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Radical-addition-fragmentation and co-polymerization of methyl methacrylate macromonomers from catalytic chain transfer polymerization (CCTP)

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Catalytic chain transfer polymerization (CCTP) of methacrylates is an efficient method to produce low molecular weight poly(methacrylates). The mechanism is such that the products each have a terminal vinyl group which is then available for subsequent further reaction. This study involves the use of matrix assisted laser/desorption ionization time-of-flight mass spectrometry (MALDI TOF MS) to investigate the effect of the addition of methyl methacrylate macromonomers as prepared by CCTP to the polymerization of perdeutero-methyl methacrylate and *n*-butyl methacrylate in the presence and absence of catalytic chain transfer agent. The experiments have demonstrated that methyl methacrylate dimer as prepared by CCTP may copolymerize with deutero-methyl methacrylate. Addition fragmentation is demonstrated to dominate over CCT, contrary to that predicted from a consideration of C_s values. No evidence for copolymerization with butyl methacrylate has been observed. Inevitably this will result in small amounts of branching during CCTP taken to high conversion. © 1997 Elsevier Science Ltd.

(Keywords: catalytic chain transfer polymerization; MALDI TOF MS; poly(methyl methacrylate))

INTRODUCTION

Catalytic chain transfer polymerization has emerged as an efficacious method to produce low molecular weight poly(methacrylates)[1–6]. The mechanism is such that the products each have a terminal vinyl group, **1** (*Figure 1*), which arises from chain transfer to [Co(II)] which is then available for subsequent further reaction. Although these macromonomers have been shown to copolymerize with non-sterically hindered monomers, such as acrylates and styrenics, their rate of copolymerization with methacrylic monomers is low and it has been reported that the incorporation of macromonomers such as **1** into polymethacrylates is zero[7]. The most favoured reaction of a macromonomer in a methacrylic copolymerization is β-scission, or radical addition fragmentation (*Figure 2*). β-Scission results in addition of the ultimate monomeric unit from the macromonomer adding to the original propagating polymeric radical releasing a macroradical, as derived from the macromonomer, which in turn can initiate residual monomer. Krstina and co-workers have used this chemistry to prepare block copolymers under emulsion polymerization conditions[8]; Haddleton and co-workers have prepared α,ω-dihydroxy telechelic poly-(methyl methacrylate) using β-scission of hydroxyethyl methacrylate dimer[10]. The chain transfer constant for these macromonomers has been shown to be chain length dependant. The chain transfer constant (C_s) for MMA dimer is reported to be 0.013 whilst for MMA trimer 0.19; there is little increase in C_s as chain length increases to tetramer, pentamer, etc.[8,9].

The participation of macromonomers such as **1** in free radical polymerization is an important consideration when carrying out CCTP to obtain useful products. Although C_s is several orders of magnitude lower than the cobalt(II) catalysts, e.g. **2**, as the reaction approaches high conversion reaction of macromonomer will increase in importance, possibly leading to unwanted grafting, etc. Previously we have reported an investigation into competition between β-scission and transfer to cobalt(II) by looking at the incorporation of methyl methacrylate tetramer **3** into poly(butyl methacrylate) in both the presence and absence of catalytic chain transfer agent, **2**, by MALDI TOF MS[11]. No evidence for copolymerization was observed and we concluded that the macromonomers themselves are effective CCTAs with the predominant product being an ABA triblock copolymer from a radical mediated polymerization process. In the presence of **2** chain transfer to [Co(II)] from propagating PBMA competes with macromonomer addition and subsequent β-scission. Although previous reports have indicated that copolymerization of the macromonomer does not occur with MMA use of the dimer **4** should maximize the possibility of observing copolymerization.

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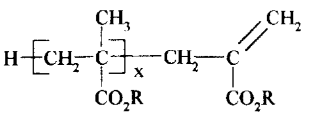
The C_s value for dimer **4** has been found to be more than an order of magnitude smaller than that for higher macromonomers[9]. It would be anticipated that reducing the size of the macromonomer would, if anything, increase the rate of addition of the macromonomer to a propagating polymeric radical. Moad and coworkers[9] have provided evidence that there is in fact little if any effect of macromonomer size on this addition rate (step 1 and step 5 in *Figure 2*). Therefore it has been concluded that the β-scission reaction is slower in the case of dimer, i.e. $k_\beta < k_{-\mathrm{add}}$ resulting in the lower C_s value whereas for higher macromonomers $k_\beta = k_{-\mathrm{add}}$. Steric interference for the copolymerization grafting reaction (step 7, *Figure 2*) would be at the minimum when employing dimer and therefore the rate coefficient k_g (where k_g is the rate constant of grafting/copolymerization) would be at a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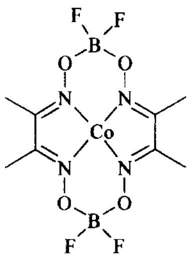
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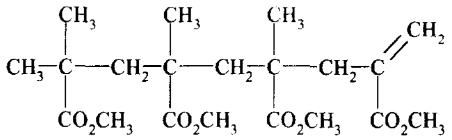
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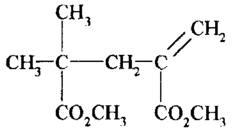
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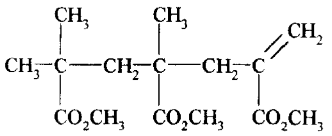
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Figure 1 Structures of macromonomer and cobalt(II) chain transfer agents

