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α,ω-dicarboxyl telechelic poly(methyl methacrylate) via radical addition–fragmentation polymerization

David M. Haddleton[a,*], Clare Topping[a], Dax Kukulj[a] and Derek Irvine[b]
[a]*Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK*
[b]*ICI Acrylics, PO Box 90, Wilton Centre, Middlesbrough, Cleveland TS90 8JE, UK*
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Catalytic chain transfer polymerization of benzyl methacrylate leads to a mixture of poly(benzyl methacrylate) macromonomers. Benzyl methacrylate dimer macromonomer has been isolated as a pure compound and used as a radical addition fragmentation chain transfer agent. This results in poly(methyl methacrylate) with both α and ω terminal benzyl methacrylate units. Catalytic hydrogenation of α,ω-benzyl methacrylate terminal poly(methyl methacrylate) results in evolution of toluene and formation of α,ω-dicarboxyl functional telechelic poly(methyl methacrylate). The products have been fully characterized by matrix-assisted laser desorption time-of-flight mass spectrometry in conjunction with ^{1}H and ^{13}C n.m.r. spectroscopy. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(methyl methacrylate); catalytic chain transfer polymerization; radical addition fragmentation)

INTRODUCTION

Telechelic polymers are, typically, low molecular weight macromolecules possessing a reactive functional group at both α and ω terminal ends[1]. Such macromolecules are usually used as prepolymers whereby they are reacted together with suitable di- and multifunctional linking agents, resulting in chain extension and/or crosslinking into three-dimensional networks[2,3]. Perhaps the most widespread use of telechelic polymers is in synthesis of polyurethanes, both foams and materials, where both macromolecular termini are usually hydroxyl functional. Nearly all telechelic materials used commercially are derived from condensation polymerization. By far the most common telechelic materials used in polyurethane synthesis are based on polyethers, with a relatively smaller number based on polyesters. Some recent developments have involved ionic polymerization[4]. However, the extremely stringent reaction conditions needed to produce telechelics with functionality equal to 2.00 are very difficult, if not impossible, to achieve. If chain extension is the ultimate objective for a telechelic material, accurate control over functionality of each macromolecule is extremely important as functionality higher than 2.00 leads to crosslinking and less than 2.00 leads to plasticization of the final product.

Telechelic polymers from radical chain polymerization have been available for a number of years from a variety of polymerization methodologies[1,5–7]. These include use of functional initiators[8], iniferters[9,10], functional chain transfer agents (telomers)[11] and incorporation of cleavable weak links along the polymer chain[12,13]. However, with the exception of the weak link approach, much of this chemistry relies on termination being solely by combination as opposed to disproportionation. We have shown that even in the case of styrene, where termination is often reported to be exclusively via combination, disproportionation is a common termination pathway, up to 10%[14]. This ultimately results in a high level of monofunctional macromolecules in the product as opposed to pure telechelic macromolecules. For more sterically hindered propagating polymers, as is the case with 1,1 disubstituted vinyl monomers such as methyl methacrylate, where disproportionation can account for more than 60% of termination[8,15,16], these approaches cannot be used to give telechelic polymers. It would be desirable to have an efficient route to telechelic methacrylates which would provide a new family of prepolymers for subsequent conversion to new materials. It is also noted that where either iniferter or telomer chemistry is utilized, end group functionality often contains undesirable atoms or functional groups with respect to final applications of the materials.

Addition fragmentation chain transfer offers a viable route to telechelic polymers via a free radical process, with all the associated advantages that radical polymerization offers[17–20]. As is the case for iniferter and telomer chemistry, most addition fragmentation chain transfer leads to polymers where at least one of the functional ends is attached via a weak link involving a heteroatom, e.g. S or O. Macromonomers from the catalytic chain transfer polymerization[21,22] of methacrylates have been shown to undergo efficient radical addition fragmentation when copolymerized with methacrylates, which ultimately leads to polymer end groups with similar or identical structure to the remainder of the macromolecule[23]. We have previously demonstrated that a dimer macromonomer, as derived from 2-hydroxyethyl methacrylate, can be used to synthesize α,ω-dihydroxy telechelic poly(methyl methacrylate)[24]. A similar approach has also been described in the patent literature by Berge, although no examples are given[25].

*To whom correspondence should be addressed. E-mail: msrgs@csv.warwick.ac.uk; tel: 01203 523256; Fax: 01203 524112

