Chain Transfer Activity of ω-Unsaturated Methacrylic Oligomers in Polymerizations of Methacrylic Monomers

Lillian Hutson, Julia Krstina, Catherine L. Moad, Graeme Moad,* Gregory R. Morrow, Almar Postma, Ezio Rizzardo, and San H. Thang

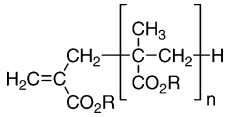
CSIRO Molecular Science, Bag 10, Clayton South, Clayton, Victoria 3169, Australia

Received January 28, 2004; Revised Manuscript Received March 31, 2004

ABSTRACT: Chain transfer constants have been determined for an unsaturated methyl methacrylate trimer, $CH_2{=}C(CO_2Me)CH_2[C(CO_2CH_3)(CH_3)CH_2]_2H$ (MMA_3), in polymerizations of methacrylate esters (ethyl, EMA; *n*-butyl, BMA; *tert*-butyl, tBMA; 2-ethylhexyl, EHMA) and for the analogous trimers of butyl methacrylate (BMA_3) and methacrylic acid (MAA_3), a hydroxyethyl methacrylate dimer ($HEMA_2$), a hydroxyethyl methacrylate−methyl methacrylate−hydroxyethyl methacrylate trimer (HEMA−MMA−HEMA), and a HEMA macromonomer in methyl methacrylate (MMA) polymerization. These data have been assessed with reference to our previously reported data on chain transfer of MMA macromonomers in MMA polymerizations. The transfer constants (C_{tr}) for MMA_3 in polymerizations of methyl, ethyl, *n*-butyl, *tert*-butyl, and 2-ethylhexyl methacrylate at 60 °C are similar (∼0.18). The C_{tr} of MAA_3 (0.28 at 60 °C in 2-butanone solvent) in MMA polymerization is ca. 50% higher than that of MMA_3 under similar conditions. Other trimers (BMA_3, HEMA−MMA−HEMA) and a low molecular weight HEMA macromonomer (degree of polymerization ca. 7) have C_{tr} similar to that of MMA_3. The transfer constants for the various trimers show no significant temperature dependence over the range 60−100 °C. The C_{tr} of the dimers (MMA_2, $HEMA_2$) in MMA polymerization are an order of magnitude lower than those of the corresponding trimers. The C_{tr} of $HEMA_2$ (0.018 at 60 °C) in MMA polymerization is ca 50% higher than that of MMA_2 (0.013 at 60 °C). The C_{tr} of both dimers increases with increasing temperature between 60 and 100 °C (C_{tr} $HEMA_2$ 0.031, MMA 0.018 at 60 °C). Issues relating to the synthesis and characterization of trimers (RMA_3) by catalytic chain transfer are discussed. Methods for synthesis of di-end-functional trimers MAA−MMA−MAA, HEMA−MMA−HEMA based on selective hydrolysis and reesterification are described. These trimers may find use in telechelic synthesis.

Introduction

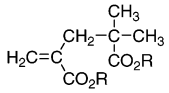
Methacrylate macromonomers of general structure (RMA_n) have found importance as chain transfer agents[1−3] and as precursors to block,[4−7] graft,[1,2,5,8−14] and end-functional polymers.[5,15−17] An excellent summary of their synthesis and application is provided by Gridnev and Ittel[18] in their recent review on catalytic chain transfer. We[3] have previously reported on the chain transfer activity of MMA macromonomers (MMA_n, n = 2, 3, 4, >4) in MMA polymerization. That work explored the effect of macromonomer chain length on the rate constants and Arrhenius parameters for chain transfer and provided insights into the mechanism of chain transfer.

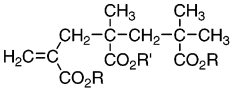


RMA_n **R = alkyl**

MMA_n **R = CH_3**

This paper concerns the synthesis, characterization and chain transfer activity of methacrylate macromonomers. We report chain transfer constants for MMA trimer (MMA_3) in polymerizations of various methacrylate esters (methyl, ethyl, *n*-butyl, *tert*-butyl, and 2-ethylhexyl) and of various trimers [*n*-butyl methacrylate trimer (BMA_3), methacrylic acid trimer (MAA_3), a hydroxyethyl−methyl methacrylate mixed trimer (HEMA−MMA−HEMA)] and a HEMA macromonomer in MMA polymerization. The aim was to assess the dependence, if any, of chain transfer activity of methacrylate macromonomers on the nature of the ester alkyl groups (R, R′) in the macromonomer or monomer. This information is of importance in developing block and graft copolymer syntheses and in designing conditions for living/controlled polymerizations based on the use of these reagents.[4−6]





MMA_2 R = CH_3

$HEMA_2$ R = CH_2CH_2OH

MAA_3 R, R′ = H

MMA_3 R, R′ = CH_3

BMA_3 R, R′ = *n*-C_4H_9

CMA_3 R, R′ = *c*-C_6H_{11}

$HEMA_3$ R, R′ = CH_2CH_2OH

MAA-MMA-MAA R=H, R′ = CH_3

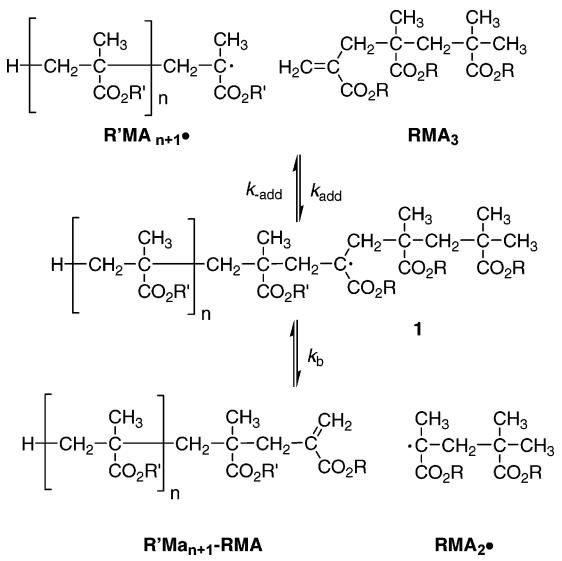
HEMA-MMA-HEMA CH_2CH_2OH, R′ = CH_3

The mechanism proposed for chain transfer to a methacrylate trimer RMA_3 involves reversible addition-fragmentation chain transfer (RAFT) as shown in Scheme 1.[1,3] The product is the dimer ($R'MA_2^{\bullet}$) radical and a macromonomer ($R'MA_{n+1}$−RMA) with a trimer-

* To whom correspondence should be addressed. E-mail: graeme.moad@csiro.au.

10.1021/ma049813o CCC: $27.50 Published 2004 by the American Chemical Society
Published on Web 05/18/2004

Scheme 1



derived end group. The mechanism for other macromonomers RMA_n is analogous. The overall RAFT process involves reversible transfer of the terminal methacrylate unit of the macromonomer to the propagating radical.

According to this mechanism there is no simple rate constant for transfer. Instead, the chain transfer process is described by the expression defined in eq 1a. The rate of chain transfer will depend on both the rate of addition to the macromonomer and the way in which the intermediate partitions between starting materials and products.[3]

$$k_{tr} = k_{add} \times k_{\beta}/(k_{-add} + k_{\beta}) \qquad (1a)$$

where k_{add}, k_{-add}, and k_{β} are defined in Scheme 1.

The adduct radicals (**1**) do not readily add methacrylate monomers.[1,4] Copolymerization has only been observed as a very minor pathway for dimers (RMA_2) and then only under forcing conditions.[15,19,20] This behavior contrasts with that observed with monosubstituted monomers such as acrylate esters or styrene where graft copolymer formation is observed.[1−3] There is evidence that radical−radical termination involving **1** is also very slow,[21,22] which is consistent with the finding that no significant retardation is found in polymerizations of methacrylates carried out in the presence of macromonomers RMA_n.[3,4]

Experimental Section

General Information. Solvents used for column chromatography and polymerization were of AR grade and were distilled. Monomers (MMA, nBMA, tBMA, and EHMA from Aldrich) were filtered through alumina, fractionally distilled under reduced pressure, and redistilled under reduced pressure immediately before use. The silica used was Kieselgel-60 (Merck), 70−230 mesh. Nuclear magnetic resonance (NMR) spectra were obtained with a Bruker AC200 or a Bruker DRX500 spectrometer. Chemical shifts are reported in ppm from external tetramethylsilane. The numbering scheme used in making NMR assignments for macromonomers is given in Figure 1. High-resolution electron impact (HREI) mass spectra were obtained with a ThermoQuest MAT95XL mass spectrometer. Atmospheric pressure chemical ionization (APCI) and electrospray (ES) mass spectra were obtained with a VG Platform Single Quadrupole mass spectrometer. Gel permeation chromatography (GPC) was performed on a Waters Associates liquid chromatograph equipped with differential refractometer and a set of six Ultrastyragel columns (10^6, 10^5, 10^4, 10^3, 500, and 100 Å). Tetrahydrofuran (flow rate of 1.0 mL/min) was used as eluent at 22 ± 2 °C. The columns were calibrated with narrow polydispersity PMMA standards (Polymer Laboratories). A third-order polynomial was used to fit the log M vs time calibration curve, which appeared to be linear across the molecular weight range $2 \times 10^2 - 2 \times 10^6$. Number molecular weight distributions were obtained from the intensity-retention time data[23−25] which were processed using KaleidaGraph.

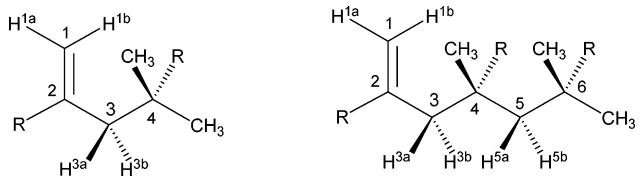


Figure 1. Numbering scheme used in making NMR assignments for methacrylic macromonomers RMA_2 and RMA_3.

Methyl Methacrylate Dimer, Trimer (2,2-Dimethyl-4-methylenepentanedioic Acid Dimethyl Ester, MMA_2, and 4,6-Bis(methoxycarbonyl)-2,2,4-trimethylhept-6-enoic Acid Methyl Ester, MMA_3). MMA_2 and MMA_3 were separated by distillation from an oligomer mixture prepared by polymerizing MMA in the presence of a catalytic chain transfer agent isopropylaquobis[difluoroboryl(dimethylglyoximato)-cobalt(III)] (iPr−Co^{III}(DMG-BF_2)$_2$−H_2O) as described previously.[3]

Methacrylic Acid Trimer (4,6-Dicarboxy-2,2,4-trimethyl-hept-6-enoic Acid, MAA_3). MAA_3 was prepared by alkaline hydrolysis of MMA_3. Thus, a solution of MMA_3 (6.0 g, 0.02 mol) and KOH (10% solution, 100 mL) was heated at 90 °C overnight (16 h). The reaction solution was acidified with concentrated HCl to pH ∼1 and the aqueous solution extracted with chloroform (3 × 80 mL) and ethyl acetate (2 × 100 mL). The combined organic layers were dried over anhydrous magnesium sulfate, filtered and concentrated to dryness on the rotary evaporator. The MAA_3 was obtained as a white solid in quantitative yield.