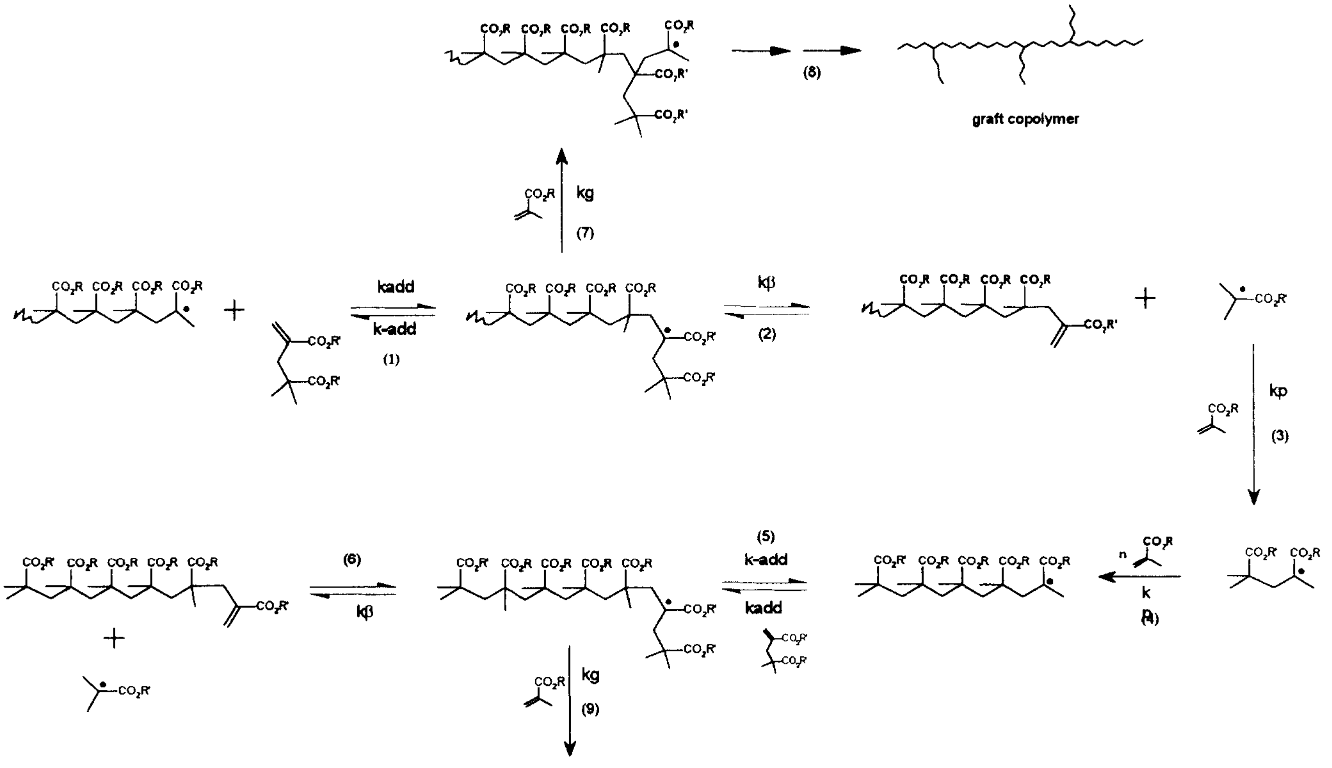


Figure 2 Possible reactions from macromonomer adduct radical

maximum. The proportion of the macroradical, produced after dimer addition, which adds further monomer will be given by $k_{\mathrm{g}}[\mathrm{MMA}]/(k_\beta + k_{-\mathrm{add}})$ which is maximized by use of dimer.

In this present study we have chosen to study the effects of the addition of methyl methacrylate dimer **4** to the polymerization of perdeutero-methyl methacrylate in the presence and absence of CCTA, **2**. d^8-MMA has been used in this study to facilitate structural interpretation of the MALDI TOF MS data. The residual mass of the repeat unit of d^8-MMA is approximately 108 Da and is thus easily distinguishable from protio methyl methacrylate with residual mass of 100.12 Da using MALDI TOF MS; a technique which is finding widespread use in the study of polymerization mechanisms[12,13]. We also report the results from catalytic chain transfer polymerization of *n*-butyl methacrylate in the presence of MMA dimer, **4**, and trimer, **5**, as investigated by MALDI TOF MS.

EXPERIMENTAL

General

All reactions were carried out using standard Schlenk line apparatus under an atmosphere of nitrogen. Reactions were performed either in Schlenk tubes fitted with rubber septa or in closed ampoules fitted with a Youngs vacuum tap. All solvents and monomers were deoxygenated thoroughly prior to use by purging with nitrogen gas for more than 60 min, or alternatively, by performing at least three freeze–pump–thaw cycles in liquid nitrogen. Addition of solvents and monomers was performed via syringe. Bis(boron difluorodiphenylglyoximate)cobaltate(II) (CoBF, **2**) was synthesized by a modification of the method of Espenson[14]. Methyl methacrylate (MMA) was obtained from ICI Acrylics (TA5) and purified by passing through a column of activated basic aluminium oxide and activated molecular sieves, 3A, Aldrich, and was stored over sieves under nitrogen prior to use. Perdeutero methyl methacrylate was obtained from Cambridge Isotopes Laboratories (D, 98%, stabilized with hydroquinone) and used without further purification.

Preparation of methyl methacrylate oligomers

MMA (150 ml, 1.4 mol), **3** (45 mg) and dimethyl 2,2′-azobisisobutyrate, AIBN (700 mg), were dissolved in degassed butanone (150 ml). The reaction mixture was heated to 75°C for a period of 24 h after which time the solvent and excess monomer was removed using a rotary evaporator. S.e.c. of the products at this stage showed a mixture of MMA oligomers which were subsequently separated by Kugelrohr distillation. MMA dimer was collected at a pressure of 1.2×10^{-1} mbar and a temperature of 130°C, MMA trimer at 1.2×10^{-1} mbar and 170°C. Purity was determined by s.e.c. and ^{1}H n.m.r.:

4: ^{1}H n.m.r. ($\mathrm{CDCl_3}$, 323 K): $\delta = 6.05$ s, 5.37 s, 3.58 s, 3.48 s, 2.46 s, 1.03 s. Intensity ratio: 1/1/3/3/2/6.

3: ^{1}H n.m.r. ($\mathrm{CDCl_3}$, 323 K): $\delta = 6.2$–5.1 m, 3.7–3.5 m, 2.46 m, 2.3–1.8 m, 1.4–0.9.

Polymerization of d^8*-MMA in the presence of MMA dimer*

A stock solution was made containing 1.0 ml of d^8-MMA (8.7×10^{-3} mol), 2.0 ml of butanone, 5.0 mg of AIBN (2.98×10^{-5} mol) and 5.64 g of **4** (1.41×10^{-2} mol). 4.0 ml of the stock solution were placed in each of two ampoules. 0.2 ml of a solution of **3** in butanone (0.005 mg in 10 ml) were added to one ampoule (reaction B), the other was polymerized in the absence of **2** (reaction A). The ampoules were heated at 60°C in a constant temperature water bath (± 0.5°C) for 24 h prior to being terminated by cooling in water at ambient temperature. S.e.c. and MALDI TOF MS analysis were performed on the final reaction mixture so as to avoid any fractionation that could be caused upon precipitation and the product isolated by precipitation into hexanes.

Polymerization of n*-butyl methacrylate in the presence of MMA oligomers*

In a typical polymerization reaction a stock solution was prepared by dissolving *n*-butyl methacrylate (6 ml, 3.77×10^{-2} mol), AIBN (30 mg, 1.79×10^{-4} mol) and the required amount of MMA macromonomer (e.g. MMA tetramer, 2.70 g, 1.35×10^{-2} mol) in butanone (12 ml). The stock solution was then deoxygenated by performing three freeze–pump–thaw cycles in liquid nitrogen. Equal volumes of solution were then removed to be used for polymerization reactions, with the required amount of **2** being added from a separate stock solution. Reactions were heated to 60°C for a period of 24 h. SEC and MALDI TOF MS analysis were performed on the final reaction mixture so as to avoid any fractionation that could be caused upon precipitation.