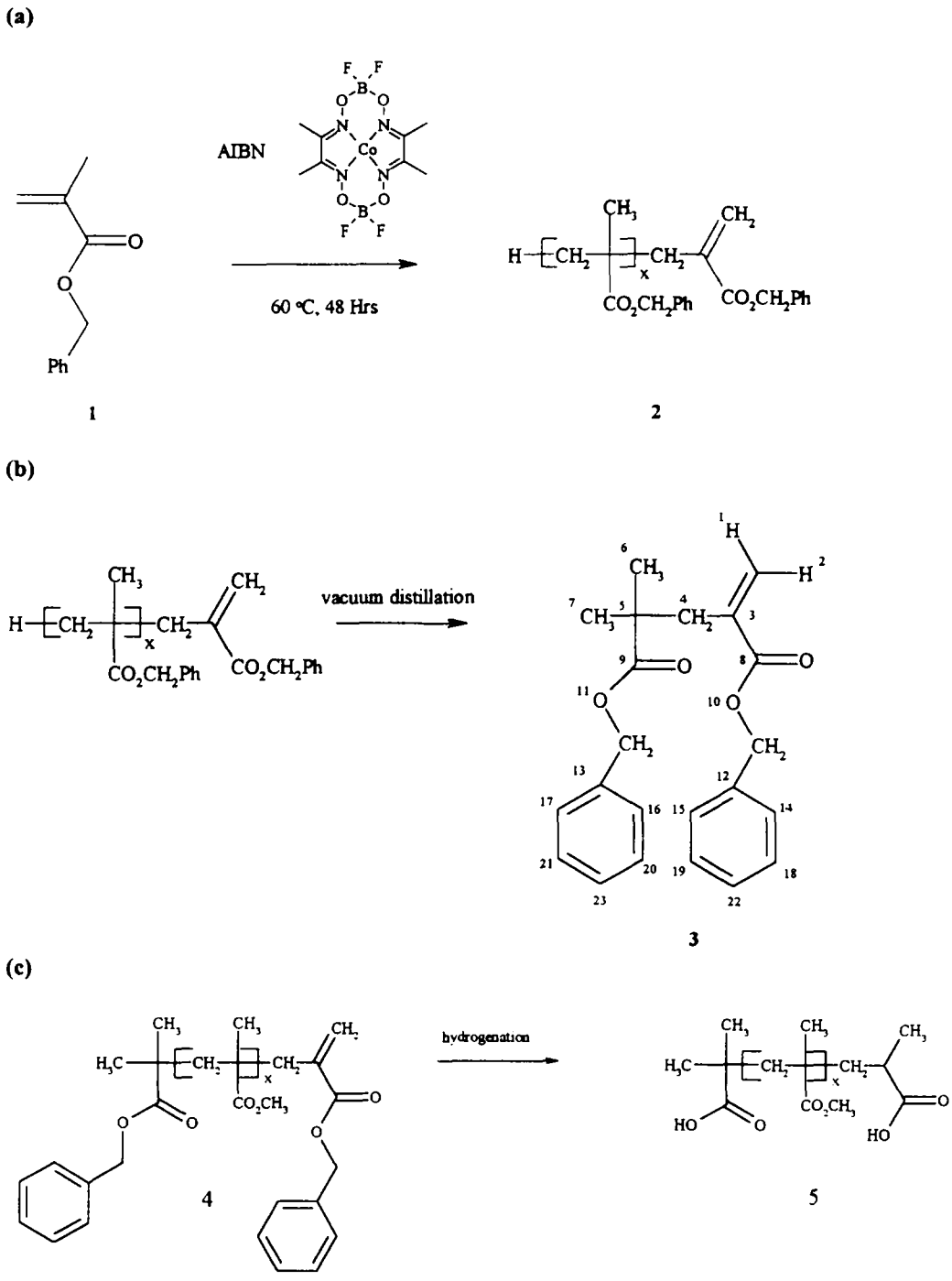

Figure 1 Reaction sequences: (a) CCTP of benzyl methacrylate; (b) isolation of **3**; and (c) hydrogenation of **4** to **5**

Radical addition fragmentation has also been described in the preparation of block copolymers[26,27]. In this paper we wish to demonstrate that α,ω-dicarboxyl poly(methyl methacrylate) may be prepared via radical addition fragmentation utilizing benzyl methacrylate dimer, **3**, as prepared via catalytic chain transfer utilizing bis(boron difluorodimethylglyoximate)cobaltate(II) as catalytic chain transfer agent, with subsequent catalytic hydrogenation.

EXPERIMENTAL

General methods and materials

All polymerizations were carried out using standard Schlenk apparatus and closed ampoules with polymerization mixtures degassed by three freeze–pump–thaw cycles. Methyl methacrylate (MMA) was obtained from ICI (TA5) and used as supplied. Benzyl methacrylate (BzMA) and palladium on activated carbon (10% Pd) and all other reagents and solvents were obtained from Aldrich and used as received. 2,2′-azobis[2-methyl-N-(2-hydroxyethyl)-propionamide] was supplied by WAKO (VA-086) and used as received without further purification. Bis(boron difluorodimethylglyoximate)cobaltate(II) (CoBF) was prepared by the method of Espenson *et al.*[28,29] and recrystallized from methanol prior to use to give the bismethanol adduct, as opposed to the bis aqua complex.

Preparation of benzyl methacrylate dimer, 3

Benzyl methacrylate dimer was prepared by catalytic chain transfer of benzyl methacrylate. Bis(boron

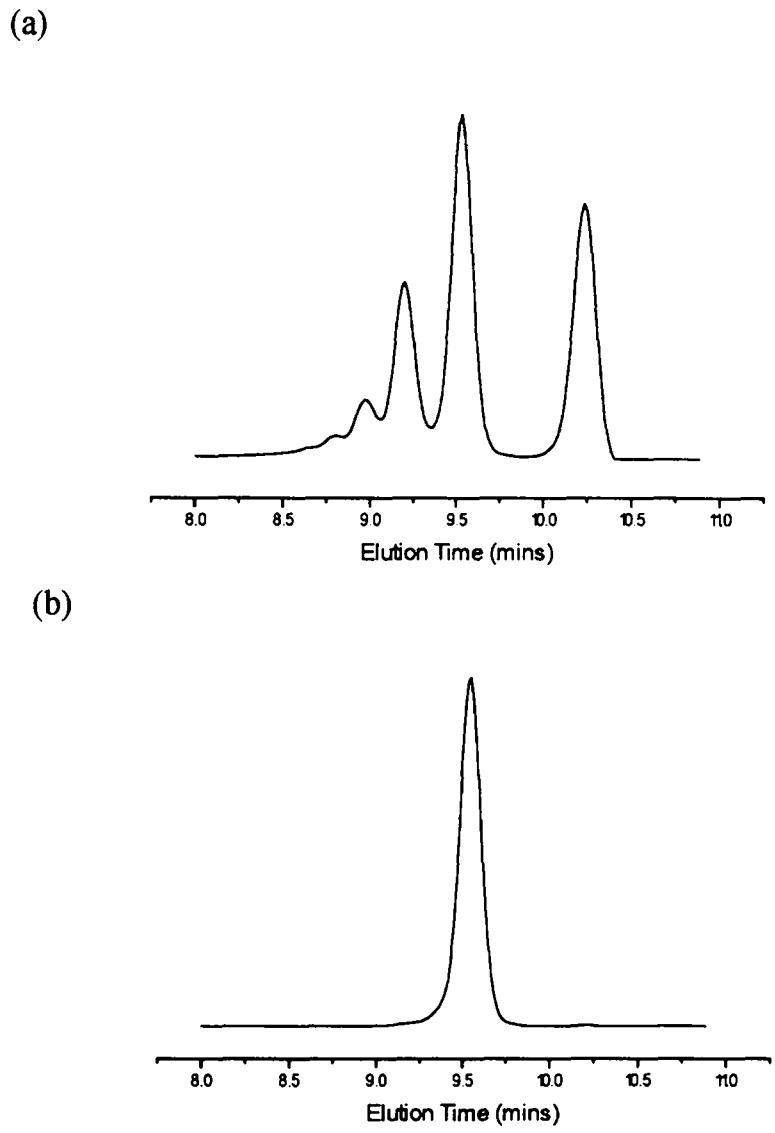

Figure 2 (a) SEC trace of benzyl methacrylate macromonomers as prepared by CCTP; monomer, dimer, trimer, tetramer and pentamer are seen as resolved peaks. (b) SEC of benzyl methacrylate dimer, **3**, recovered by vacuum distillation from the mixture in (a)

difluorodimethylglyoximate)cobaltate(II) (CoBF) (80 mg) and 2,2′-azoisobutyronitrile (AIBN) (257 mg) were dissolved in a mixture of benzyl methacrylate (100 ml) and butanone (100 ml). All reagents were deoxygenated prior to use. The reaction mixture was heated to 60°C for 48 h, after which time the solvent was removed by rotary evaporation. Benzyl methacrylate and **3** were isolated using a Kugelrohr; monomer was collected at 95–120°C and 0.8 mbar, dimer at 244°C and 0.3 mbar.