^{1}H NMR (CD_3OD): δ 1.06 (s, 3H, $C^4C\mathbf{H}_3$), 1.13 (s, 3H, $C^6C\mathbf{H}_3$), 1.19 (s, 3H, $C^6C\mathbf{H}_3$), 2.11 (ABq, 2H, $C^5\mathbf{H}_2$), 2.56 (ABq, 2H, $C^3\mathbf{H}_2$), 5.59 (br d, 1H, =C$\mathbf{H^{1b}}$H^{1a}), 6.22 (d, J = 1.45 Hz, 1H, =CH$^{1b}\mathbf{H^{1a}}$.

^{13}C NMR (CD_3OD): δ 19.28 ($C^4\mathbf{C}H_3$), 22.80 ($C^6\mathbf{C}H_3$), 30.77 ($C^6\mathbf{C}H_3$), 42.43 (**C^6**), 43.77 (**C^3**), 47.57 (**C^4**H_2), 49.41 (**C^5**H_2), 129.0 (**C^1**H_2=C), 138.7 (CH_2=**C^2**), 170.9 (C^2**C**=O), 180.8 (C^4**C**=O), 182.6 (C^6**C**=O). Signals were assigned on the basis of connectivities seen in HMBC and HSQC spectra.

Mass spectrum (AP$^+$): m/z 259.2 (M+1). Mass spectrum (AP$^-$): m/z 257.3 (M − 1).

Methacrylic Acid Dimer (2,2-Dimethyl-4-methylenepentanedioic Acid, MAA_2). MAA_2 was prepared by alkaline hydrolysis of MMA_2 using a similar procedure to that described for the hydrolysis of MMA_3.

Butyl Methacrylate Trimer (4,6-Bis(butoxycarbonyl)-2,2,4-trimethylhept-6-enoic Acid Butyl Ester, BMA_3). A mixture of MAA_3 (0.5 g, 1.9 mmol), 1-iodobutane (3.0 g, 0.016 mol), and tetramethylammonium hydroxide (2.3 g, from 20 mL of ∼25 wt % solution in methanol, 0.058 mol) in tetrahydrofuran (2 mL) was heated at 100 °C in a sealed tube for 120 min. The crude product (which contained >95% of the required triester by ^{1}H NMR) was purified by on silica with 4:1 hexane:$CHCl_3$ as eluent. Isolated yield: ca. 0.5 g, 80%.

^{1}H NMR ($CDCl_3$): δ 0.89, 0.91, 0.92 (3×s, 9H, 3×OCH_2CH_2-CH_2C$\mathbf{H}_3$), 0.97 (s, 3H, $C^4\mathbf{H}_3$), 1.04 (s, 3H, $C^6\mathbf{H}_3$), 1.14 (s, 3H, $C^6\mathbf{H}_3$), 1.36 (m, 6H, 3×OCH_2CH_2C$\mathbf{H}_2$CH_3), 1.60 (m, 6H, 3×OCH_2C$\mathbf{H}_2$CH_2CH_3), 2.07 (ABq, 2H, $C^5\mathbf{H}_2$), 2.52 (s, 2H, $C^3\mathbf{H}_2$), 3.95, 4.02, 4.08 (3×tr, 6H, 3×OC$\mathbf{H}_2$CH_2CH_2CH_3), 5.44 (br d, 1H, =C$\mathbf{H^{1b}}$H^{1a}), 6.15 (d, J = 1.52 Hz, 1H, =CH$^{1b}\mathbf{H^{1a}}$).

^{1}H NMR (CD_3OD): δ 0.95, 0.97, 0.98 (3×s, 9H, 3×OCH_2-CH_2CH_2C$\mathbf{H}_3$), 1.00 (s, 3H, $C^4\mathbf{H}_3$), 1.05 (s, 3H, $C^6\mathbf{H}_3$), 1.16 (s, 3H, $C^6\mathbf{H}_3$), 1.43, 1.64 (2×m, 12H, 3×OCH_2C$\mathbf{H}_2$C$\mathbf{H}_2$CH_3), 2.11 (ABq, 2H, $C^5\mathbf{H}_2$), 2.55 (s, 2H, $C^3\mathbf{H}_2$), 3.98 (tr, 2H, OC$\mathbf{H}_2$CH_2-

CH_2CH_3), 4.06, 4.13 (2×m, 4H, 2×OC**H**$_2$$CH_2CH_2CH_3$), 5.54 (br d, 1H, =C**H**^{1b}H^{1a}), 6.17 (d, J = 1.52 Hz, 1H, =CH^{1b}**H**^{1a}).

^{13}C NMR ($CDCl_3$): δ 13.66 (3×$OCH_2CH_2CH_2$**C**H_3), 18.54 (C^4**C**H_3), 19.15, 19.20, 19.25 (3×OCH_2CH_2**C**H_2CH_3), 22.12 (C^6**C**H_3), 29.91 (C^6**C**H_3), 30.39, 30.47, 30.60 (3×OCH_2**C**H_2CH_2-CH_3), 41.46 (**C**^{6}), 42.98 (**C**^{3}H_2), 46.28 (**C**^{4}), 48.14 (**C**^{5}H_2), 64.37, 64.43, 64.65 (3×O**C**$H_2CH_2CH_2CH_3$), 127.8 (**C**^{1}H_2=C), 137.0 (CH_2=**C**^{2}), 167.4 (C^2**C**=O), 176.5 (C^4**C**=O), 178.2 (C^6**C**=O). Signals were assigned by analogy with the CD_3OD spectrum.

^{13}C NMR (CD_3OD): δ 14.21 (3×$OCH_2CH_2CH_2$**C**H_3), 19.65 (C^4**C**H_3), 20.43, 20.50, 20.56 (3×OCH_2CH_2**C**H_2CH_3), 23.08 (C^6**C**H_3), 30.53 (C^6**C**H_3), 31.69, 31.80, 31.96 (3×OCH_2**C**H_2CH_2-CH_3), 42.78 (**C**^{6}), 44.35 (**C**^{3}H_2), 47.48 (**C**^{4}), 49.38 (**C**^{5}H_2), 65.80, 65.91, 65.97 (3×O**C**$H_2CH_2CH_2CH_3$), 129.0 (**C**^{1}H_2=C), 138.6 (CH_2=**C**^{2}), 168.9 (C^2**C**=O), 178.2 (C^4**C**=O), 179.9 (C^6**C**=O). Signals assigned on the basis of connectivities seen in HMBC and HSQC spectra.

Mass spectrum (HR, EI): m/z 426.2977 ($C_{24}H_{42}O_6$ requires 426.2981).

Hydroxyethyl Methacrylate Dimer (2,2-Dimethyl-4-methylenepentanedioic Acid Bis(2-hydroxyethyl) Ester, HEMA$_2$). (a) A mixture of MAA$_2$ (0.14 g, 0.8 mmol), 2-bromoethanol (0.92 g, 7.3 mmol), and tetramethylammonium hydroxide (1.32 g, from 15 mL of ∼25% solution in methanol, 0.033 mol) in tetrahydrofuran (4 mL) and methanol (4 mL) was placed in a 25 mL vial with crimped Teflon seal and heated at 100 °C for 30 min. The mixture was then cooled to room temperature and filtered, rinsed with methanol, and the filtrate evaporated at 55 °C, 0.1 mmHg, 6 h to leave HEMA$_2$ (0.2 g, 95%). NMR indicates quantitative yield.

(b) An aqueous solution of cesium carbonate (9.8 g, 0.03 mol in 30 mL water) was slowly added to a solution of MAA dimer (5.2 g, 0.03 mol) in ethanol (90 mL). The resulting mixture was stirred at room temperature for 1 h then evaporated to dryness to leave the dicesium salt of the MAA dimer (13 g, 100% yield).

2-Bromoethanol (6.4 mL, 0.09 mol) was added to a suspension of the dicesium salt of the MAA dimer (17.4 g, 0.04 mol) in *N*-methylpyrrolidone (NMP, 40 mL) and the resulting mixture heated at 100 °C for 2 h. The mixture was filtered, the filtrate was transferred to a 100 mL round-bottom flask, and the NMP was removed by vacuum distillation (bp 32−42 °C, 0.1 mmHg). Water (50 mL) was added to the residue, and the resultant mixture was extracted with ethyl acetate five times. The combined organic layers were dried over magnesium sulfate. After removal of the solvent under reduced pressure the crude product was purified by bulb-to-bulb distillation on the Kugelrohr (Buchi model B-580, oven temperature 215 °C, 0.01 mmHg) to give HEMA$_2$ (6.2 g, 60%) as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 1.17 (s, 6H, 2×C^4**H**$_3$), 2.60 (s, 2H, C^3**H**$_2$), 3.55 (br s, 2H, O**H**), 3.77 (dd, 2H, C^4CO_2CH_2C**H**$_2$−OH), 3.80 (dd, 2H, C^2CO_2CH_2C**H**$_2$−OH), 4.13 (dd, 2H, C^4CO_2C**H**$_2$$CH_2$−OH), 4.20 (dd, 2H, C^2$CO_2$C**H**$_2$$CH_2$−OH), 5.57 (br d, 1H, =C**H**^{1b}H^{1a}), 6.23 (d, J = 1.29 Hz, 1H, =CH^{1b}**H**^{1a}).

^{1}H NMR (CD_3OD): δ 1.18 (s, 6H, 2×C^4**H**$_3$), 2.67 (s, 2H, C^3**H**$_2$), 3.73 (dd, 2H, C^4CO_2CH_2C**H**$_2$−OH), 3.77 (dd, 2H, C^2-CO_2CH_2C**H**$_2$−OH), 4.09 (dd, 2H, C^4CO_2C**H**$_2$$CH_2$−OH), 4.19 (dd, 2H, C^2$CO_2$C**H**$_2$$CH_2$−OH), 5.65 (br d, 1H, =C**H**^{1b}H^{1a}), 6.28 (d, J = 1.5 Hz, 1H, =CH^{1b}**H**^{1a}).

^{13}C NMR ($CDCl_3$) δ 25.07 (2×**C**^{4}H_3), 41.76 (**C**^{3}H_2), 42.64 (**C**^{4}), 60.72, 60.76, (2×O**C**H_2), 66.35 (C^4CO_2CH_2**C**H_2−OH), 66.62 (C^2-CO_2CH_2**C**H_2−OH), 128.6 (**C**^{1}H_2=C), 137.0 (CH_2=**C**^{2}), 167.8 (C^2**C**=O), 177.5 (C^4**C**=O). Signals were assigned by analogy with the CD_3OD spectra.

^{13}C NMR (CD_3OD): δ 25.47 (2×**C**^{4}H_3), 42.18 (**C**^{3}H_2), 44.21 (**C**^{4}), 61.11, 61.14 (2×O**C**H_2), 67.33 (C^4CO_2CH_2**C**H_2−OH), 67.60 (C^2CO_2CH_2**C**H_2−OH), 129.2 (**C**^{1}H_2=C), 139.1 (CH_2 = **C**^{2}), 169.2 (C^2**C**=O), 178.9 (C^4**C**=O). Signals were assigned on the basis of connectivities seen in HMBC and HSQC spectra.

Mass spectrum (HR, EI): m/z 242.1159 (M − H_2O) ($C_{12}H_{18}O_5$ requires 242.1154). Mass spectrum (ES$^+$): m/z 261.0 (M + 1).