ANALYSIS

Size exclusion chromatography was carried out using THF as an elutant at 1 ml min^{-1} with toluene (0.2 wt%) as an internal standard and flow marker in each sample. Two Polymer Laboratories PLgel 5 μm Mixed-C columns (300 × 7.5 mm) and a PLgel 5 μm guard column (50 × 7.5 mm) were employed and calibrated with Polymer Laboratories PMMA standards from 200–1 577 000. N.m.r. was carried out at 400.135 MHz ^{1}H in TCE, $\delta = 5,97$ and 100.614 MHz ^{13}C in TCE $\delta = 74,2$ at 373 K ^{2}H in $\mathrm{CDCl_3}$ at 298 K. Quantitative n.m.r. was gated so as to remove NOE with a relaxation delay (RD) of 10 s, ^{13}C, and a RD of 30 s, ^{1}H.

Matrix-assisted laser desorption ionization time-of-flight mass spectrometry was carried out on a Kratos (Manchester) Kompact III spectrometer in reflection mode. Samples were deposited in a 2,5-dihydroxybenzoic acid matrix from acetone and doped with NaCl or KCl which results in each species being observed as a $\mathrm{Na^+}$ or $\mathrm{K^+}$ adduct at molecular masses M + 23 and M + 39 respectively. The spectrometer was calibrated internally using bovine insulin (*m/z* 5734), Na (*m/z* 23.9898) and K (*m/z* 39.0983). The width of the peaks at approx. *m/z* 4000 are approx. 10 Da at half peak height. These factors combine to allow an accuracy of to within 2–3 Da (0.075%) for each individual macromolecular species. All MALDI TOF MS of d^8-MMA were performed with the addition of sodium chloride to the sample leading to all peak being observed as $\mathrm{Na^+}$ adducts.

RESULTS AND DICSUSSION

Polymerization of d^8*-MMA in the presence of added* **4**

d^8-Methyl methacrylate has a repeat unit mass of

108.17 Da as compared to 100.12 Da for MMA, thus any incorporation of MMA dimer into the d^8-MMA polymer chain produces distinguishable peaks in a MALDI TOF mass spectrum. **4** was added to the polymerization of d^8-MMA at high concentration, [4]:[d^8-MMA] = 3/1 mole ratio, in order to magnify the effect of the macromonomer in the reaction and thus simulate very high conversion in a catalytic transfer reaction. Polymerizations were performed in the presence and absence of **2**. Reaction conditions and

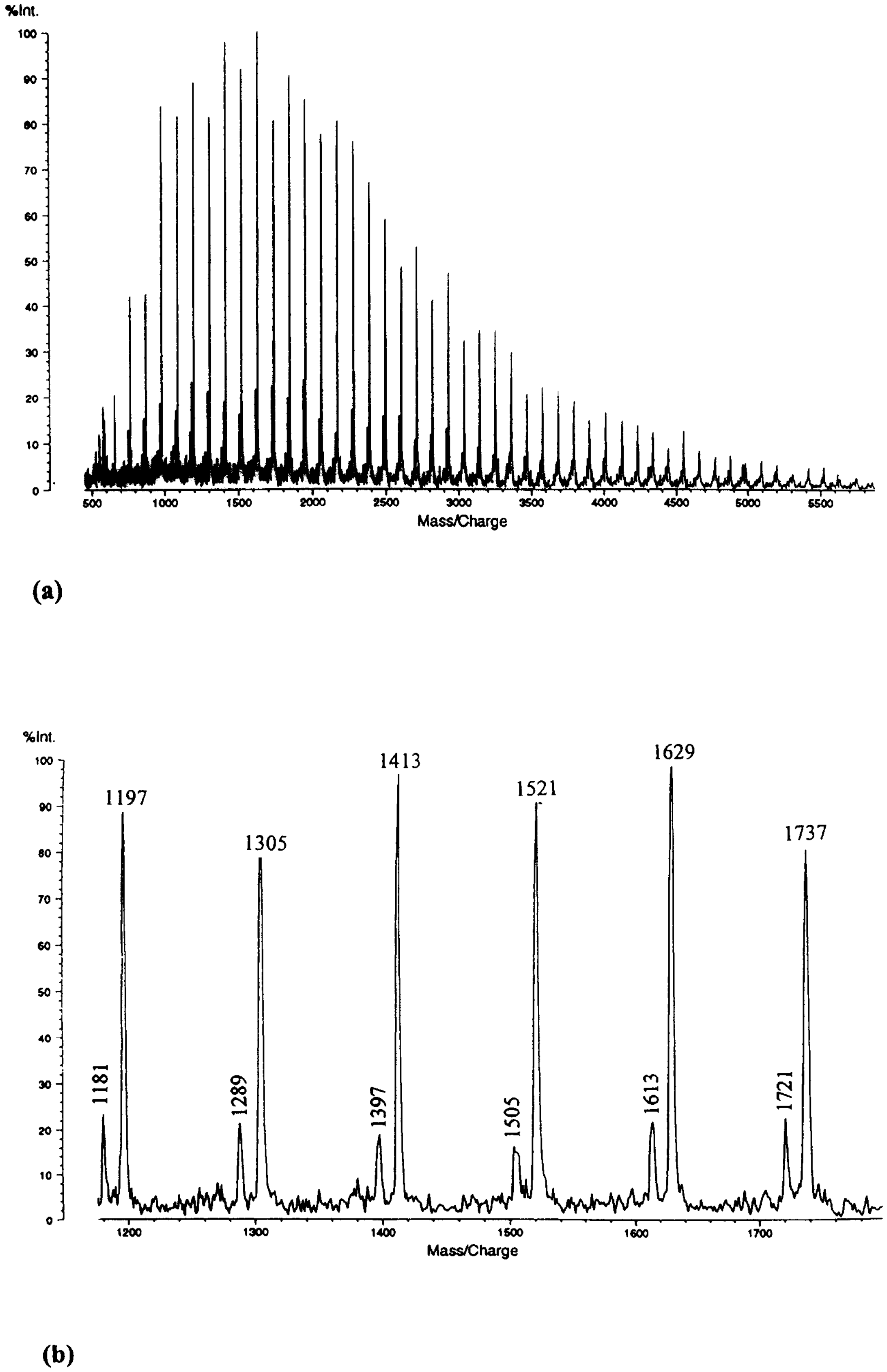


Figure 3 MALDI TOF MS of polymer from reaction A, (a) full spectrum, (b) expansion between DP = 11 and 16

Table 1 Reaction conditions and molecular weight data for the polymerization of d^8-MMA in the presence and absence of **2**

	Butanone (ml)	d^8-MMA (ml)	**4** (g)	AIBN (mg)	**2** (mg)	Mn^a	PDI^a
A	2.0	0.5	2.82	2.5	0	3200	1.82
B	2.0	0.5	2.82	2.5	0.10	1160	1.94

^{a} Residual MMA dimer peak was excluded from the SEC analysis

molecular weight data are summarized in *Table 1*. Molecular weight data were obtained from s.e.c. analysed relative to protio-PMMA standards.

