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Synthesis of branched poly(methyl methacrylate)s *via* controlled/living polymerisations exploiting ethylene glycol dimethacrylate as branching agent

Francoise Isaure,[a] Peter A. G. Cormack,[a] Susan Graham,[a] David C. Sherrington,*[a] Steven P. Armes[b] and Vural Bütün[c]

[a] *Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow, UK G1 1XL. E-mail: d.Sherrington@strath.ac.uk; Fax: 0141 548 4246; Tel: 0141 548 2799*
[b] *Department of Chemistry, School of Life Sciences, University of Sussex, Falmer, Brighton, UK BN1 9QJ*
[c] *Department of Chemistry, Faculty of Arts and Sciences, Osmangazi University, Campus of Meselik, 26480 Eskisehir, Turkey*

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With appropriate choice of reaction composition and conditions, copolymerisation of methyl methacrylate and ethylene glycol dimethacrylate using Cu-based ATRP or GTP methodologies yields soluble branched polymers in facile one-pot reactions.

Recently Sherrington and his coworkers[1] have reported a facile, generic and cost effective route to branched vinyl polymers *via* conventional free radical polymerisation using a multi-functional vinyl comonomer as the branching species, with gelation inhibited by use of a thiol chain transfer agent or indeed a catalytic chain transfer species.[2] The mole ratio of (doubly reacted branching comonomer incorporated)/(thiol residues incorporated) (from ^{1}H NMR spectra) is a measure of the average number of branching units per primary chain, N_c.[3] In principle providing $N_c \leq 1$, for a difunctional brancher, the product will have a branched architecture. For $N_c > 1$ the product is likely to be a crosslinked gel or microgel. Though this analysis seems rather naïve it is confirmed in practice, and this led us to argue that if we could define and control the number of primary chains *e.g. via* use of controlled or living polymerisations, then by controlling also the level of branching comonomer employed, we should produce branched rather than crosslinked polymer. Hence for ethylene glycol dimethacrylate (EGDMA) and methyl methacrylate (MMA) use of a mole ratio EGDMA/initiator ≤ 1 in a controlled or living polymerisation should yield soluble branched product, with insoluble crosslinked material or microgel resulting when this ratio is >1. Unlike conventional free radical polymerisation no additional chain regulator should be required to avoid network formation. In this context we now report on the polymerisation of MMA/EGDMA using Cu-based ATRP and GTP as examples of controlled and living polymerizations respectively. Gelation involving controlled free radical copolymerization of a monofunctional and a difunctional comonomer has been reported previously,[4] and similar methodology has been employed to end-link a narrow molar mass polystyrene with blocks of crosslinked poly(divinylbenzene).[5] However the only existing approach which relates directly to the novel one we now describe is the use of so-called self-condensing vinyl polymerisation.[6]

ATRP of MMA/EGDMA mixtures were carried out in toluene at 90 °C using the initiator system 2,2′-bipyridyl (bipy)/Cu(I)Cl/ethyl-2-bromopropionate (EBP) = 3/1/1 mole ratio. Reaction mixtures were filtered to remove the bulk of the Cu residues then precipitated into hexane. Product recoveries were rather low, 25–55%, because polymerizations were terminated after 4 h, and because careful purification of products was required before samples could be analysed by SEC. The results are shown in Table 1. As predicted reaction mixtures ATRP2–4 remained isotropic and the dried products could be readily redissolved in a range of organic solvents, these PMMAs being prepared using EGDMA/EBP ≤ 1. The product from ATRP5 was also soluble but the EGDMA/EBP was 1.16/1 (see SEC data). In contrast the product from ATRP6 (EGDMA/EBP $>$ 1) was a gel and was insoluble in the solvents tested. Remarkably therefore even with ~5 mol% of EGDMA appropriate choice of reaction composition and conditions allows crosslinking to be avoided and fully soluble branched polymer to be prepared. The ^{1}H NMR spectra (CDCl$_3$, 400 MHz) of these soluble PMMAs confirm their branched structure. A PMMA prepared using MMA/EGDMA/EBP = 100/5.86/5.04 (*i.e.* on the limit EGDMA/EBP = 1.16/1) and isolated after 4 h shows the appropriate ^{1}H NMR resonances which we have previously identified[2] as characteristic of the branching –OCH$_2$CH$_2$O– group in the EGDMA residues (δ = 4.1 ppm), along with resonances characteristic of the –OCH$_2$CH$_2$O– group in pendent unreacted EGDMA residues (δ = 4.2 and 4.35 ppm) and the corresponding vinylic hydrogen atoms (δ = 5.5 and 6.2 ppm). Allowing the