Methacrylic Acid—Methyl Methacrylate—Methacrylic Acid Trimer (6-Carboxy-4-methoxycarbonyl-2,2,4-trimethylhept-6-enoic acid, MAA—MMA—MAA). A mixture of MMA$_3$ (10 g, 0.033 mol) in aqueous potassium hydroxide (100 mL) was stirred vigorously at room temperature for 16 h when the mixture was extracted with diethyl ether (2 × 50 mL) to remove any unreacted MMA$_3$ (this step is essential for high product purity). The aqueous phase was then acidified to pH ∼ 1 with concentrated HCl and extracted with ethyl acetate (3 × 100 mL). The extracts were dried over anhydrous $MgSO_4$, filtered, and evaporated under vacuum to leave MAA−MMA−MAA (8.9 g, ∼100%), mp 100−102 °C. MAA$_3$ could not be detected by NMR.

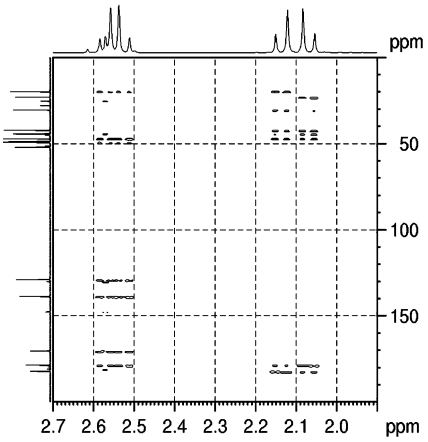


Figure 2. Portion of the gHMBC spectrum of MAA−MMA−MAA showing connectivities of methylene hydrogens. Spectrum recorded in CD_3OD (referenced to δ_H 3.30 and δ_C 49.15) at 25 °C/29 8K using a Bruker DRX500 spectrometer at 500.13 MHz for ^{1}H and 125.6 MHz for ^{13}C (see Experimental Section and text for further experimental details and assignments). Sample is contaminated by impurity **3** (see text).

^{1}H NMR (CD_3OD): δ 1.03 (s, 3H, C^6**H**$_3$), 1.11 (s, 3H, C^4**H**$_3$), 1.18 (s, 3H, C^6**H**$_3$), 2.10 (ABq, 2H, C^5**H**$_2$), 2.55 (ABq, 2H, C^3**H**$_2$), 3.60 (s, 3H, C^4CO_2C**H**$_3$), 5.53 (br d, 1H, =C**H**^{1b}H^{1a}), 6.20 (d, J = 1.20 Hz, 1H, =CH^{1b}**H**^{1a}).

^{13}C NMR (CD_3OD): δ 19.87 (**C**^{4}H_3), 23.09 (**C**^{6}H_3), 30.54 (**C**^{6}H_3), 42.35 (**C**^{6}), 44.52 (**C**^{3}H_2), 47.23 (**C**^{4}), 49.46 (**C**^{5}H_2), 52.14 (C^4CO_2**C**H_3), 129.1 (**C**^{1}H_2=C), 138.8 (CH_2 = **C**^{2}), 170.6 (C^2**C**=O), 178.7 (C^4**C**=O), 182.3 (C^6**C**=O). Signals were assigned on the basis of connectivities seen in HMBC and HSQC spectra—see text and Figure 2.

Mass spectrum (HREI): m/z 272.1263 ($C_{13}H_{20}O_6$ requires 272.1260). Mass spectrum (ES$^+$): m/z 273.1 (M + 1). Mass spectrum (ES$^-$): m/z 271.1 (M − 1).

Hydroxyethyl Methacrylate—Methyl Methacrylate—Hydroxyethyl Methacrylate Trimer (6-(2-Hydroxyethoxycarbonyl)-4-methoxycarbonyl-2,2,4-trimethyl-hept-6-enoic Acid 2-Hydroxyethyl Ester, HEMA—MMA—HEMA). An aqueous solution of cesium carbonate (1.2 g, 3.7 mmol, in 5 mL water) was added slowly to a solution of MAA−MMA−MAA trimer (1.0 g, 3.7 mmol) in ethanol (10 mL). The resulting mixture was stirred at room temperature for 1 h. Removing solvent on rotary evaporator until dryness gave the dicesium salt of MAA−MMA−MAA trimer (1.97 g, ∼100% yield).

A suspension of the dicesium salt of MAA−MMA−MAA trimer (1.97 g, 3.67 mmol) in *N*-methylpyrrolidone (NMP, 10 mL) was added to 2-bromoethanol (0.92 g, 0.52 mL, 7.35 mmol). The resulting mixture was heated at 100 °C for 4.5 h. The solution was filtered, the filtrate transferred to a 100 mL round-bottom flask, and the NMP was removed by vacuum distillation (0.05 mmHg, bath temperature 75 °C) to give HEMA−MMA−HEMA (1.35 g, ∼100% yield) as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 1.07 (s, 3H, C^{4}C**H**$_3$), 1.08 (s, 3H, C^{6}C**H**$_3$), 1.19 (s, 3H, C^{6}C**H**$_3$), 2.09 (ABq, 2H, C^5**H**$_2$), 2.56 (ABq, 2H, C^3**H**$_2$), 2.96 (br s, 4H, O**H**), 3.61 (s, 3H, C^4CO_2C**H**$_3$), 3.83 (m, 4H, C^6CO_2C**H**$_2$C**H**$_2$), 4.21 (m, 4H, C^6CO_2C**H**$_2$C**H**$_2$), 5.52 (br d, Hz, 1H, =C**H**^{1b}H^{1a}), 6.24 (d, J = 0.63 Hz, 1H, =CH^{1b}**H**^{1a}).

Table 1. Mark−Houwink−Sakurada (K, α) Coefficients Reported for Polystyrene and Poly(alkyl methacrylate)s in THF at 30 °C

polymer	K (g/L) × 10^8	α
PSty[41]	11.4	0.716
PMMA[42]	9.44	0.719
PEMA[41]	9.70	0.714
PnBMA[41]	14.8	0.664
PtBMA[a]	5.84	0.76
PEHMA[41]	5.18	0.720

[a] Mark−Houwink-Sakurada parameters for PtBMA have been reported as shown,[43,44] these were not obtained under GPC conditions and have not been used in our calculations, Instead, it is recommended that values for PMMA are used (see text).

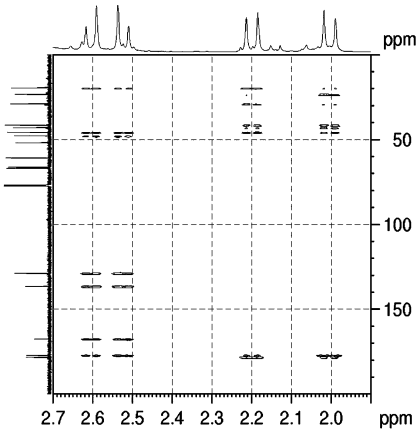


Figure 3. Portion of the gHMBC spectrum of HEMA−MMA−HEMA showing connectivities of methylene hydrogens. Spectrum recorded in $CDCl_3$ referenced to δ_H 7.26 and δ_C 77.03) at 25 °C/298 K using a Bruker DRX500 spectrometer at 500.13 MHz for ^1H and 125.6 MHz for ^{13}C (see Experimental Section and text for further experimental details and assignments).

^{13}C NMR ($CDCl_3$): δ 19.68 ($C^4\mathbf{C}H_3$), 23.38 ($C^6\mathbf{C}H_3$), 29.02 ($C^6\mathbf{C}H_3$), 41.62 ($\mathbf{C^6}$), 43.11 ($\mathbf{C^3}H_2$), 45.77 ($\mathbf{C^4}$), 47.90 ($\mathbf{C^5}H_2$), 51.96 ($C^4CO_2\mathbf{C}H_3$), 60.96, 61.02 (2×$\mathbf{C}H_2OH$), 66.34 (C^6-$CO_2\mathbf{C}H_2$), 66.82 ($C^2CO_2\mathbf{C}H_2$), 128.9 ($\mathbf{C^1}H_2$=C), 136.6 (CH_2=$\mathbf{C^2}$), 167.6 ($C^2\mathbf{C}$=O), 177.3 ($C^4\mathbf{C}$=O), 178.4 ($C^6\mathbf{C}$=O). Signals were assigned on the basis of connectivities seen in HMBC and HSQC spectra−see text and Figure 3.

Mass spectrum (HREI): m/z 360.1789 ($C_{17}H_{28}O_8$ requires 360.1784).

HEMA Macromonomer (HEMA$_n$). HEMA macromonomer was synthesized using the procedure described previously[6] from HEMA (35.2 g) in water (75 g) at 80 °C but with a higher concentration of iPrCo^{III}(DMG-BF_2)$_2$ (24 mg in initial mixture, 27.1 mg in feed). The crude macromonomer (95% conversion after 6 h, GPC $\bar{M}_n$ 900, $\bar{M}_w/\bar{M}_n$ 1.3) was isolated by freeze-drying it and then twice dissolving it in acetone and precipitating it into n-hexane. The molecular weight of the purified macromonomer was estimated by ^1H NMR (from relative intensity of olefinic resonances vs $C\mathbf{H}_2O$ resonances) to be 920. GPC: $\bar{M}_n$ (PMMA equivalents) 760; $\bar{M}_w/\bar{M}_n$ 1.3.

^1H NMR ($(CD_3)_2CO$): δ 1.05 (m, $C\mathbf{H}_3$), 2.05 (m, $C\mathbf{H}_2$), 2.84 (br s, O**H**), 3.76 (m, $CO_2C\mathbf{H}_2CH_2OH$), 4.05 (m, $CO_2CH_2C\mathbf{H}_2$-OH), 5.62 (s, =C$\mathbf{H^{1b}}$H^{1a}), 6.21 (s, =CH^{1b}$\mathbf{H^{1a}}$).

Transfer Constant Measurements. The following procedures are typical.

(a) Aliquots (1 mL) of a stock solution of AIBN (20.4 mg) in BMA (10.00 mL) were added to preweighed quantities of MMA_3 (0 mg, 10.1 mg, 19.2 mg and 30.5 mg) to give the concentrations shown in Table 2. After dissolution, the solutions were transferred to ampules, degassed with three freeze−pump−thaw cycles, and sealed under vacuum. The ampules were then heated at 60 °C for 60 min when the polymerization was quenched by cooling in liquid nitrogen. Samples of the monomer/polymer mixture were diluted with THF or $CDCl_3$ (for GPC and NMR analysis respectively).

(b) MMA (15 g) and AIBN (50.2 mg) were transferred to a 50 mL volumetric flask which was made up to the mark with 2-butanone (27.2 g) to give stock solution 1. $HEMA_2$ (100 mg) was placed in a 10 mL volumetric flask which was made up with solution 1 (8.37 g) to give stock solution 2. Aliquots of the two stock solutions were combined to give 5 mL of solution at the concentrations indicated in Table 4. The solutions were transferred to ampules and degassed with three freeze−pump−thaw cycles, and the ampules were sealed under vacuum. The ampules were then heated at 60 °C for 60 min when the polymerization was quenched by cooling in liquid nitrogen. Samples of the monomer/polymer mixture were diluted with THF or $CDCl_3$ (for GPC and NMR analysis respectively).