The MALDI TOF mass spectrum of polymer A, i.e. with no **2** present, is shown in *Figure 3*. Two separate series of peaks are observed. The main series of peaks, e.g. m/z 1629, 1521, 1413, 1305, etc., correspond to incorporation of two units of protio MMA into perdeuteropoly(methyl methacrylate) giving molecular structures $(d^8\text{MMA})_x$+$(\text{MMA})_2$ + Na^+. For example, the peak at m/z 1629 corresponds to $(d^8\text{MMA})_{13}$+ $(\text{MMA})_2$ + Na^+ (calculated mass = 1629.45 Da). Macromolecules of this type arise from the addition-fragmentation (β-scission) of **4** to give one unit of protio-MMA on each end of the polymer chain, **6**[11] (*Figure 4*) as illustrated in steps 3–6 of *Figure 2*. A second less intense series of peaks appears at masses of m/z 1613, 1505, 1397, 1289, etc. corresponding to structures of $(d^8\text{-MMA})_n + (\text{MMA})_4 + \text{Na}^+$. For example the peak at m/z 1613, corresponds to $(d^8\text{-MMA})_{11} + (\text{MMA})_4 + \text{Na}^+$ (calculated mass 1613.35 Da). Macromolecules giving rise to this series must include one intact unit of protio-MMA dimer being copolymerized within the d^8-MMA chain together with two terminal protio-MMA units arising from the addition fragmentation pathway (structure **7**, *Figure 4*). This is strong evidence that copolymerization of the dimer **4** has occurred in competition with addition fragmentation in the polymerization of d^8-MMA. No evidence was found within the MALDI TOF mass spectrum for macromolecules containing greater than four units of protio-MMA. This absence, together with

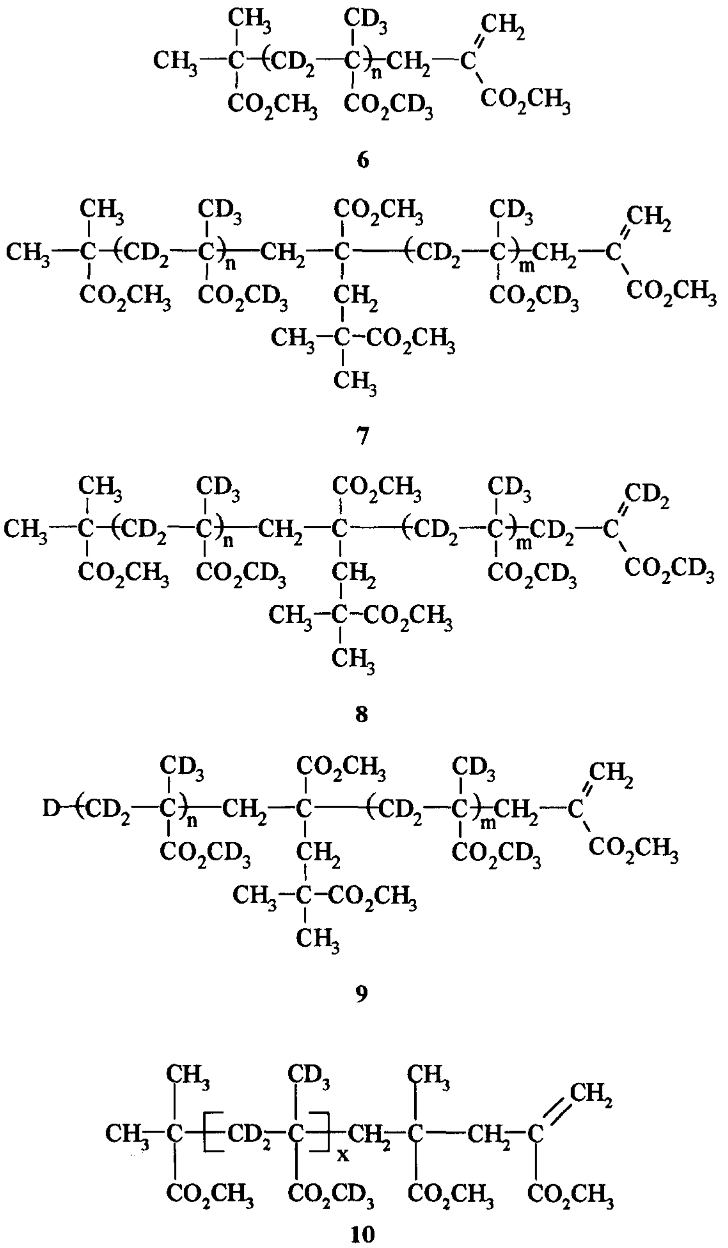


Figure 4 Structures of macromolecules from polymerization of perdeutero methyl methacrylate in the presence of **4**

the observation that the series of peaks showing incorporation of one intact dimer unit is the minor series, shows that copolymerization although present is not highly favoured. Also no evidence was found within the MALDI TOF mass spectrum for macromolecules containing one or three units of protio-MMA. Although one would expect to find polymers containing one unit of protio-MMA derived from normal bimolecular termination via disproportionation this route of termination clearly accounts for only a very small proportion of the polymer chains produced. Equally the lack of observation of peaks in the mass spectrum