$C_{22}H_{24}O_4$	Calc. C 74.98	H 6.86
	Found C 75.09	H 6.98

^{1}H n.m.r. (TCE, 298 K): δ: 7.41–7.35 (m, H^{14}–H^{23}), 6.31 (s, H^1), 5.55 (s, H^2), 5.20 (s, H^{11}), 5.12 (s, H^{10}), 2.74 (s, H^4), 1.26 (s, H^6), 1.26 (s, H^7). Intensity ratio: 10 : 1 : 1 : 2 : 2 : 2 : 3 : 3 ^{13}C n.m.r. (TCE, 298K): δ: 176.26 (C^9), 166.75 (C^8), 136.73 (C^3), 135.88 (C^{13}), 135.62 (C^{12}), 128.18 (C^1), 127.81, 127.65, 127.36 (C^{14}–C^{23}), 66.12, 65.71 (C^{10}, C^{11}), 42.46 (C^5), 40.57 (C^4), 24.50 (C^6, C^7)
I.r. (NaCl, film): 3090, 3065, 3033 (s, aromatic C–H), 2973, 2873 (vs, aliphatic C–H), 1721 (vs, C=O), 1627 (s, C=C), 1498, 1472, 1456 (aromatic C=C), 1390, 1375, 1338, 1289, 1197, 1145, 1081, 1020, 957, 916, 818, 751 and 697 cm^{-1}.

Polymerizations

For a typical polymerization in the presence of **3** (see *Table 1*), methyl methacrylate (MMA) (1.0162 g, 10.15 mmol) and **3** (1.0046 g, 2.85 mmol) were placed in a preweighed ampoule together with 0.9958 g DMF and 1.9949 g of 2,2′-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] solution (0.10 g in 40 g DMF). The reaction mixture was degassed, closed under vacuum and heated at 80°C for 8 days. The polymer was isolated by precipitation into petroleum ether and dried under vacuum.

Hydrogenation

Benzyl methacrylate terminated PMMA (**4**, 0.3 g) was dissolved in dichloromethane, precipitated from methanol and redissolved in dichloromethane in a Parr hydrogenation flask. Palladium on activated carbon (0.03 g, 10% Pd) was

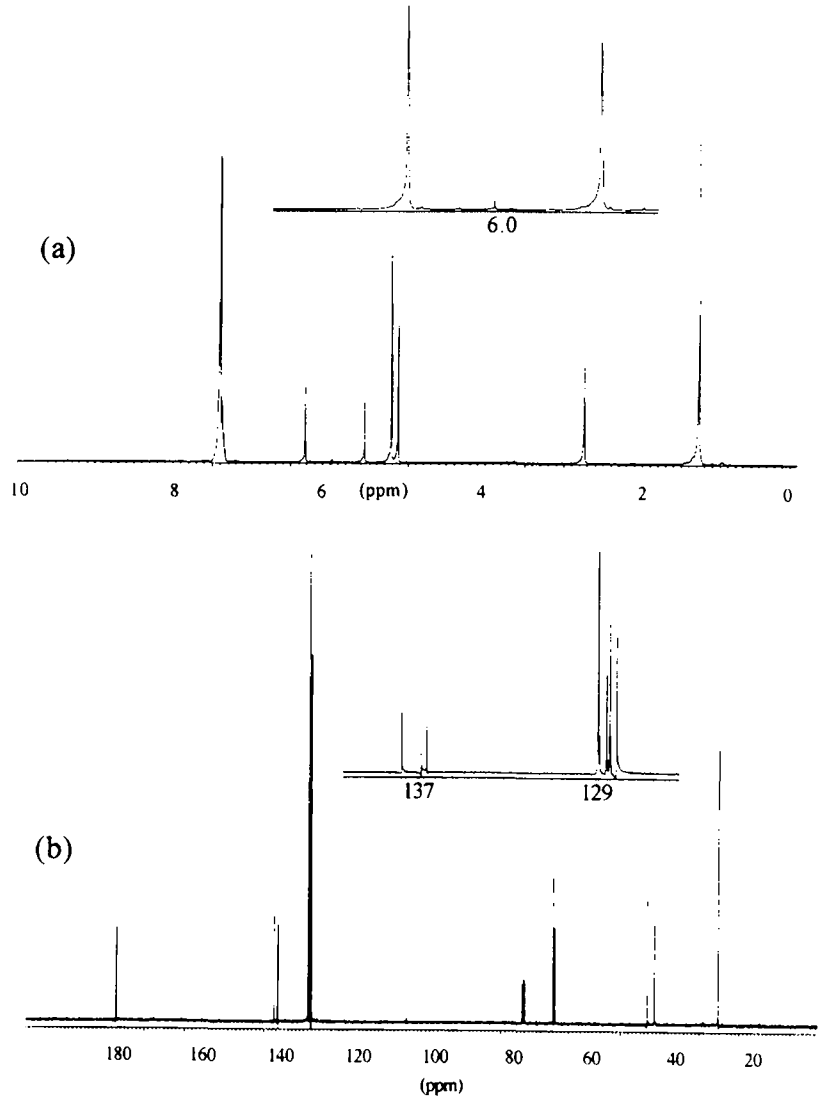

Figure 3 (a) 400 MHz ^{1}H n.m.r. of **3**; (b) 100 MHz ^{13}C n.m.r. of **3**

Table 1 Reaction conditions for polymerizations of MMA in the presence of **3**

	MMA (g)	**3** (g)	Initiator (g)	DMF (g)	Time (min)	Initiator half-lives
A	1.0268	1.0075	0.0052	2.9979	1020	1
B	1.0208	1.0046	0.0051	2.9803	2460	2
C	1.0242	1.0050	0.0051	2.9904	11 520	11.5
D	0.5077	1.0197	0.0026	3.5406	11 520	11.5
E	0.6511	1.3051	0.0055	3.1706	11 520	11.5

added to the flask prior to being shaken under a hydrogen atmosphere for 4 days. The majority of the solvent was removed by rotary evaporation before the catalyst was removed by passing the solution through a column of Celite, acetone being used as eluent. The polymer was isolated by precipitation into hexanes.

Analysis

Size exclusion chromatography was carried out using THF as eluent at 1 ml min^{-1} with toluene (0.2 vol%) 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 to 1 577 000. N.m.r. was carried out at 400.135 MHz in ^{1}H TCE, $\delta = 5.97$ and 100.614 MHz ^{13}C in TCE, $\delta = 74.2$, at 298 K. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry was carried out on a Kratos Kompact III spectrometer in reflectron mode. Samples were deposited in a 2,5-dihydroxy benzoic acid matrix from acetone and doped with NaCl, which resulted in species being observed as an Na^{+} adduct at $m/z = M + 23$. 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 approximately 4000 Da are approximately 10 Da at half peak height. These factors combine to allow an accuracy of within 2–3 Da for each individual macromolecular species[30].