The initiator was selected according to the polymerization temperature: for 60 °C, azobis(isobutyronitrile) (AIBN); for 100 °C, *tert*-butyl peroxybenzoate (tBPB). Initiator concentrations were selected to give polymerization times ranging from

Table 2. Chain Transfer Constants of MMA Trimer (MMA3) in Polymerizations of Methacrylate

monomer	[MMA_3]/[MMA] × 10^3	$\bar{M}_n$[a]	$\bar{M}_w/\bar{M}_n$	convn (%)	$C_{tr(Mayo)}$[b,c]	C_{tr}(log CLD)[b,d]	C_{tr}(log CLD)[b,e]
MMA (bulk, 60°C)[3]						0.19[c]	0.19
EMA (bulk, 60°C)[f]	0	465 000	1.86	9.9	0.15	0.14	0.14
	0.068	74 600	1.79	n.d[h]			
	0.133	41 400	1.74	n.d[h]			
	0.206	28 000	1.74	n.d[h]			
nBMA (bulk, 60°C)[f]	0	578 000	1.81	10.0	0.16	0.19	0.17
	0.068	60 700	1.83	8.7			
	0.155	32 100	1.72	6.8			
	0.196	26 300	1.74	7.0			
tBMA (bulk, 60°C)[f]	0	445 000	1.84	9.8	0.18 ± 0.02	0.17 ± 0.02	0.17 ± 0.02[h]
	0.081	62 000	1.74	11.0			
	0.134	47 100	1.80	13.5			
	0.209	32 900	1.74	12.9			
2-EHMA (bulk, 60°C)[f]	0	1 030 000	1.63	(16.7)	0.25 ± 0.02	0.23	0.17
	0.068	55 100	1.79	6.5			
	0.152	23 700	1.96	7.6			
	0.207	16 700	1.91	3.8			
tBMA (bulk, 100°C)[g]	0	647 000	1.89	n.d[h]	0.16 ± 0.02	0.18	0.18[i]
	0.056	80 400	1.83	n.d[h]			
	0.096	55 300	1.73	n.d[h]			
	0.141	35 400	1.85	n.d[h]			

[a] Molecular weight in PMMA equivalents and rounded to three significant figures. [b] Errors are standard deviations from mean. Where no error is indicated it is less than ±0.01. [c] Chain transfer constant obtained from by direct application of Mayo method with $1/\bar{X}_n$ calculated from PMMA equivalent molecular weights shown. [d] Chain transfer constant obtained from number molecular weight distribution by log *C*LD method. [e] Chain transfer constant obtained after calibration had been corrected using Mark−Houwink−Sakurada coefficients (Hutchinson). [f] Initiator [AIBN] = 6.1 × 10^{-3} M, polymerization time 60 min. [g] Initiator [tBPB] = 3.4 × 10^{-3} M, polymerization time 45 min. [h] Not determined directly but estimated to be <10%. [i] Mark−Houwink−Sakurada parameters not available. Those for PMMA assumed to give correct molecular weight (see text).

Table 3. Chain Transfer Constants of Methacrylic Trimers (RMA_3) and HEMA Macromonomer ($HEMA_n$) in MMA Polymerization

trimer	([RMA_3]/[MMA]) × 10^3	$\bar{M}_n$[a]	$\bar{M}_w/\bar{M}_n$	convn (%)	C_{tr}(log CLD)[b,c]	$C_{tr(Mayo)}$[b,d]	$C_{tr(Mayo)}$[b,e]
MMA_3 (bulk, 60 °C)[3]					0.19	0.20	0.19
MMA_3 (3 M MMA in 2-butanone, 60 °C)[f]	0	84 800	1.82	9.9	0.19	0.14 ± 0.04	0.18 ± 0.02
	6.77	43 100	1.74	11.5			
	12.98	27 500	1.82	13.1			
	26.40	32 700	1.61	13.8			
MMA_3 (3 M MMA in 2-butanone, 100 °C)[g]	0	122 000	1.70	10.0	0.19 ± 0.02	0.19 ± 0.05	0.21 ± 0.02
	6.44	38 300	2.04	20.6			
	13.21	21 500	2.24	21.5			
	21.75	20 500	1.74	19.4			
MAA_3 (3 M MMA in 2-butanone, 60 °C)[h]	0	82 400	1.71	8.2	0.26 ± 0.02	0.27 ± 0.04	0.27 ± 0.02
	6.45	38 000	1.71	10.1			
	9.81	27 000	1.84	9.2			
	12.64	21 800	1.87	9.4			
MAA_3 (3 M MMA in 2-propanol, 60 °C)[i,j]	0	110 000	1.76	4.6		0.20 ± 0.02	0.22 ± 0.02
	6.58	43 300	1.78	5.0			
	12.64	31 800	1.73	6.3			
	26.31	15 900	1.89	8.3			
MAA_3 (3 M MMA in 2-butanone, 100 °C)[k]	0	232 000	2.02	10.3	0.27 ± 0.01	0.28 ± 0.05	0.32 ± 0.02
	5.18	53 200	1.90	11.0			
	7.78	33 200	2.03	17.1			
	12.96	25 000	1.79	17.7			
BMA_3 (3 M MMA in 2-butanone, 60°C)[l]	0	65 200	2.05	14.1	0.18	0.16 ± 0.01	0.20
	7.88	33 900	1.90	9.0			
	14.97	25 400	1.73	8.5			
	23.78	18 400	1.75	4.8			
BMA_3 (3 M MMA in 2-butanone,100°C)[m]	0	141 000	3.07	11.4	0.20 ± 0.02	0.17 ± 0.02	0.21 ± 0.02
	6.44	51 100	1.65	8.5			
	13.21	26 400	1.77	4.5			
	21.75	18 800	1.93	3.5			
HEMA−MMA−HEMA (3 M MMA in 2-butanone, 60 °C)[n]	0	134 000	1.64	11.4	0.19 ± 0.02	0.16	0.18
	4.52	63 000	1.79	12.3			
	6.78	53 900	1.74	14.1			
	11.30	38 000	1.81	14.4			
HEMA−MMA−HEMA (3 M MMA in 2-butanone, 100 °C)[o]	0	224 000	1.70	15.7	0.23	0.21	0.22
	3.81	87 600	1.78	15.6			
	5.72	63 200	1.74	14.9			
	9.53	41 600	1.85	15.1			
$HEMA_n$ ($\bar{M}_n$ 920) (3 M MMA in 2-propanol, 60 °C)[p]	0	154 000	2.97	n.d[q]	0.23	0.18 ± 0.02	0.26 ± 0.03
	4.36	64 300	1.74	n.d[q]			
	6.54	51 600	1.67	n.d[q]			
	10.90	38 500	1.56	n.d[q]			

[a] Molecular weights rounded to three significant figures. [b] Errors in C_{tr} are standard deviations from mean. Where no error is indicated, it is less than ±0.01. [c] log CLD (chain length distribution) method. [d] Chain transfer constant obtained from by direct application of conventional Mayo method by taking slope of plot of $1/\bar{X}_n$ vs [RMA_3]/[MMA]. [e] Chain transfer constant obtained by application of modified Mayo method by taking slope of plot of $2/\bar{X}_w$ vs [RMA_3]/[MMA]. [f] Initiator [AIBN] = 1.25×10^{-2} M; polymerization time 50 min. [g] Initiator [tBPB] = 3.1×10^{-3} M; polymerization time 60 min. [h] Initiator [AIBN] = 1.25×10^{-2} M; polymerization time 45 min. [i] Initiator [AIBN] = 1.20×10^{-2} M; polymerization time 45 min. [j] Some precipitation of polymer observed. [k] Initiator [tBPB] = 1.6×10^{-3} M; polymerization time 60 min. [l] Initiator [AIBN] = 1.24×10^{-2} M; polymerization time 60 min. [m] Initiator [tBPB] = 1.6×10^{-3} M; polymerization time 40 min. [n] Initiator [AIBN] = 6.1×10^{-3} M; polymerization time 60 min [o] Initiator [tBPB] = 3.4×10^{-3} M; polymerization time 60 min. [p] Initiator [AIBN] = 6.1×10^{-3} M; polymerization time 60 min. [q] Not determined directly but estimated to be <15%.

30 to 60 min and ranged from 0.1 to 5 × 10^{-3} mol/L. Polymerization times were selected such that conversion of monomer to polymer was less than 15%.[26] Details appear in Tables 2−4.

The conversion of monomer to polymer was determined by ^{1}H NMR on polymerization mixtures diluted with $CDCl_3$ and confirmed gravimetrically. The conversion was estimated from the relative intensities of the ester OCH_2R resonances for monomer and polymer. Where individual OCH_2R resonances of monomer and polymer were not sufficiently resolved, the intensity of the olefinic protons was used to correct for the monomer contribution.

Two Dimensional NMR. ^{1}H and ^{13}C NMR spectra of MAA−MMA−MAA were recorded in CD_3OD (referenced to δ_H 3.30 and δ_C 49.15) and of HEMA−MMA−HEMA were recorded in $CDCl_3$ (referenced to δ_H 7.26 and δ_C 77.03) at 25 °C/298 K using a Bruker DRX500 spectrometer at 500.13 MHz for ^{1}H and 125.6 MHz for ^{13}C. For **^{1}H** spectra, 32K data points were collected for the FID, over a sweep width of 7500 Hz (0.23 Hz/pt). For **^{13}C** spectra, 64K data points were collected for the FID over a sweep width of 30300 Hz (0.46 Hz/pt). The 2D experiments used standard Bruker library sequences with the following parameters: COSY (cosygpqf) 4096 FID data points, 3500 Hz sweep width, 0.58 s acquisition time, 0.7 s relaxation delay, 1 scan, 512 experiments, multiplied by an unshifted sine function in both dimensions and Fourier transformed over 2098 × 1024 points; HSQC (invietgp) 2048 FID data points, 3500 Hz sweep width, 0.29 s acquisition time, 1.0 s relaxation delay, $^1J_{CH}$ = 140 Hz, 1 scan, 512 experiments, multiplied by an $\pi/2$-shifted sine-squared function in both dimensions and Fourier transformed over 2098 × 1024 points; HMBC (inv4gplplrndqf) 4098 FID data points, 3500 Hz sweep width, 0.58 s acquisition time, 0.7 s relaxation delay, 2 scans, 512 experiments, 3.57 ms low-pass J-filter ($^1J_{CH}$ = 140 Hz), 62.5 ms delay for evolution of long-range coupling ($^nJ_{CH}$ = 8 Hz), multiplied by an $\pi/2$-shifted sine function in both dimensions and Fourier transformed over 2098 × 1024 points.

Portions of the HMBC spectra of MAA−MMA−MAA and HEMA−MMA−HEMA are shown in Figures 2 and 3, respectively.