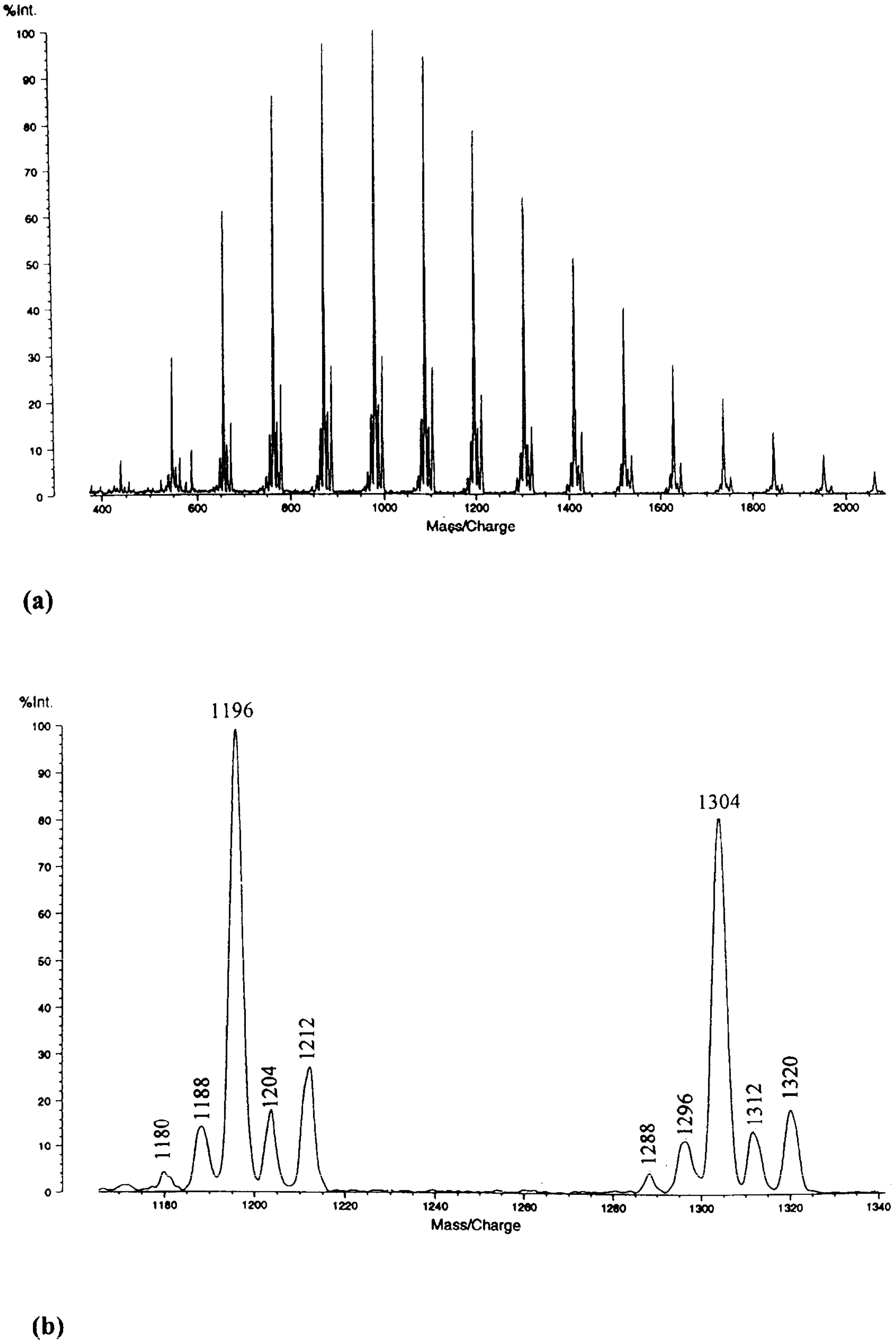


Figure 5 MALDI TOF MS of polymer from reaction B, (a) full spectrum, (b) expansion between DP = 11 and 12

corresponding to macromolecules containing an isobutyronitrile fragment derived from the initiator AIBN shows that the vast majority of chains are initiated via the transfer process.

The MALDI TOF mass spectrum of polymer B is shown in *Figure 5*. The addition of **2** to the system gives rise to a number of different additional macromolecular species. Each macromolecule may now be initiated by either the fragmentation product from β-scission or by transfer from cobalt and termination may occur by either transfer to **2** *or* **4**. Other, more normal modes of termination will be present terminating the kinetic chain; however, the number of macromolecules arising from these mechanisms will be very small and are undetected by MALDI TOF MS or ^{1}H n.m.r. ^{1}H n.m.r. analysis of these product mixtures is complicated by the presence of unreacted dimer which is present in a massive excess in terms of number of molecules. This is of course not true as a mass fraction, the residual mass of **4** being only 200 Da. Although ^{1}H n.m.r. can be used to distinguish between the different methoxy groups of macromolecules **6–10** it is not possible to use ^{1}H n.m.r. as a useful mechanistic probe without prior separation of products from residual **4**. This would inherently involve fractionation of the product and analysis on an unrepresentable sample and was thus avoided. Both initiation and termination by β-scission will lead to **6**. Initiation by β-scission and termination by transfer to [Co(II)] or initiation by transfer from [Co(III)]–H and termination by β-scission will lead to macromolecules containing one protio-MMA unit. Initiation and termination by transfer from and to cobalt will lead to pure homo poly(perdeuteromethyl methacrylate). Copolymerization of **4** will manifest itself as incorporation of higher than two units of protio-MMA. The predominant series of peaks corresponds to two protio-MMA being incorporated as described above, i.e. the series 980, 1088, 1196, 1304 Da, etc. A smaller series of peaks is seen that corresponds to d^8-MMA homopolymer with no incorporation of MMA arising from normal CCT polymerization, e.g. the peak at m/z 1212 is from $(d^8\mathrm{MMA})_{11} + \mathrm{Na}^+$ (calculated mass = 1212.87). Macromolecules are also seen corresponding to incorporation of one, three and four units of protio-MMA into the d^8-MMA chain, e.g. m/z 1204, 1188 and 1180 respectively. Three units of protio-MMA may be incorporated in three different ways, these are indistinguishable by MALDI TOF MS, **8**, **9** and **10**. Macromolecule **8** arises from chain transfer to **2** in preference to reaction with **4**. ^{2}H n.m.r. of polymer A shows no evidence for vinylic deuterium which would occur at approximately 6.2 and 5.5 ppm, vinylic hydrogens are present in the ^{1}H n.m.r. spectrum. Thus structure **8** is not present in sufficient quantities to be detected as a possible product within the limitations of ^{2}H n.m.r. This implies that under the reaction conditions employed the rate of transfer to **2** from propagating polymer radicals is slow relative to addition of **4**[11]. β-Scission is the predominant mode of termination under these conditions leading to **9** as the most probable method of incorporating three units of protio MMA, i.e. copolymerization of **4**.