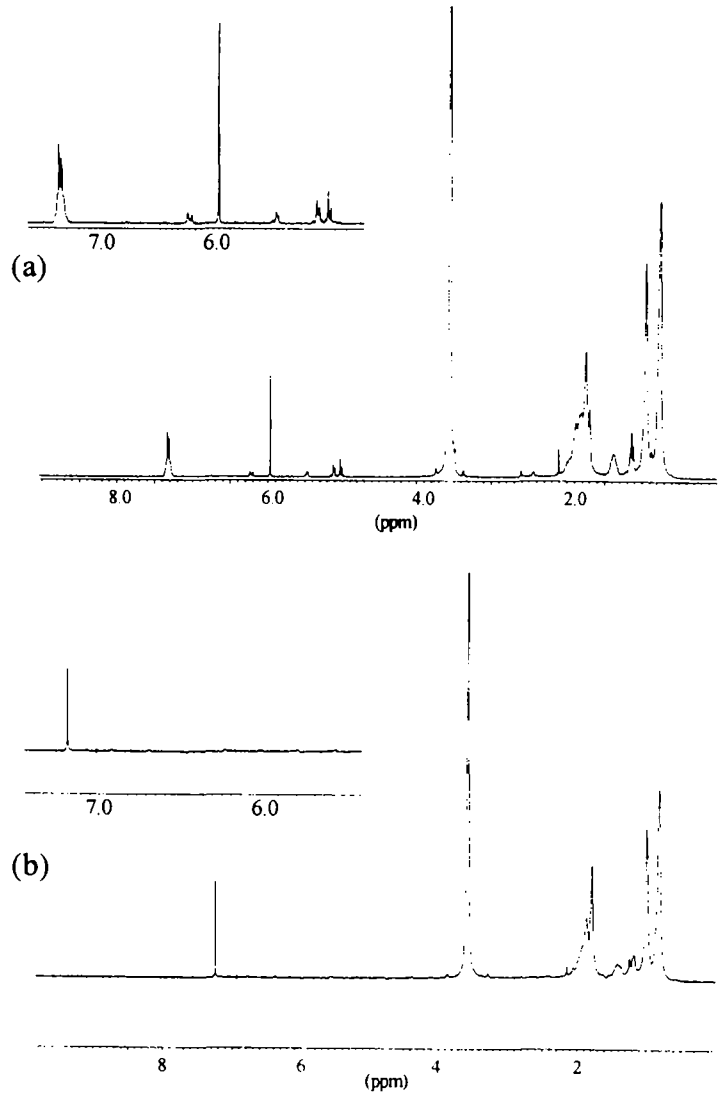

Figure 4 (a) 400 MHz ^{1}H n.m.r. of the precipitated reaction product from D, in TCE; (b) 250 MHz ^{1}H n.m.r. of the precipitated reaction product from D after hydrogenation, in $CDCl_3$

Table 2 Molecular weight data for products from reactions A-E

	[3] (mol%)	M_n	PDI	Conversion (%)
A	21.8	20170	1.97	43.1
B	21.8	16350	2.02	74.8
C	21.8	10240	2.83	85.1
D	56.4	6100	2.66	72.9
E	36.28	6670	2.26	79.5

RESULTS AND DISCUSSION

The use of benzyl methacrylate as a precursor for carboxyl functional polymers was chosen since the benzyl ester has been previously shown to be easily removed by catalytic hydrogenation to give the carboxylic acid[31,32]. An alternative strategy would have been to employ catalytic chain transfer (CCT) with methacrylic acid to give acid dimer macromonomers. However, although this is feasible, catalytic chain transfer agents have been demonstrated to be susceptible towards acid hydrolysis[28], which necessitates the use of a catalyst feed, thus complicating the polymerization process[33]. A simple batch polymerization was preferred in this work. Benzyl methacrylate macromonomer, **2**, was prepared by CCT utilizing CoBF as catalytic chain transfer agent in butanone solution, *Figure 1a*. Solution CCTP resulted in a mixture of macromonomers as observed by SEC analysis, *Figure 2a*. Benzyl methacrylate dimer macromonomer, **3**, can be isolated by distillation under reduced pressure, *Figure 1b*, and has been fully characterized by SEC, *Figure 2b*, showing a single peak, and by both ^{1}H and ^{13}C n.m.r., *Figure 3a* and *b*, which show only one vinyl group, indicative of a pure compound with little contamination of either benzyl methacrylate monomer or higher order macromonomers. Higher order macromonomers have distinctive resonances in the n.m.r. and SEC retention times. It is important to remove higher order macromonomers from the product as methacrylate trimer macromonomers have chain transfer coefficients, C_s, one order of magnitude greater than dimer