Results and Discussion

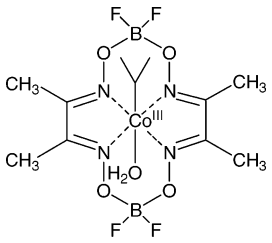
Macromonomer Synthesis and Characterization. The MMA macromonomers MMA_2 and MMA_3

Table 4. Chain Transfer Constants of Methacrylic Dimers (RMA)2 in MMA Polymerization

dimer	$[RMA_2]/[MMA] \times 10^3$	$\bar{M}_n$[a]	$\bar{M}_w/\bar{M}_n$	% convn	C_{tr}[b]
MMA_2 (bulk, 60 °C)					0.013[c,3]
					0.008[d,3]
					0.015[e,3]
					0.012 ± 0.002[f]
MMA_2[3] (bulk, 100 °C)					0.018[c,3]
					0.018[d,3]
					0.018[e,3]
$HEMA_2$ (bulk MMA, 60 °C)[g]	0	361 000	1.68	13.5	0.019 ± 0.002[c]
	2.05	344 000	1.78	10.3	0.015 ± 0.002[d]
	4.71	276 000	1.82	13.1	0.018 ± 0.002[e]
	10.14	224 000	1.95	12.4	
	29.59	140 000	1.76	13.3	
$HEMA_2$[e](3 M MMA in 2-butanone,60°C)[g,h]	0	111 000	1.81	7.77	0.014 ± 0.002[c]
	2.56	108 000	1.77	8.78	0.009 ± 0.001[d]
	10.25	100 000	1.72	7.57	0.014 ± 0.002[e]
	12.81	98 800	1.71	6.47	
$HEMA_2$ (3 M MMA in 2-butanone,80°C)[i]	0	195 000	1.87	4.15	0.017 ± 0.001[c]
	5.54	163 000	1.87	9.07	0.015 ± 0.002[d]
	8.31	156 000	1.88	8.68	0.018 ± 0.002[e]
	13.85	138 000	1.83	7.80	
$HEMA_2$ (3 M MMA in 2-butanone,100°C)[j]	0	264 000	1.83	10.8	0.031 ± 0.008[c]
	5.13	190 000	1.99	10.2	0.027 ± 0.012[d]
	7.69	149 000	2.22	12.9	0.027 ± 0.002[e]
	12.83	142 000	1.87	14.5	

[a] Molecular weights rounded to three significant figures. [b] Errors are standard deviation from mean. [c] Chain transfer constant obtained with log CLD (chain length distribution) method. [d] Chain transfer constant obtained from by direct application of conventional Mayo method by taking slope of plot of $1/\bar{X}_n$ vs $[RMA_2]/[MMA]$. [e] Chain transfer constant obtained from by application of modified Mayo method by taking slope of plot of $2/\bar{X}_w$ vs $[RMA_2]/[MMA]$. [f] Chain transfer constant from rate of consumption of MMA_2 as a function of monomer conversion. [g] Initiator [AIBN] = 6.1×10^{-3} M; polymerization time 60 min. [h] Some baseline artifacts evident in GPC traces. [i] Initiator [AIBN] = 3.8×10^{-4} M; polymerization time 60 min. [j] Initiator [tBPB] = 3.4×10^{-3} M; polymerization time 45 min.

were separated by fractional distillation from reaction mixtures prepared by bulk polymerization of MMA in the presence of *i*Pr−Co^{III}(DMG-BF_2)$_2$−H_2O as described

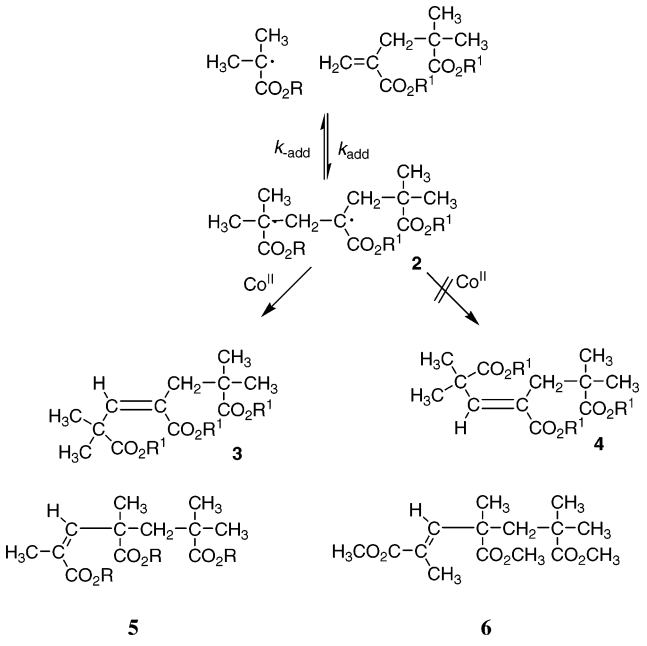


***i*Pr-Co^{III}(DMG-BF_2)$_2$-H_2O**

previously. MAA_2 and MAA_3 were prepared by exhaustive alkaline hydrolysis of MMA_2 and MMA_3 using reflux conditions. Hydrolysis of MMA_3 under mild conditions (room temperature, 24 h) gave selective hydrolysis of the end group methyls to give MAA−MMA−MAA. Selective hydrolysis or transesterification of the chain ends of PMMA has previously been reported in the patent literature.[27] The $HEMA_2$, $HEMA_3$, HEMA−MMA−HEMA, and BMA_3 were prepared by esterification of the corresponding MAA macromonomers by alkylation of the cesium or trimethylammonium salts. These reactions proceeded in near quantitative yield with 2-bromoethanol or 1-iodobutane as the alkylating agent as appropriate. No exchange of the central MMA was observed in the case of HEMA−MMA−HEMA. The process of mild hydrolysis followed by esterification offers a convenient route to di-end-functional macromonomer transfer agents useful for telechelic synthesis.

HEMA macromonomer $HEMA_n$ was prepared by catalytic chain transfer with *i*Pr−Co^{III}(DMG-BF_2)$_2$−H_2O in aqueous solution as previously described.[6] The use of the cobalt(III) complex, which generates the active cobalt(II) species in situ, offers significant advantages over the direct use of the corresponding cobalt(II)

Scheme 2



complex[28,29] because of its enhanced air stability as a solid and in solution at room temperature.

Samples of the MMA trimer isolated from high (>90%) conversion polymerizations were contaminated with significant amounts (up to 5%) of a compound that is assigned the structure **3** (R = R^1 = CH_3). This compound is isomeric with the trimer MMA_3 but has an internal double bond. The compound is different from the internal double bond trimer **6** synthesized by McCord et al.[30] by isomerization of MMA_3 (stereochemistry unspecified, but reported NMR chemical shifts are consistent with olefinic H cis to CO_2Et). We believe that **3** is derived from radical **2** which is formed by the monomeric radical adding to MMA_2 as shown in Scheme 2. The isomer **4** (R = R^1 = CH_3) was not observed. The preferential formation of **3** is rationalized on steric

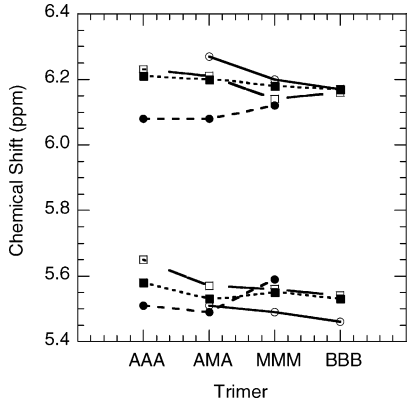


Figure 4. ^{1}H NMR chemical shifts of olefinic protons of methacrylate trimers (AAA = MAA_3, AMA = MAA−MMA−MAA, MMM = MMA_3, BBB = BMA_3) as a function of solvent: (a) $CDCl_3$ (○, ——); (b) acetone-d_6 (□, — —); (c) CD_3OD (■, – –); (d) DMSO-d_6 (●, - - -). In all solvents, the high-field signal is $\mathbf{H}^{1b}$ (trans to CO_2R) and the low-field signal is $\mathbf{H}^{1a}$ (cis to CO_2R)—refer to Figure 1.

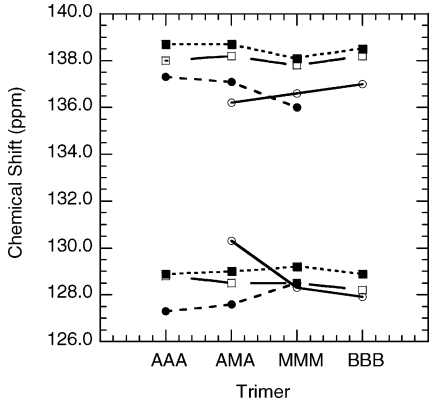


Figure 5. ^{13}C NMR chemical shifts of olefinic carbons of methacrylate trimers (AAA = MAA_3, AMA = MAA−MMA−MAA, MMM = MMA_3, BBB = BMA_3) as a function of solvent: (a) $CDCl_3$ (○, ——); (b) acetone-d_6 (□, — —); (c) CD_3OD (■, – –); (d) DMSO-d_6 (●, - - -). Concentrations used were 28.5 and 75 mg mL^{-1}. In all solvents, the high-field signal is $-\mathbf{C}^{2}=$ and the low-field signal is $=\mathbf{C}^{1}H_2$—refer to Figure 1 for the numbering scheme.

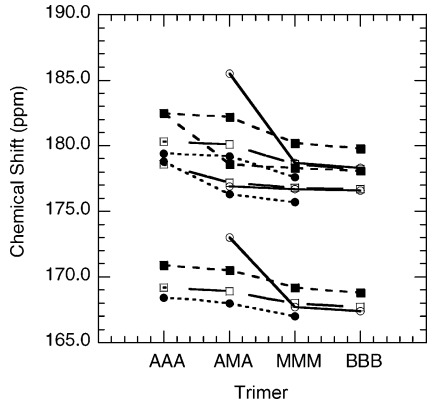


Figure 6. ^{13}C NMR chemical shifts of carbonyl carbons of methacrylate trimers (AAA = MAA_3, AMA = MAA−MMA−MAA, MMM = MMA_3, BBB = BMA_3) as a function of solvent: (a) $CDCl_3$ (○, ——); (b) acetone-d_6 (□, — —); (c) CD_3OD (■, – –); (d) DMSO-d_6 (●, - - -). Concentrations used were 28.5 and 75 mg mL^{-1}. In all solvents, the high-field signal is $=C^{2}(\mathbf{C}O)-$ and the low-field signal is $-C^{6}(\mathbf{C}O)(CH_3)_2$—refer to Figure 1 for numbering scheme.

grounds since it has the two largest groups in a trans configuration. The radical **2** has been reported[21,31] as long-lived and is substantially more stable to fragmentation relative to similar adducts formed from higher macromonomers. This may explain why analogous byproducts are not observed as contaminants in syntheses of higher molecular weight macromonomers. The amount of the contaminant **3** can be minimized by limiting the conversion. The contaminant appears inert under the polymerization conditions.

Two studies on polymerization of methacrylates with catalytic chain transfer in the presence of high concentrations MMA_2 have appeared.[20,32] Neither study reported formation of products analogous to **3**. However, such products were not considered as possibilities and they would not be distinguishable from the products proposed to be formed by mass spectrometric analysis performed. Further analysis of these reactions is warranted.

The positions of the ester groups of the mixed trimers MAA−MMA−MAA and HEMA−MMA−HEMA was proved by 2D NMR long range $^{13}C-^{1}H$ correlation spectroscopy (HMBC). Portions of the HMBC spectra are shown as Figures 2 and 3. Hydrogens H^{3a} and H^{3b} (refer to Figure 1) are nonequivalent and show connectivity with the olefinic carbons C^1 and C^2, the carbonyls at C^2 and C^4, and the methyl at C^4. Hydrogens H^{5a} and H^{5b} are also nonequivalent and show connectivity with the carbonyls at C^4 and C^6, the methyl at C^4 and the methyls at C^6. Thus, the carbonyl of the MMA unit (C^4) in MAA−MMA−MAA and HEMA−MMA−HEMA shows connectivity to each of the methylene hydrogens H^{3a}, H^{3b}, H^{5a}, and H^{5b}.