Thus at very high concentrations of **4**, copolymerization of macromonomer is observed in competition with β-scission as well as catalytic chain transfer. In the absence of CCTA the radical **11** may undergo one of two possible events, (1) β-scission or (2) propagation, *Figure 6*. Contrary to earlier results the rate of reaction 3 is not zero and an appreciable amount of copolymerization

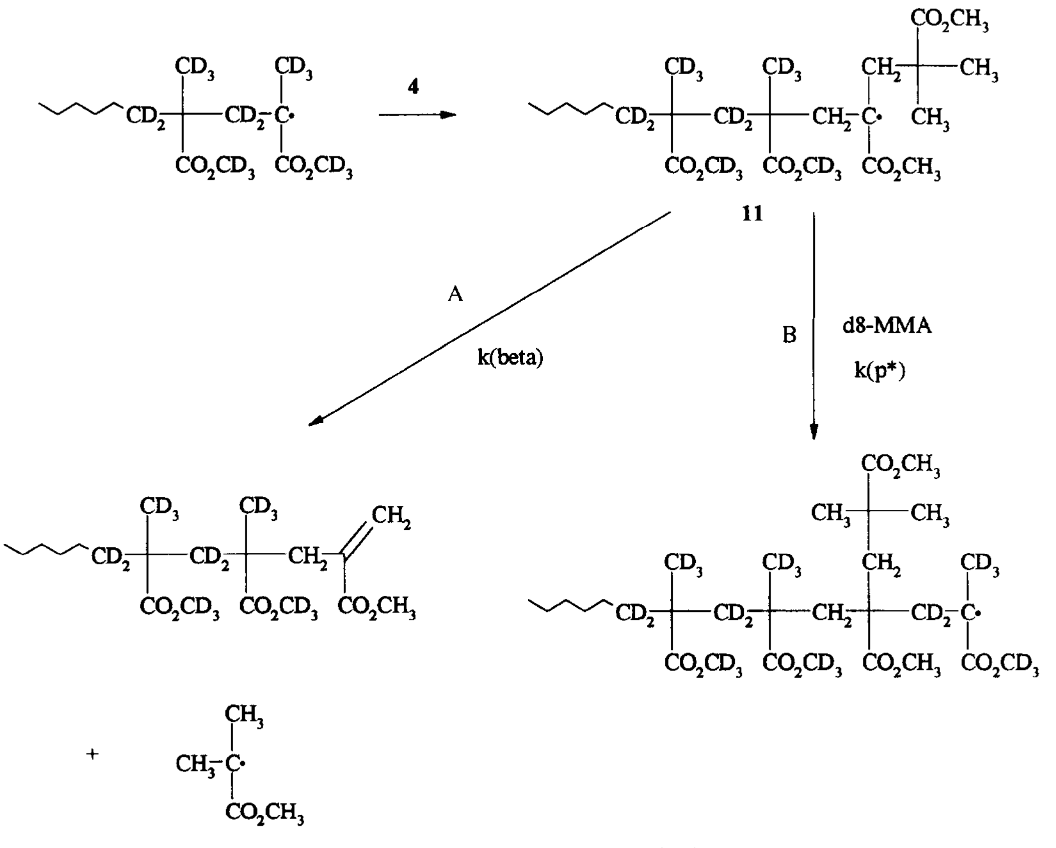


Figure 6 Reaction scheme from **11** with competition between β-scission and copolymerization

does occur[7]. The rate of β-scission is equal to $k_{(\mathrm{beta})}[\mathbf{11}]$ and propagation is equal to $k_{(\mathrm{p}*)}[\mathbf{11}]$ $[d^8\text{-MMA}]$. Both reactions should be first order with respect to [**11**] and the ratio of these two reaction rates should remain constant irrespective of the [**4**]; thus the high concentrations of **4** used in this work should not adversely change this ratio. Results in the presence of **2** increase the number of products available and confirm that copolymerization takes place on the same time scale as β-scission. From the concentrations of **2** and **4** used one might have expected that CCT should dominate over addition fragmentation from the published C_s values for both **2** and **4**[2,8,9]. However, these

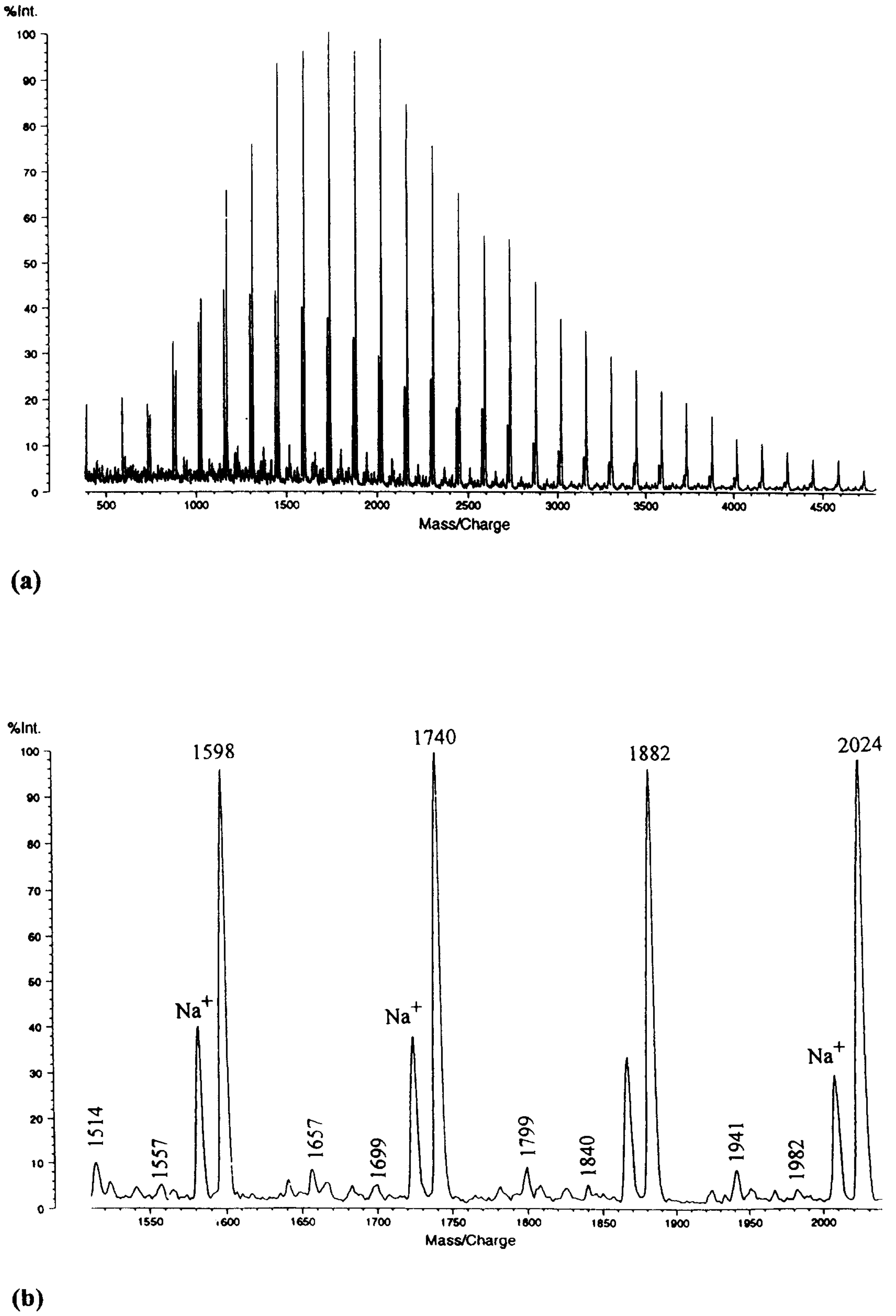


Figure 7 MALDI TOF MS of polymer from polymer E, (a) spectrum between m/z 400 and 4700, (b) expansion between DP = 11 and 14, major peaks from K^+ adducts