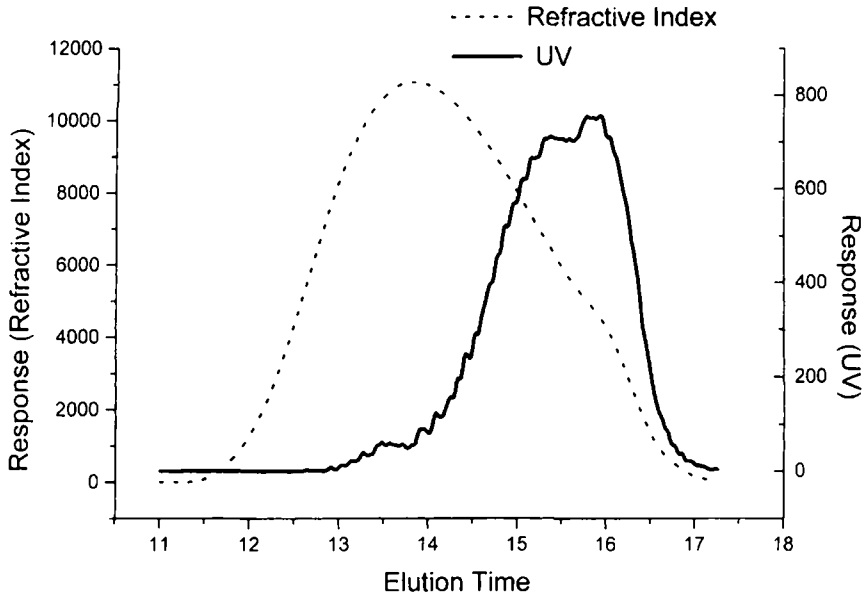

Figure 5 Dual channel DRI and u.v./visible detection SEC traces for polymer D

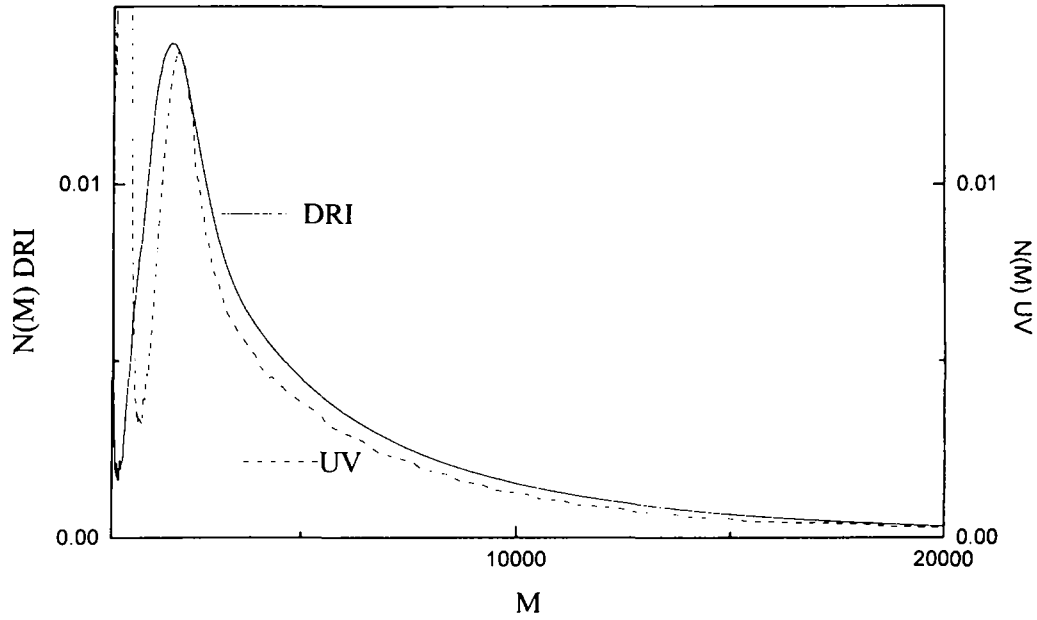

Figure 6 Overlay of the number distribution for polymer A as derived from both the DRI and u.v. detectors

macromonomers; C_s for MMA dimer is reported to be 0.013 and for MMA trimer 0.19 for transfer to poly(methyl methacrylate)[27]. Chain transfer to trimer or higher order macromonomers leads to multifunctional products as opposed to telechelic macromolecules.

Radical polymerization of methyl methacrylate in the presence of **3** was initiated by 2,2′-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] in order to ensure that even polymer chains initiated by primary radical fragments contain useful α functionality. Polymerization for one half-life at 80°C (17 h) in the presence of 21.8 mol% **3**, reaction A, leads to polymeric product in 43.1% yield (see *Table 2*). When the reaction is carried out for longer times, 2 and 11 half-lives, at the same level of **3**, reactions B, C, M_n drops and the PDI broadens. Over the longer time periods the radical flux is greatly reduced, which might be expected to lead to higher molecular weight products. However, as the C_s for **3** is approximately 0.015 it is consumed at a much lower rate than monomer, resulting in an increase in the relative molar amount of **3** with respect to monomer; this increase in chain transfer agent concentration results in the observed drop in M_n. The increase in PDI is explained as the molecular weight distribution shifting to lower molecular mass throughout the experiment. At higher levels of **3**, reactions D and E (duplicates), we see the expected drop in M_n over 11 half-lives.

^{1}H n.m.r. of the precipitated reaction product from D, *Figure 4a*, shows the incorporation of benzyl ester groups within the polymer, 7.2–7.4 ppm and 5.0–5.2 ppm, as well as an ω-terminal vinylic group at approximately 6.24 and 5.47 ppm. SEC with dual channel differential refractive index (DRI) and u.v./visible detection show incorporation of aromatic groups across the molecular weight range, *Figure 5*. The difference between the DRI and u.v. traces

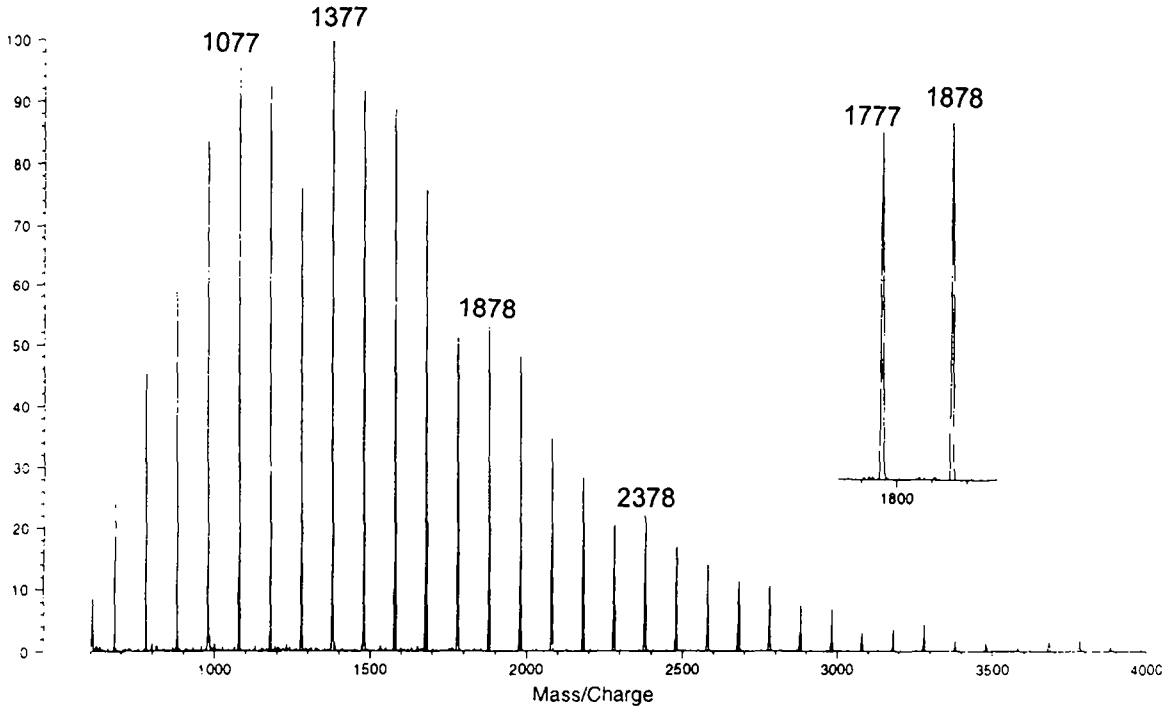

Figure 7 MALDI TOF MS of D. Expanded region shows peaks corresponding to **4**, where $x = 14$ and 15