There have been several previous studies on the NMR of MMA macromonomers.[30,33] The methylene hydrogens and the terminal methyls of MMA oligomers are nonequivalent. This is due to their adopting strongly preferred conformation with little configurational exchange on the NMR time scale. These preferred conformations depend on the particular macromonomer. This is indicated by the ^{1}H NMR chemical shift separation of the methylene hydrogens (H^{5a} and H^{5b}, refer to Figure 1) and to a lesser extent (H^{3a} and H^{3b}) being most marked in the case of the MMA-centered trimers (MMA_3, HEMA−MMA−HEMA, and MAA−MMA−MAA) and smallest in the case of BMA_3 and MAA_3.

The NMR spectra of the various oligomers were determined in various solvents and concentrations. There appears to be some dependence of the spectra on solvent (acetone-d_6, $CDCl_3$, DMSO-d_6, CD_3OD) but no significant dependence on concentration (28.5−75 mg mL^{-1}). The chemical shifts of the olefinic hydrogens and carbons are reported in Figures 4 and 5. Those of the carbonyl carbons are given in Figure 6.

Transfer Constant Determination. Chain transfer constants ($C_{tr} = k_{tr}/k_p$) are traditionally obtained using the number-average degree of polymerization and the Mayo equation (eq 1b)[34]

$$\frac{1}{\bar{X}_n} = \frac{1}{\bar{X}_{n0}} + C_{tr}\frac{[S]_0}{[M]_0} \qquad (1b)$$

where $\bar{X}_n$ is the average degree of polymerization, $\bar{X}_{n0}$ is the average degree of polymerization in the absence of added transfer agent, $[S]_0$ is the initial concentration of transfer agent, and $[M]_0$ is the initial monomer concentration. We showed in an earlier publication that a method based on analysis of number molecular weight

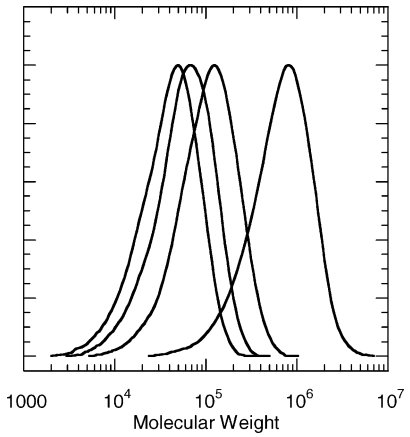


Figure 7. Normalized GPC molecular weight distributions for polymerizations of EMA in the presence of MMA trimer. Experimental conditions are reported in Table 2. Molecular weight axis is in PMMA equivalents.

distributions (the log CLD method) can provide improved accuracy and precision with respect to data obtained with the traditional Mayo analysis.[3,35] The method is based on the use of eq 2, which has its origin in the work of Gilbert and co-workers.[23]

$$\frac{\mathrm{d}(\ln P_i)}{\mathrm{d}i} \propto -\left(C_\mathrm{M} + C_\mathrm{tr}\frac{[\mathrm{S}]_0}{[\mathrm{M}]_0}\right) \qquad (2)$$

where P_i is the concentration of chains of length i. The method also eliminates problems due to low molecular weight contaminants (e.g., the residual macromonomer) and minor baseline fluctuations in the GPC trace.[3,35] The greatest reproducibility is obtained by taking the slope in a region around the maximum peak intensity. However, for proportionality between $\mathrm{d}(\ln P_i)/\mathrm{d}i$ and $[\mathrm{S}]_0/[\mathrm{M}]_0$ to be maintained, it is important when applying this method to be systematic in choosing the region over which the slope is taken. In the present work, we have taken the slope by least squares regression analysis over the top 10% of the GPC distribution plot. Some reported difficulties in applying the log CLD method may be attributed to not being systematic in this regard. We also showed empirically[3,35] that use of values $2/\bar{X}_\mathrm{w}$ rather than $1/\bar{X}_\mathrm{n}$ can provide data which are less dependent on baseline selection. This strategy has also recently been promoted by others[36,37] as a means of obtaining reproducible transfer constants. Figure 7 shows GPC traces, Figure 8 the slope plots, and Figure 9 the Mayo type plots for the polymerization of EMA in the presence of MMA_3 at 60 °C (refer to Table 2).

The conventional methods for measuring transfer constants are not strictly applicable to systems which give reversible chain transfer.[38,39] The macromonomer product from chain transfer to dimer will be a much better chain transfer agent than the dimer itself. However, when transfer constants are low (<1) and conversions are small ($MMA_n \sim 0$) , errors introduced are negligible. The expression (eq 3)[38,39]

$$\frac{\mathrm{d}[\mathrm{MMA_3}]}{\mathrm{d}[\mathrm{MMA}]} \approx C_\mathrm{tr}\frac{[\mathrm{MMA_3}]}{[\mathrm{MMA}] + C_\mathrm{tr}[\mathrm{MMA_3}] + C_{-\mathrm{tr}}[\mathrm{MMA_n}]} \qquad (3)$$

where $C_{-\mathrm{tr}}$ describes how the expelled radical ($MMA_2^\bullet$) partitions between adding MMA_3 and MMA then devolves to eq 4.

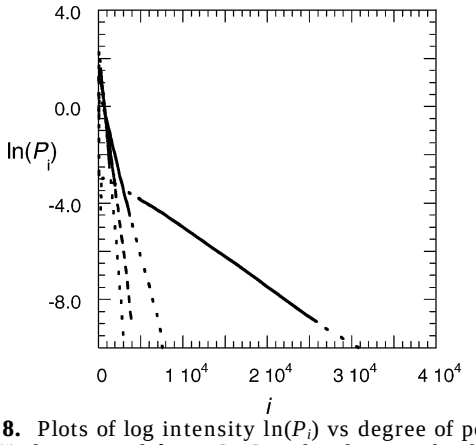


Figure 8. Plots of log intensity $\ln(P_i)$ vs degree of polymerization (i) determined from GPC molecular weight distributions for polymerizations of EMA in the presence of MMA trimer. Experimental conditions are reported in Table 2. The solid line indicates the region from which the slope was taken corresponding to the peak of the molecular weight distributions (Figure 7).

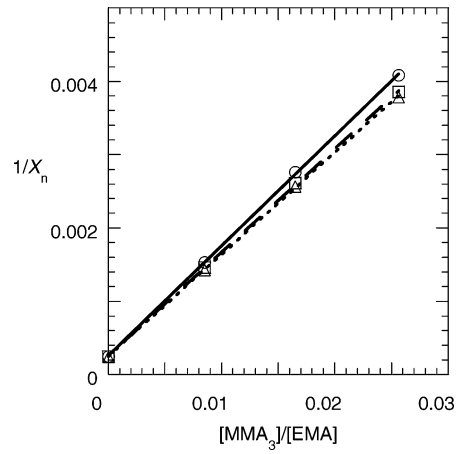


Figure 9. Mayo-like plots of normalized slopes $[-(\mathrm{d}(\ln P_i)/\mathrm{d}i)]$ and $1/\bar{X}_\mathrm{n}$ vs $[\mathrm{MMA_3}]_0/[\mathrm{EMA}]_0$ for polymerizations of EMA in the presence of MMA trimer. Experimental conditions and derived transfer constants are reported in Table 2: (□, — —) slopes from log CLD plots based on uncorrected molecular weight distributions in PMMA equivalent molecular weight; (△, - - -) slopes from log CLD plots based on molecular weight distributions corrected using Mark–Houwink-Sakaruda constants shown in Table 1, (○, —) values of $1/\bar{X}_\mathrm{n}$).

$$\frac{\mathrm{d}[\mathrm{MMA_3}]}{\mathrm{d}[\mathrm{MMA}]} \approx C_\mathrm{tr}\frac{[\mathrm{MMA_3}]}{[\mathrm{MMA}]} \qquad (4)$$

or

$$C_\mathrm{tr} \approx \frac{\mathrm{d}(\ln[\mathrm{MMA_3}])}{\mathrm{d}(\ln[\mathrm{MMA}])} \qquad (5)$$

and the slope plot of $\ln[\mathrm{MMA_3}]$ vs $\ln[\mathrm{MMA}]$ yields the transfer constant as in the classical treatment.[40] Transfer constants of MMA_2 and MMA_3 in bulk polymerization of MMA at 60 °C were evaluated by determining the rate of consumption of the reagent as a function of monomer conversion. The concentration of macromonomer at various conversions was calculated form the found and calculated molecular weights as described previously[38] and the experimental data used are provided in our earlier publication.[3] Values of transfer constants obtained, 0.200±0.004 for MMA_3 (Figure 10)

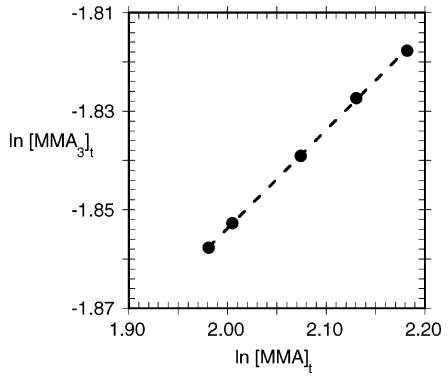


Figure 10. Double log plot of transfer agent concentration vs monomer concentration for bulk polymerization of MMA in the presence of MMA_3 (**1**) at 60 °C. $[MMA_3]_0 = 0.162$ M, $[MMA]_0 = 8.86$ M, and [AIBN] = 0.00625 M. The line of best fit is −2.2539 + 0.20008 ln[M]; correlation coefficient = 0.99988.

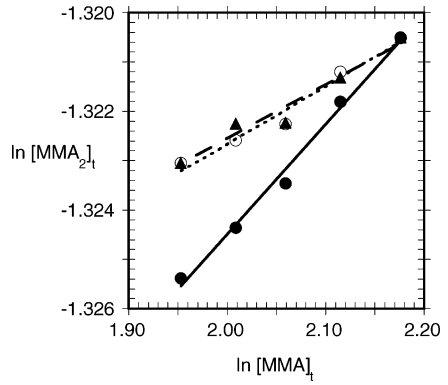


Figure 11. Double log plots of transfer agent concentration vs monomer concentration for bulk polymerization of MMA in the presence of MMA_2 dimer 60 °C. $[MMA_2]_0 = 0.267$ M, $[MMA]_0 = 8.81$ M, [AIBN] = 0.00625 M. Key: (a) with no allowance for initiator derived chains (●, —; line of best fit −1.3692 + 0.02333 ln[M], correlation coefficient 0.99586), with number of initiator derived chains (I) calculated with the relationship $I = df[AIBN]_0(1 - \exp(1\text{-}k_d t)$ with $df = 1.0$ and $k_d = 9.7 \times 10^{-6}$ s^{-1} (○, – –; line of best fit −1.3462 + 0.01178 ln[M], correlation coefficient 0.98459), with number of initiator-derived chains calculated on the basis of control experiments carried out in the absence of transfer agent using the relationship $I = ([MMA]_0\text{-}[MMA]_t)/\bar{X}_n$ (▲, - - -; line of best fit −1.3445 + 0.010981 ln[M], correlation coefficient 0.97801).

and 0.012±0.002 for MMA_2 (Figure 11), are in very close agreement with those obtained by application of the Log CLD method and other methods (compare with data in Table 2).[3]

In this work, the GPC was calibrated with narrow polydispersity PMMA standards. Universal calibration was used to correct for hydrodynamic volume differences between the various poly(alkyl methacrylates) and PMMA. This requires reliable values of the required Mark−Houwink−Sakurada coefficients. There are discrepancies between literature values (e.g., for polystyrene or PMMA) even when parameters are ostensibly obtained under the same experimental conditions (THF, 25−30 °C). In this work we have, where possible, used Mark−Houwink−Sakurada coefficients reported by Hutchinson et al.[41,42] These values are summarized in Table 1. As a simple test of the validity of Mark−Houwink−Sakurada parameters under our chromatographic conditions, a polystyrene calibration formed with polystyrene standards was exactly transformed into a PMMA calibration by universal calibration. The GPC Mark−Houwink−Sakurada coefficients reported for poly(*tert*-butyl methacrylate) (Table 1)[43,44] were obtained under different experimental conditions and may not be directly applicable under our chromatographic conditions. We have analyzed poly(*tert*-butyl methacrylate) using triple detector (viscometry−light scattering) GPC and found that the molecular weight is the same within experimental error as that predicted by conventional calibration with PMMA standards. The molecular weights reported for poly(*tert*-butyl methacrylate) are therefore given as PMMA equivalents.

