under which F_1 does not deviate by more than ±3% from its instantaneous value throughout the first 90% of conversion. For HEMA–AMS this requirement holds, if the initial value of f_1 lies in the range 0.710–0.990 inclusive (Fig. 1, curves 5–10). The range is more restricted in the system HEMA–MMS, which dictates that the initial value of f_1 be within the interval 0.850–0.990 inclusive (Fig. 2, curves 6–9). On the basis of these findings, it is proposed to investigate the transparency or opacity exhibited in these systems, when copolymerisation to different levels of conversion is effected by γ-irradiation.

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