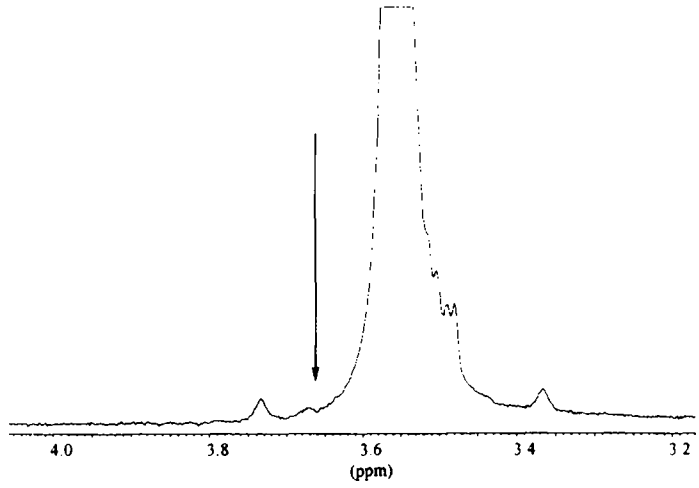

Figure 8 Expanded region of 400 MHz ^{1}H n.m.r. of D. The arrow shows where a methoxy α to a terminal vinylic group would be expected

in *Figure 5* is due to the u.v. detector giving a number distribution. As there are only two benzyl ester groups per chain, irrespective of molecular mass, we see a relatively weaker signal at higher mass than is seen in the DRI trace which is a true concentration detector. The difference between the traces seems quite remarkable. However, the molecular weight of the polymer at 12 min elution time is approximately 64 000 g mol^{-1}. This represents a lowering of the u.v. chromophore by two orders of magnitude from the lower molecular mass oligomers. In order to achieve efficient separation on the SEC columns for acceptable DRI analysis the sample concentration is approximately 1 mg ml^{-1}. This decrease in concentration explains the decrease in signal-to-noise ratio in the spectrum and the eventual loss of signal. This effect can be better understood if both traces are converted to number distributions.

The number distribution from the DRI detector was calculated according to the method of Shortt[34]. The DRI detector is a mass sensitive detector and so the raw SEC chromatogram is a differential weight distribution, i.e. dw/dV_{el}, where w is the weight of polymer and V_{el} is the elution volume. The chromatogram is first normalized to give the weight of polymer per unit volume increment:

$$\frac{dw}{dV_{el}} = \frac{h(V_{el})}{\int h(V_{el})dV_{el}} \quad (1)$$

By dividing the normalized chromatogram by the first derivative of the calibration curve, $d(\log M)/dV_{el}$, the distribution in terms of log molecular weight is obtained:

$$W(\log M) = \frac{dw}{d(\log M)} = -\frac{dw}{dV_{el}}\frac{dV_{el}}{d(\log M)} \quad (2)$$

The log weight distribution, $W(\log M)$, can be converted

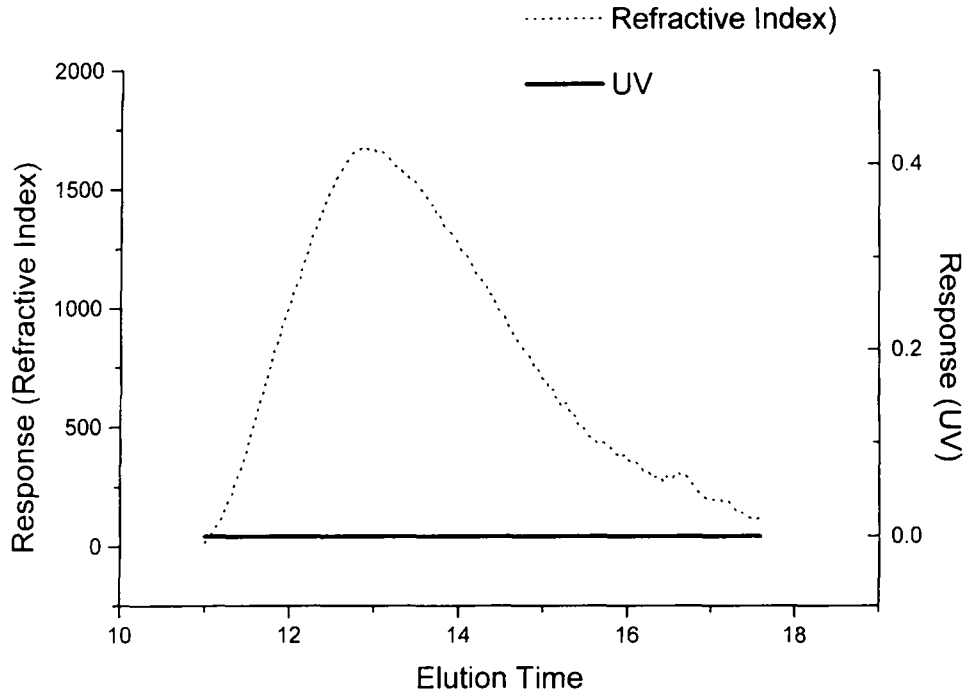

Figure 9 Dual channel DRI and u.v./visible detection SEC traces for polymer D following hydrogenation