Transfer constants measured for MMA_3 with various methacrylate monomers are given in Table 2. Transfer constants for various trimers (RMA_3) and dimers (RMA_2) in MMA polymerization are provided in Tables 3 and 4, respectively.

Apparent transfer constants evaluated from the molecular weight distributions in PMMA equivalents show a small increase with increasing length of the alkyl group in the series Et < Bu < 2EH (see Table 2). This small dependence disappears when the molecular weight distributions are transformed to absolute units using universal calibration. We conclude that the dependence is not due to differences in the transfer constants, rather it reflects differences in the hydrodynamic volume of the polymers. This result suggests a need for care when considering literature transfer constant data where molecular weight data are quoted only in polystyrene (or other) equivalents rather than in absolute units.

Discussion

For the case of addition of a MMA propagating radical to a MMA macromonomer (MMA_n), the intermediate radical (**3**) is expected to partition equally between starting materials and products. The transfer constant will therefore be determined mainly by the rate constant for addition of the propagating radical to the macromonomer (k_{add}). This suggests that k_{add} is ca. 40% of the value of the rate constant for addition to monomer (k_p).

The length of the ester alkyl group in either the alkyl methacrylate monomer or the trimer (RMA_3) has little if any effect on values of the transfer constant (refer to Table 5). This can indicate either that the alkyl group has little effect on the value of k_{add} or the partitioning of the adduct radical or that any effect on k_{add} is balanced by an effect on the partition coefficient.

Our results for C_{tr} may be compared with literature data on the reactivity of alkyl methacrylates in free radical polymerization (Tables 5 and 6). Propagation rate constants (k_p.) for various alkyl methacrylates, MAA, and HEMA have been determined by pulsed laser photolysis. Values at 60 °C are summarized in Table 6. Those for alkyl methacrylates show a trend to increase slightly with the length of the alkyl chain. Since values of C_{tr} appear independent of the length of the ester chain, we must conclude that the values of k_{tr} for MMA_3 in the alkyl methacrylates show a similar dependence to k_p. Reported propagation rate constants for MAA and HEMA are significantly higher than those of the alkyl methacrylates (and show solvent dependence). The rate constants k_{tr} are therefore also higher in these monomers. We conclude that the rate constants k_p and k_{tr} (and most likely k_{add}) are more strongly influenced by structural features of the propagating radical than of the macromonomer or monomer.

There are no direct data on k_{add} for the reaction of propagating radicals with RMA_n. However, we antici-

Table 5. Effects of Ester Alkyl Group on Transfer Constants of Methacrylates

	C_{tr}							
monomer	MMA_3[a] (60 °C)	RMA_3[b] (60 °C)	BMP[a,c] (70 °C)	iOMP[a,d] (70 °C)	tDDM[a,e] (70 °C)	$Co^{II}(DMG\text{-}BF_2)_2$[a,f] (60 °C)		
MMA	0.19	0.19	0.54[53]	0.86[53]	0.11[53]	28 100[43]	39 600[56]	34 000[55]
EMA	0.14							27 000[55]
nBMA	0.17	0.18	0.28[53]	0.47[53]	0.11[53]	16 100[43]	27 700[56]	16 000[55]
EHMA	0.17						11 800[56]	
tBMA	0.18					15 100[43]		
MAA		0.26						
HEMA		0.19				610[28]		

[a] Transfer constant of reagent in polymerization of monomer (column 1). [b] Transfer constant of trimer based on monomer (column 1) in MMA polymerization. [c] Butyl 3-mercaptopropionate. [d] Isooctyl 3-mercaptopropionate. [e] *tert*-Dodecyl mecaptan. [f] bis[difluoroboryl(dimethylglyoximato)cobalt(II) [$Co^{II}(DMG\text{-}BF_2)_2$].

Table 6. Effects of Ester Alkyl Group on Reactivity of Methacrylates

	C_{tr} MMA_3[a] (60 °C)	k_{tr} ($M^{-1}s^{-1}$) MMA_3[a] (60 °C)	C_{tr} RMA_3[b] (60 °C)	k_{tr} ($M^{-1}s^{-1}$) RMA_3[b] (60 °C)	k_p ($M^{-1}s^{-1}$)[a] (60 °C)	r_{MMA}, r_{RMA}[b] (60°C)
MMA	0.19	160	0.19	160	830[57]	(1.0)
EMA	0.14	120			870[57]	0.81, 0.86
						1.16, 1.00
						1.08, 1.08
						0.94, 1.01[c]
nBMA	0.17	140	0.18	180	980[57]	0.87, 0.93[53]
						0.93, 1.22[58]
						0.91, 1.09[c]
EHMA	0.17	140			1184[41]	
tBMA	0.18	150			1100,[59] 840[43]	0.96, 1.35
MAA			0.26	260	1000[60,61,d]	0.78, 0.33[d,48]
					1500[60,e]	0.31, 0.63[e,48]
					6900[60,f]	0.87, 1.10[c]
HEMA			0.19	690	3300[62]	0.82, 0.63[g]
						0.19, 0.81[h]
						0.75, 1.50[i]
						0.31, 1.68[c]
						0.90, 1.07[j]

[a] In bulk. Calculated from Arrhenius parameters given in the references indicated and rounded to two significant figures. [b] Numbers taken from the *Polymer Handbook*[49] unless indicated otherwise. [c] Calculated from $Q-e$ values of Greenley.[51] [d] In methanol. [e] In dimethyl sulfoxide. [f] In water. [g] In *N*,*N*-dimethylformamide. On the basis of data in the original paper[63] reactivity ratios may be reversed. [h] In bulk. [i] In bulk at 80 °C. [j] Calculated from $Q-e$ values of Young.[50]

pate that the values of k_{add} for dimers (RMA_2) should be similar or greater than that of trimers (RMA_3) and macromonomers (RMA_n) (k_{add} ~40% k_p—see above). The values of k_{add} for *tert*-butoxy radicals adding MMA_2 and CMA_2 are reported to be approximately 2-fold higher than those for adding MMA_3 and CMA_3 respectively.[45] The very much lower transfer constant of the dimers (RMA_2) is therefore attributed to the partition coefficient lying in favor of the starting materials and is explicable in terms of steric factors.[3,38,46,47] The increase in transfer constant of RMA_2 with increasing temperature is attributed to the partitioning of the adduct becoming less selective.

The transfer constant of MAA_3 in MMA polymerization in 2-butanone is significantly higher than that of the other trimers included in the present study (Table 3). In 2-propanol, the transfer constant of MAA_3 appears lower (similar to that of other trimers). Macromonomer aggregation caused by H-bonding may be important. In 2-propanol, H-bonding between macromonomer molecules may be disrupted.

If similar factors affect both macromonomer [k_{add}-(RMA_3)] and monomer addition rates [k_p(RMA)], then C_{tr} for the various methacrylate trimers [=$k_{add}(RMA_3)/k_p(MMA)$] in MMA polymerization should scale inversely as values of r_{MMA}. While there is considerable variation in reported reactivity ratios for methacrylate esters, values of r_{MMA} and r_{RMA} are generally close to unity. Experimental reactivity ratios and those calculated from $Q-e$ values are presented in Table 6. Reactivity ratios r_{MMA} [=$k_p(MMA)/k_p(MAA)$] for copolymerization of MAA[48] show substantial solvent dependence. In 2-propanol and acetone the MMA propagating radical shows a significant preference for adding MAA (Table 6).[48] Reactivity ratios for HEMA copolymerizations show substantial variation which may also be due to reaction conditions (Table 6).[49] Very different $Q-e$ values for HEMA have been reported by in the second edition of the *Polymer Handbook* by Young[50] and in more recent editions by Greenley.[51] Recent studies using the HEMA $Q-e$ values for predictive purposes have employed Young's values.[52] These values suggest that reactivity ratios for HEMA are not very different from other alkyl methacrylates. We conclude that the experimental data are too scattered to make a judgment.

There have been a few previous studies on C_{tr} to other substrates in alkyl methacrylate polymerizations which consider the effect of the nature of the alkyl group. Dependence of transfer constants on the length of the alkyl chain of alkyl methacrylate monomers was reported in the case of chain transfer to certain alkanethiols[53] and in catalytic chain transfer[43,54−56] (Table 5). Transfer constants to 3-mercaptopropionate esters are approximately a factor of 2 higher in MMA polymerization than in BMA polymerization.[53] There is considerable variation in reported C_{tr} for $Co^{II}(DMG\text{-}BF_2)_2$ which is attributed to the influence of reagent purity and reaction conditions. Nonetheless, all studies conclude

that C_{tr} is higher in MMA polymerization than in polymerizations of higher methacrylates.[43,55,56] In the latter case, variations in transfer constants have been correlated with changes in solvent viscosity and related to diffusion control of the transfer process.[55,56] Steric hindrance of chain transfer has also been suggested as a possible explanation for reduced C_{tr} seen with the higher methacrylates.[54,56]

As was observed in our earlier work with MMA macromonomers,[3] there is no significant retardation of polymerization of methacrylates caused by the presence of the methacrylate macromonomers. This suggests that fragmentation of the adduct radicals (**1**, Scheme 1) is sufficiently rapid that **1** is not consumed in side reactions with other radicals. We have already noted above that *i*Pr−Co^{III}(DMG-BF_2)$_2$−H_2O also does not react with the adduct radicals other than as shown in Scheme 2 (monomeric radical adding to MMA_2). This finding is of importance to the utilization of these macromonomers in block copolymer synthesis.

Conclusions

We have determined the transfer constants of various methacrylate dimers (RMA_2) and trimers (RMA_3) in MMA polymerization and those of MMA_3 in polymerizations of various methacrylate esters. The values of the transfer constants show little dependence on the nature of the ester alkyl group in monomer or macromonomer or on reaction temperature and are similar to that reported previously for MMA dimer (MMA_2) or trimer (MMA_3) in MMA polymerization. The transfer constant of methacrylic acid trimer (MAA_3) in MMA polymerization is higher than those of the methacrylate ester trimers. The end-functional trimers (MAA−MMA−MAA, HEMA−MMA−HEMA) that can be readily prepared by selective hydrolysis and esterification may provide a route to telechelics.