Table 2 Reaction conditions and molecular weight data for the CCTP of *n*-BMA at with added MMA macromonomer at varying [**2**]

	Butanine (ml)	*n*-BMA (ml)	Macromonomer (ml)	AIBN (mg)	**2** (mg)	M_n	PDI
C	4.0	2.0	0.2 (**4**)	10	0.025	11 200[a]	1.89[a]
D	4.0	2.0	0.2 (**4**)	10	0.05	3560[a]	1.85[a]
E	4.0	2.0	0.2 (**4**)	10	0.10	1510[a]	1.94[a]
F	4.0	2.0	0.2 (**5**)	10	0.025	5078[b]	1.85[b]
G	4.0	2.0	0.2 (**5**)	10	0.050	837[b]	2.00[b]
H	4.0	2.0	0.2 (**5**)	10	0.075	766[b]	1.78[b]

[a] The s.e.c. traces of polymers C, D and E each contained a peak corresponding to residual MMA dimer in the sample. In no case does this overlap with the polymer peak and was thus omitted from the analysis

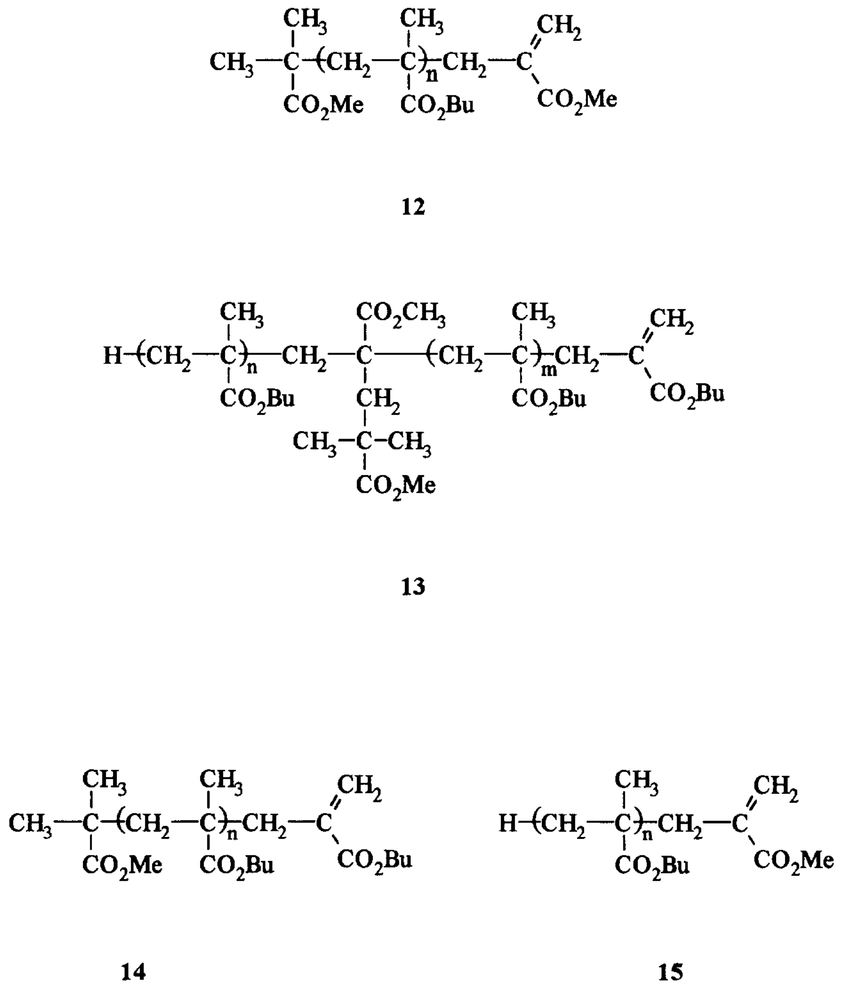
[b] Residual MMA trimer in the s.e.c. traces of polymers G and H overlapped with the polymer peak and were included in these analyses

results from MALDI TOF MS show that addition fragmentation is indeed the predominant pathway.

Polymerization of n*-butyl methacrylate in the presence of MMA oligomers*

The combination of methyl methacrylate macromonomers with butyl methacrylate allows the direct observation of methyl methacrylate incorporation into poly(butyl methacrylate) by MALDI TOF MS, the residual mass of MMA being 100.12 and BMA 142.20. In our previous studies addition of methyl methacrylate tetramer to the radical polymerization of butyl methacrylate resulted in macromolecules of molecular formula BMA_xMMA_4 with no evidence for MMA monomer, dimer or trimer incorporation[11]. Also there was no evidence for BMA_xMMA_8 from the incorporation of two macromonomers into the propagating chain, copolymerization. When the reaction is carried out in the presence of **2** at [BMA] : [**3**] : [**2**] of 170 250 : 30 000 : 1 (mole ratio) peaks from four main poly(butyl methacrylate) polymers were observed by MALDI TOF; BMA_xMMA_4, BMA_xMMA_3, BMA_xMMA_1 and BMA_xMMA_0 with no macromolecules containing two MMA units incorporated observed. The absence of BMA_xMMA_2 is strong evidence for β-scission being the predominant reaction pathway. Similar reactions have now been carried out with MMA dimer and trimer in this present study.