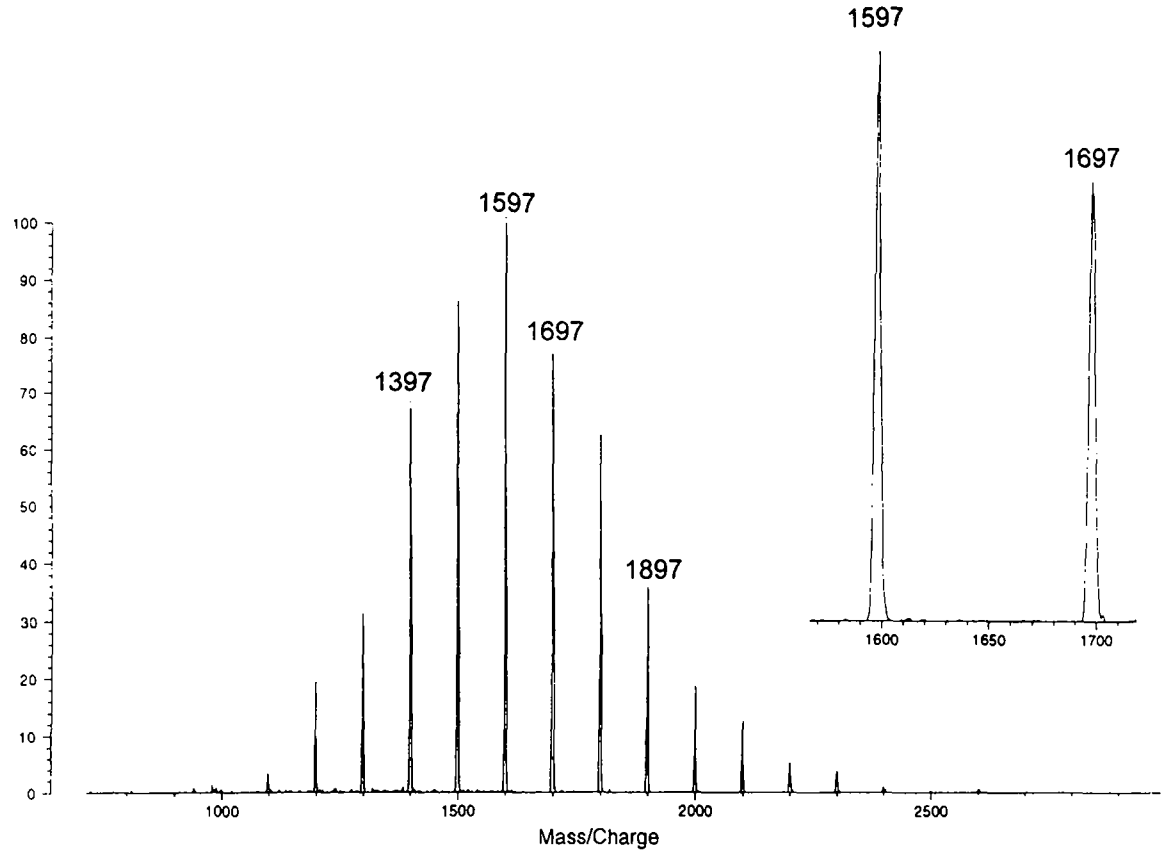

Figure 10 MALDI TOF MS of D following hydrogenation, **5**, expanded region where $x = 14$ and 15

into a linear weight distribution, $W(M)$, as follows:

$$W(M) = \frac{dw}{dM} = \frac{dw}{d(\log M)} \frac{d(\log M)}{dM}$$

$$= \frac{dw}{d(\log M)} \frac{\log e}{M} = W(\log M) \frac{\log e}{M} \quad (3)$$

From the linear weight distribution, $W(M)$, the number distribution $N(M)$ can be calculated:

$$N(M) = \frac{W(M)}{M} \quad (4)$$

The majority of chains have a benzyl methacrylate unit on both endgroups; i.e., there are two u.v. chromophores per

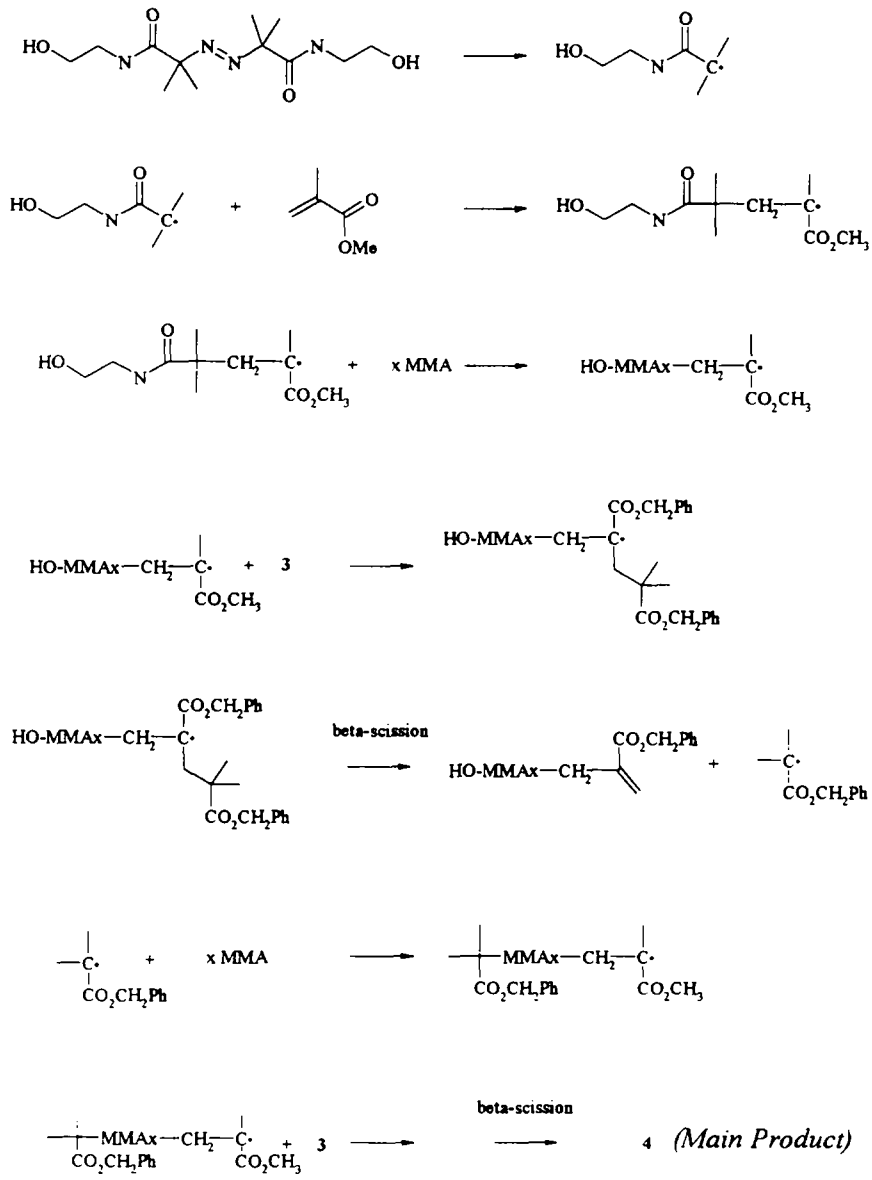

Figure 11 Reaction sequence for the polymerization of methyl methacrylate in the presence of **3**, showing initiation, propagation and termination steps

chain. Thus, when a u.v. detector is used on the SEC the resulting chromatogram reflects the number distribution (dn/dV_{el}).

For a u.v./vis. detector the chromatogram is again normalized to give the number of polymer chains per unit volume increment. Similar calculations follow.

The effect of these calculations is illustrated in *Figure 6* where the number distributions from both detectors are shown for polymer A, showing an excellent agreement, contrary to the impression obtained from examination of the chromatograms.

MALDI TOF MS of polymer D, *Figure 7*, gives a very simple spectrum showing the presence of only one type of macromolecular species corresponding to sodium adducts of MMA_xBzMA_2. It is noted that the MALDI TOF spectrum gives a number distribution directly and there is excellent agreement for the maximum in the number distribution with both the DRI and u.v. traces, *Figure 6*. We see no evidence for primary radical incorporation; for example, the peak at m/z 1377 corresponds to $MMA_{10}BzMA_2$.Na which has a calculated m/z of (10 × 100.12 + 2 × 176.22 + 22.99) = 1376.63, i.e. **4** where $x = 10$; the peak at $m/z = 1777$ has a calculated $m/z = 1777.1$ where $x = 14$. MALDI TOF is unprecedented in providing compositional information but does not provide information concerning the position of the two benzyl methacrylate units within the macromolecule. We have previously shown that where the ω-terminal vinyl group is α to a methoxy ester (i.e. a methyl methacrylate unit) we observe a singlet approximately 0.1 ppm to low field of the main signal from the methoxy protons, i.e. at approximately 3.65 ppm[24]. *Figure 8* clearly shows an absence of this. We have also previously shown that, on addition of a methacrylic macromonomer to a radically propagating poly(methacrylate) fragmentation (β-scission) is almost exclusively favoured relative to propagation[35]. On the basis of these observations we conclude that the product from these reactions has both α and ω benzyl ester groups, **4**. Catalytic hydrogenation of the product leads to loss of toluene, leaving terminal carboxyl functionality as seen by ^{1}H n.m.r., *Figure 4b*. Dual detection SEC shows no u.v. signal, confirming the loss of the aromatic groups from the polymer, *Figure 9*. MALDI TOF again shows a very simple spectrum, *Figure 10*. There is no evidence for any starting material remaining: note the lack of a peak at $m/z = 1777$. The MALDI TOF spectrum supports **5** as the main product where the peak at $m/z = 1597$ corresponds to **5** with $x = 14$.

calculated m/z = 1596.85, i.e. the hydrogenation product from the peak at m/z = 1777 in **4**.