Acknowledgment. We thank DuPont Performance Coatings for their support of this work. We are grateful to Joan Hansen (Dupont Performance Coatings), Ian Willing, Roger Mulder, and Jo Cosgriff (CSIRO) for assistance with NMR characterization and helpful discussions.

References and Notes

(1) Cacioli, P.; Hawthorne, D. G.; Laslett, R. L.; Rizzardo, E.; Solomon, D. H. *J. Macromol. Sci., Chem.* **1986**, *A23*, 839−852.
(2) Rizzardo, E.; Meijs, G. F.; Thang, S. H. *Macromol. Symp.* **1995**, *98*, 101−123.
(3) Moad, G.; Moad, C. L.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1996**, *29*, 7717−7726.
(4) Krstina, J.; Moad, G.; Rizzardo, E.; Winzor, C. L.; Berge, C. T.; Fryd, M. *Macromolecules* **1995**, *28*, 5381−5385.
(5) Darmon, M. J.; Berge, C. T.; Antonelli, J. A. US 5 362 826, 1994; *Chem. Abstr.* **1993**, *120*, 299554.
(6) Krstina, J.; Moad, C. L.; Moad, G.; Rizzardo, E.; Berge, C. T.; Fryd, M. *Macromol. Symp.* **1996**, *111*, 13−23.
(7) Moad, G.; Moad, C. L.; Krstina, J.; Rizzardo, E.; Berge, C. T.; Darling, T. R. WO 9615157, 1996; *Chem. Abstr.* **1996**, *125*, 115512.
(8) Rizzardo, E.; Harrison, D. S.; Laslett, R. L.; Meijs, G. F.; Morton, T. C.; Thang, S. H. In *Progress in Pacific Polymer Science*; Anderson, B. C., Imanishi, Y., Eds.; Springer-Verlag: Berlin, 1991; p 77.
(9) Abbey, K. J.; Trumbo, D. L.; Carlson, G. M.; Masola, M. J.; Zander, R. A. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 3417−3424.
(10) Trumbo, D. L.; Abbey, K. J. *J. Polym. Sci., Part C: Polym. Lett.* **1987**, *25*, 229−232.
(11) Rajatapiti, P.; Dimonie, V. L.; El-Aasser, M. *J. Macromol. Sci., Chem.* **1995**, *A32*, 1445−1460.
(12) Huybrechts, J.; Bruylants, P.; Kirshenbaum, K.; Vrana, J.; Snuparek, J. *Prog. Org. Coatings* **2002**, *45*, 173−183.
(13) Muratore, L. M.; Steinhoff, K.; Davis, T. P. *J. Mater. Chem.* **1999**, *9*, 1687−1691.
(14) Muratore, L. M.; Davis, T. P. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 810−817.
(15) Haddleton, D. M.; Topping, C.; Hastings, J. J. *Macromol. Chem. Phys.* **1996**, *197*, 3027−3042.
(16) Haddleton, D. M.; Topping, C.; Kukulj, D.; Irvine, D. *Polymer* **1998**, *39*, 3119−3128.
(17) Monteiro, M. J.; Bussels, R.; Wilkinson, T. S. In *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2813−2820.
(18) Gridnev, A. A.; Ittel, S. D. *Chem. Rev.* **2001**, *101*, 3611−3659.
(19) Haddleton, D. M.; Maloney, D. R.; Suddaby, K. G. *Macromolecules* **1996**, *29*, 481−483.
(20) Haddleton, D. M.; Maloney, D. R.; Suddaby, K. *Polymer* **1997**, *38*, 6207−6217.
(21) Sato, E.; Zetterlund, P. B.; Yamada, B. *Polymer* **2003**, *44*, 2883−2889.
(22) Zetterlund, P. B.; Yamazoe, H.; Yamada, B. *Macromol. Rapid Commun.* **2003**, *24*, 197−201.
(23) Clay, P. A.; Gilbert, R. G. *Macromolecules* **1995**, *28*, 552−569.
(24) Heuts, J. P. A.; Clay, P. A.; Christie, D. I.; Piton, M. C.; Hutovic, J.; Kable, S. H.; Gilbert, R. G. In *Progress in Pacific Polymer Science*; Ghiggino, K., Ed.; Springer-Verlag: Berlin, 1994; Vol. 3, p 203.
(25) Whang, B. C. Y.; Ballard, M. J.; Napper, D. H.; Gilbert, R. G. *Aust. J. Chem.* **1991**, *44*, 1133−1137.
(26) In general it is recommended that for transfer constant estimation by the Mayo or log CLD methods, the conversions are as low as practicable. By use of the integrated expression for determining chain transfer constants (appendix of ref 3), it is possible to calculate that for a transfer constant of 0.2 the transfer constants will be overestimated by 4% if polymerizations are taken to 10% conversion and 6% if to 15% conversion. If the transfer constant is 0.02, the overestimation will be 5% at 10% conversion and 8% at 15% conversion.
(27) Esselborn, E.; Fock, J. 1997; *Chem. Abstr.* **1996**, *54*, 011752.
(28) Biasutti, J. D.; Roberts, G. E.; Lucien, F. P.; Heuts, J. P. A. *Eur. Polym. J.* **2003**, *39*, 429−436.
(29) Haddleton, D. M.; Depaquis, E.; Kelly, E. J.; Kukulj, D.; Morsley, S. R.; Bon, S. A. F.; Eason, M. D.; Steward, A. G. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2378−2384.
(30) McCord, E. F.; Anton, W. L.; Wilczek, L.; Ittel, S. D.; Nelson, L. T. J.; Raffell, K. D.; Hansen, J. E.; Berge, C. *Macromol. Symp.* **1994**, *86*, 47−64.
(31) Tanaka, H.; Kagawa, T.; Sato, T.; Ota, T. *Macromolecules* **1986**, *19*, 936.
(32) Gridnev, A. A.; Simonsick, W. J.; Ittel, S. D. *J. Polym. Sci., Part A: Polym. Chem.*. **2000**, *38*, 1911−1918.
(33) Cacioli, P.; Hawthorne, D. G.; Johns, S. R.; Solomon, D. H.; Rizzardo, E.; Willing, R. I. *Chem. Commun.* **1985**, 1355−1356.
(34) Mayo, F. R. *J. Am. Chem. Soc.* **1943**, *65*, 2324−2329.
(35) Moad, G.; Moad, C. L. *Macromolecules* **1996**, *29*, 7727−7733.
(36) Heuts, J. P. A.; Davis, T. P.; Russell, G. T. *Macromolecules* **1999**, *32*, 6019−6030.
(37) de la Fuente, J. L.; Madruga, E. L. *Macromol. Chem. Phys.* **2000**, *201*, 2152−2159.
(38) Chong, Y. K.; Krstina, J.; Le, T. P. T.; Moad, G.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2003**, *36*, 2256−2272.
(39) Chiefari, J.; Mayadunne, R. T. A.; Moad, C. L.; Moad, G.; Rizzardo, E.; Postma, A.; Skidmore, M. A.; Thang, S. H. *Macromolecules* **2003**, *36*, 2273−2283.
(40) O'Brien, J. L.; Gornick, F. *J. Am. Chem. Soc.* **1955**, *77*, 4757.
(41) Hutchinson, R. A.; Beuermann, S.; Paquet, D. A.; Jr; McMinn, J. H. *Macromolecules* **1997**, *30*, 3490−3493.
(42) Hutchinson, R. A.; McMinn, J. H.; Paquet, D. A.; Beuermann, S.; Jackson, C. *Ind. Eng. Chem. Res.* **1997**, *36*, 1103−1113.
(43) Roberts, G. E.; Davis, T. P.; Heuts, J. P. A.; Ball, G. E. *Macromolecules* **2002**, *35*, 9954−9963.
(44) Karandinos, A.; Nan, S.; Mays, J. W. *Macromolecules* **1991**, *24*, 2007.

(45) Sato, E.; Zetterlund, P. B.; Yamada, B.; Busfield, W. K.; Jenkins, I. D. *Macromol. Chem. Phys.* **2003**, *204*, 1882−1888.
(46) The explanation we provided in ref 3 on page 7723 is correct. However, "pathway a" and "pathway b" in the text should be interchanged.
(47) Moad, G.; Chiefari, J.; Moad, C. L.; Postma, A.; Mayadunne, R. T. A.; Rizzardo, E.; Thang, S. H. *Macromol. Symp.* **2002**, *182*, 65−80.
(48) Georgiev, G. S.; Dakova, I. G. *Macromol. Chem. Phys.* **1994**, *195*, 1695−1707.
(49) Greenley, R. Z. In *Polymer Handbook*, 4th ed.; Brandup, J., Immergut, E. H., Grulke, E. A., Eds.; John Wiley and Sons: New York, 1999; pp II/181−308.
(50) Young, L. J. In *Polymer Handbook*, 2nd ed.; Brandup, J., Immergut, E. H., Eds.; John Wiley and Sons: New York, 1975; pp II/387−404.
(51) Greenley, R. Z. In *Polymer Handbook*, 4th ed.; Brandup, J., Immergut, E. H., Grulke, E. A., Eds.; John Wiley and Sons: New York, 1999; pp II/309−320.
(52) Heuts, J. P. A.; Muratore, L. M.; Davis, T. P. *Macromol. Chem. Phys.* **2000**, *201*, 2780−2788.
(53) Vail, N. K.; Barlow, J. W.; Beaman, J. J.; Marcus, H. L.; Bourell, D. L. *J. Appl. Polym. Sci.* **1994**, *52*, 789−812.
(54) Mironychev, V. Y.; Mogilechev, M. M.; Smirnov, B. R.; Shapiro, Y. Y.; Golikov, I. V. *Polym. Sci. USSR* **1986**, *28*, 2103-2107.
(55) Heuts, J. P. A.; Forster, D. J.; Davis, T. P. *Macromolecules* **1999**, *32*, 3907−3912.
(56) Pierik, S. C. J.; Vollmerhaus, R.; van Herk, A. M. *Macromol. Chem. Phys.* **2003**, *204*, 1090−1101.
(57) Beuermann, S.; Buback, M.; Davis, T. P.; Gilbert, R. G.; Hutchinson, R. A.; Kajiwara, A.; Klumperman, B.; Russell, G. T. *Macromol. Chem. Phys.* **2000**, *201*, 1355−1364.
(58) Haddleton, D. M.; Crossman, M. C.; Hunt, K. H.; Topping, C.; Waterson, C.; Suddaby, K. G. *Macromolecules* **1997**, *30*, 3992−3998.
(59) Pascal, P.; Winnik, M. A.; Napper, D. H.; Gilbert, R. G. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 213-215.
(60) Kuchta, F. D.; van Herk, A. M.; German, A. L. *Macromolecules* **2000**, *33*, 3641−3649.
(61) Beuermann, S.; Paquet, D. A., Jr.; McMinn, J. H.; Hutchinson, R. A. *Macromolecules* **1997**, *30*, 194−197.
(62) Buback, M.; Kurz, C. H. *Macromol. Chem. Phys.* **1998**, *199*, 2301−2310.
(63) Okano, T.; Aoyagi, J.; Shinohara, I. *Nippon Kagaku Kaishi* **1976**, 161−165.

MA049813O