Polymerization of *n*-BMA was carried out with added



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$CH_3-\overset{CH_3}{\underset{CO_2Me}{C}}-(CH_2-\overset{CH_3}{\underset{CO_2Bu}{C}})_n-CH_2-C(=CH_2)CO_2Me$

13

14

$CH_3-\overset{CH_3}{\underset{CO_2Me}{C}}-(CH_2-\overset{CH_3}{\underset{CO_2Bu}{C}})_n-CH_2-C(=CH_2)CO_2Bu$

15

$H-(CH_2-\overset{CH_3}{\underset{CO_2Bu}{C}})_n-CH_2-C(=CH_2)CO_2Me$

Figure 8 Structures of macromolecules from polymerization of *n*-butyl methacrylate in the presence of methyl methacrylate macromonomers

MMA dimer in the presence of **2**, at a molar ratio of [**4**]/[*n*-BMA] of 8.33 × 10^{-2}, under the conditions shown in *Table 2*. The MALDI TOF mass spectrum of polymer E is shown in *Figure 7*, K^+ has previously been shown to lead to better MALDI TOF spectra than with Na^+. The exact mode of attachment of the cation to a polymer is not fully understood and the optimum conditions for each polymer type, including cation selection, has to be determined for each analyte[15,16]. The main series of peaks corresponding to pure poly(butyl methacrylate) (both K^+ and Na^+ adducts) with no incorporation of **4** (*m/z* 1598, 1740, 1882, etc.). These macromolecules arise from normal CCT polymerization of *n*-BMA. The emergence of two smaller distributions of peaks can be seen from two separate macromoleculer species. Series (1) *m/z* 1514, 1657, 1799, 1941, etc. corresponds to BMA_xMMA_2, i.e. $x(142.2)+2(100.12)+39$. Again, the Na^+ adducts of these peaks are observed at *m/z* 16 lower for each individual peak. Structures containing two units of MMA can arise via two possible mechanisms: (1) By the addition-fragmentation (β-scission) of an MMA dimer unit causing termination of the PBMA chain by the addition of one MMA unit and release of an MMA monomer which reinitiates polymerization. Both initiation and termination occur via the β-scission mechanism the product from this reaction is **12**, *Figure 8*. Alternatively, incorporation of two MMA units may be occurring by copolymerization of an MMA dimer within the PBMA chain with initiation and termination proceeding by the normal CCT mechanism **13**. It is possible that these two mechanisms are in competition and that both contribute towards the final product. MALDI TOF MS cannot be used to differentiate between the two possible structures since they will have identical molecular masses. The second series of peaks in the mass spectrum, series (2), i.e. *m/z* 1557, 1699, 1840, 1982, etc. corresponds to $BMA_xMMA_1 + K^+$, i.e. $x(142.2)+100.12+39$. Macromolecules of this type are proposed to arise from a combination of CCTP and addition-fragmentation of an MMA dimer, **14** or **15**. Initiation/termination from primary radicals only occurs to a very limited extent in this reaction. The other very low intensity peaks in *Figure 7* cannot be assigned.

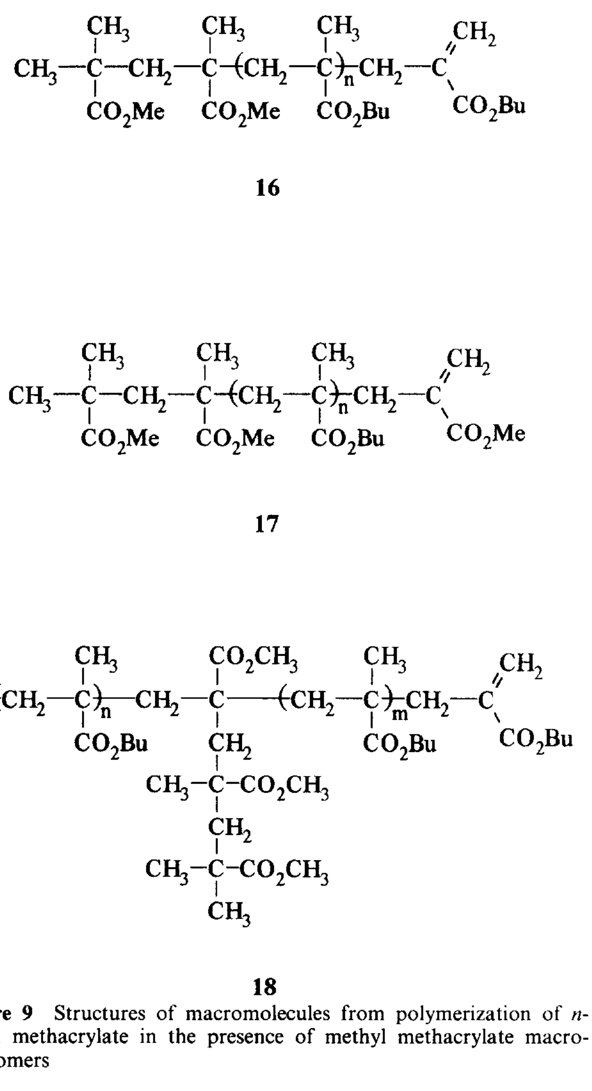

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Figure 9 Structures of macromolecules from polymerization of *n*-butyl methacrylate in the presence of methyl methacrylate macromonomers

CCTP of *n*-BMA was carried out with added MMA trimer, **5**, at a molar ratio of [*n*-BMA]/[**5**] of 0.06, under the conditions shown in *Table 2*. A number of series of peaks can be seen in the MALDI TOF spectrum. The main distribution of peaks is again from poly(butyl methacrylate) homopolymer. A second distribution of peaks include *m/z* 1556, 1598, 1840, etc. correspond to a molecular formula $BMA_xMMA_1 + K^+$, i.e. $x(142.2)+100.12+39$, these are formed by initiation by CCT followed by termination via addition-fragmentation, **14**. The MMA dimer radical produced during β-scission reaction can reinitiate to form new polymer chains which may terminate to form polymers of the third series by transfer to cobalt, **16** (*m/z* 1514, 1656, 1798, etc.), or the fourth series, further addition-fragmentation reaction, **17** (*m/z* 1472, 1614, 1756, etc.). Series 4 may also have a contribution from macromolecules derived from the copolymerization of one MMA trimer unit within the poly(butyl methacrylate) chain where initiation and termination occurs via CCT, **18**.

If copolymerization does occur to a significant extent then it would be expected that poly(butyl methacrylate) containing more than three units of MMA would be formed. No evidence is seen in the MALDI TOF spectrum for incorporation of more than three units of MMA. Thus it is assumed that copolymerization of MMA trimer does not play a significant role in this reaction.

CONCLUSIONS

The experiments have demonstrated that methyl methacrylate dimer as prepared by CCTP may copolymerize with deutero-methyl methacrylate. No evidence for copolymerization with butyl methacrylate has been observed. This is ascribed to the increased steric hindrance with butyl methacrylate relative to methyl methacrylate slowing the rate of copolymerization relative to β-scission. Thus although the rate of copolymerization is slow it does occur on a similar time scale to β-scission and transfer to cobalt during CCTP. These effects will inevitably lead to small amounts of branching during CCTP taken to high conversion. The results indicate that addition fragmentation dominate over CCT under these reaction conditions, contrary to what would be expected from C_s values. MALDI TOF MS is invaluable for performing these studies with many of the macromolecular species being unidentifiable other than by mass spectrometry, this is especially true when used in conjunction with n.m.r. However, the resolution of MALDI TOF MS is limiting to a certain extent limiting mechanistic information. Higher resolution mass detectors will be required to obtain isotropic resolution, e.g. Fourier transform ion-cyclotron-resonance.

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