CONCLUSIONS

We have demonstrated that α,ω-dicarboxyl telechelic poly(methyl methacrylate) may be prepared via radical addition–fragmentation polymerization from the reaction sequence shown in *Figure 11*. Benzyl methacrylate dimer may be easily prepared by CCTP, isolated as a pure compound and used as an effective chain transfer agent. Chain transfer activity arises from an addition–fragmentation process which results in the macromonomer dimer splitting in half. One half of the dimer finishes as the ω-terminal end of each macromolecule whilst the other half of the dimer is released as a functional initiating radical. These two events are very efficient and only telechelic product of structure **5** is observed. A combination of n.m.r. and MALDI TOF MS proved invaluable in the elucidation of the structure of the product. The products from CCTP have been shown to be useful in subsequent controlled polymer synthesis.

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REFERENCES

1. Goethals, E. J., *Telechelic Polymers: Synthesis and Applications*. CRC Press, Boca Raton, 1989.
2. Caeter, P.V., *Trends Polym. Sci.*, 1995, **3**, 227.
3. Athey, R.D. Jr, *J. Coat. Technol.*, 1982, **54**, 47.
4. Sawamoto, M. and Kamigaito, M., in *Precision Polymer Synthesis by Living Cationic Polymerisation*, Vol. 2, ed. J. R. Ebdon. Blackie, Glasgow, 1995, p. 2/37 ff.
5. Boutevin, B., *Adv. Polym. Sci.*, 1990, **94**, 69.
6. Ameduri, B., Boutevin, B. and Gramain, P., *Adv. Polym. Sci.*, 1997, **127**, 87.
7. Heitz, W., *Makromol. Chem., Macromol. Symp.*, 1987, **10/11**, 297.
8. Moad, G. and Solomon, D. H., *Chemistry of Bimolecular Termination*. Vol. 3, ed. G. C. Eastmond, A. Ledwith, S. Russo and P. Sigwalt. Pergamon, Oxford, 1989, p. 11/147 ff.
9. Otsu, T. and Tazaki, T., *Polym. Bull. (Berlin)*, 1986, **16**, 277.
10. Nair, C.P.R. and Clouet, G., *J. Macromol. Sci. Rev. Macromol. Chem. Phys.*, 1991, **C31**, 311.
11. Baudin, G., Boutevin, B., Mistral, J.P. and Sarraf, L., *Makromol. Chem.*, 1985, **186**, 1445.
12. Ebdon, J.R., Flint, N.J. and Hodge, P., *Eur. Polym. J.*, 1989, **25**, 759.
13. Ebdon, J.R., Flint, N.J. and Rimmer, S., *Macromol. Rep.*, 1995, **A32**, 603.
14. Zammit, M.D., Davis, T.P., Haddleton, D.M. and Suddaby, K.G., *Macromolecules*, 1997, **30**, 1915.
15. Moad, G. and Solomon, D. H., *The Chemistry of Free Radical Polymerisation*. Pergamon, Oxford, 1995.
16. Odian, G., *Principles of Polymerization*, 2nd edn. John Wiley & Sons, New York, 1981.
17. Rizzardo, E., Meijs, G.F. and Thang, S.H., *Macromol. Symp.*, 1995, **98**, 101.
18. Meijs, G.F., Morton, T.C., Rizzardo, E. and Thang, S.H., *Macromolecules*, 1991, **24**, 3689.
19. Yamada, B., Tagashira, S. and Aoki, S., *J. Polym. Sci. A. Polym. Chem.*, 1994, **32**, 2745.
20. Yamada, B., Kobatake, S. and Otsu, T., *Polym. J.*, 1992, **24**, 281.
21. Davis, T.P., Kukulj, D., Haddleton, D.M. and Maloney, D. R., *Trends Polym. Sci.*, 1995, **3**, 365.
22. Haddleton, D.M., Maloney, D.R. and Suddaby, K.G., *Macromol. Chem. Phys. Macromol. Symp.*, 1996, **111**, 37.
23. Haddleton, D. M., Maloney, D. R. and Suddaby, K. G., *Macromolecules*, 1996, **29**, 481.
24. Haddleton, D.M., Topping, C., Hastings, J.J. and Suddaby, K.G., *Macromol. Chem. Phys.*, 1996, **197**, 3027.
25. Berge, C. T., Darmon, M. J. and Antonelli, J. A., US Patent No. 5 371 151, 1994.
26. Krstina, J., Moad, C.L., Moad, G., Rizzardo, E., Berge, C.T. and Fryd, M., *Macromol. Symp.*, 1996, **111**, 13.
27. Krstina, J., Moad, G., Rizzardo, E. and Winzor, C.L., *Macromolecules*, 1995, **28**, 5381.
28. Bakac, A., Brynildson, M.E. and Espenson, J.H., *Inorganic Chemistry*, 1986, **25**, 4108.
29. Bakac, A. and Espenson, J.H., *J. Am. Chem. Soc.*, 1984, **106**, 5197.
30. Lloyd, P.M., Suddaby, K.G., Varney, J.E., Scrivener, E., Derrick, P.J. and Haddleton, D.M., *Eur. Mass Spectrom.*, 1995, **1**, 293.
31. Mykytiuk, J., Armes, S.P. and Billingham, N.C., *Polym. Bull.*, 1992, **29**, 139.
32. Rannard, S.P., Billingham, N.C., Armes, S.P. and Mykytiuk, J., *Eur. Polym. J.*, 1993, **29**, 407.
33. Suddaby, K.G., Haddleton, D.M., Hastings, J.J., Richards, S.N. and O'Donnell, J.P., *Macromolecules*, 1996, **29**, 8083.
34. Shortt, D.W., *J. Liquid Chromat.*, 1993, **16**, 3371.
35. Haddleton, D.M., Maloney, D.R. and Suddaby, K.G., *Macromolecules*, 1996, **29**, 481.