Table 1 Controlled ATRP and living GTP of MMA/EGDMA

Entry	Feed ratio (mol) MMA/EGDMA/I	Feed ratio (mol) C=C/I	Feed ratio (mol) EGDMA/I	Solubility (0.5 g ml^{-1})	$M_n \times 10^{-4}$	$M_w \times 10^{-5}$	M_w/M_n
ATRP1[a]	100/0.00/1.00	100/1.00	0	Yes	3.0	0.53	1.7
ATRP2[b]	100/1.10/4.04	100/3.95	0.27/1	Yes	8.5	1.1	1.2
ATRP3[b]	100/2.94/5.00	100/4.72	0.58/1	Yes	3.1	1.0	3.2
ATRP4[b]	100/2.82/3.95	100/3.74	0.71/1	Yes	1.8	1.2	6.5
ATRP5[b]	100/5.86/5.04	100/4.50	1.16/1	Yes	1.4	9.1	63.3
ATRP6[b]	100/4.88/3.85	100/3.50	1.26/1	No	–	–	–
GTP1[c]	100/0.00/1.15	100/1.15	0	Yes	1.5	0.15	1.1
GTP2[c]	100/2.68/1.15	100/1.09	2.33/1	Yes	4.2	1.0	2.5
GTP3[c]	100/3.94/1.17	100/1.08	3.37/1	Yes	5.4	1.9	3.5
GTP4[c]	100/4.96/1.15	100/1.05	4.31/1	Yes	5.7	2.2	4.0

[a] MMA: 5.0 g, 50 mmol; MMA/bipy/CuCl/I = 100/3/1/1, I = EBP; T = 90 °C; toluene (15 ml); time = 4 h; N$_2$ atmosphere; solubility tests in toluene, THF, chloroform and DCM. [b] MMA: 1.5 g, 15 mmol; toluene (7.5 ml); others as in *a*. [c] MMA: 15.0 g, 150 mmol; I = MTS; T = 20 °C; THF (150 ml); time = 2 h; dry N$_2$ atmosphere; solubility tests in THF and CDCl$_3$.

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polymerisation to proceed for 8 h yielded a PMMA whose ^{1}H NMR spectrum indicates essentially no pendent unreacted EGDMA residues.

The SEC molar mass distribution curves for branched PMMAs (ATRP2–5) and the linear PMMA control (ATRP1) are shown in Fig. 1. The data were obtained using a double detection system (refractive index and DAWN multi-angle light scattering (Wyatt Corp., CA, USA)). The required d*n*/d*c* data were obtained off-line. In this sense the molar mass distribution curves are 'absolute'. The curve for the linear control polymer is symmetric and yields M_n, M_w and M_w/M_n of 30 K, 53 K and 1.7 respectively. The M_n is greater than that expected from the monomer/EBP ratio, and the polydispersity is somewhat higher than the best ATRP literature examples. We suspect this is due to some inefficiency in the use of the EBP, and the poor solubility of the catalyst/ligand. Nevertheless the data provide an in-house generated benchmark for comparing the branched products. The molar mass distributions of the latter are clearly much broader and there is some suggestion of multimodality (Fig. 1). The breadth of the distributions grows systematically as the EGDMA level used is increased, and is reflected in the molar mass and dispersity index data in Table 1. Indeed the extremely broad distribution of sample ATRP5 (extending beyond the upper molar mass range of the SEC columns used) almost certainly reflects the presence of microgel, and this is consistent with the EGDMA/EBP ratio >1 used in this polymerisation. Overall the results agree well with the large volume of data we have now generated on branched vinyl polymers[2] and these distributions confirm the complexity of the architectures generated in these polymerisations.

GTP of MMA/EGDMA comonomer mixtures were carried out in dry THF at room temperature using 1-methoxy-1-trimethylsiloxy-2-methylpropane (MTS) as initiator and *n*-tetrabutylammonium bibenzoate (TBABB)[7] as catalyst. The THF was dried over Na wire and refluxed over K before distillation; MMA and EGDMA were dried over CaH_2 and distilled; and MTS was distilled prior to use. Polymerisations were performed in flame-dried glassware under dry N_2 with component transfers made by cannula. Typical procedural details have been reported previously.[8] Polymerisations were quenched with methanol and the PMMA was recovered by removal of the solvent under vacuum to provide essentially quantitative conversion and recovery of this set of polymers. The results are shown in Table 1. All isolated copolymers (GTP1–4) could be readily redissolved in THF and chloroform. The ^{1}H NMR spectra ($CDCl_3$, 300 MHz) of the PMMAs confirm the presence of the branching EGDMA residues ($\delta = 4.1$) but there is no indication of any unreacted pendent vinyl groups.

The SEC data yielded a value for M_n of 15 K, somewhat higher than expected. Nevertheless the narrow molar mass distribution ($M_w/M_n \sim 1.10$) (Table 1 and Fig. 2) confirms the high level of control achieved in these polymerisations. For the branched copolymers obtained from GTP2–3 the molar mass distributions (Fig. 2) again shift to much higher mass, broaden considerably and become multi-modal, much like the PMMAs obtained from the ATRP syntheses. The M_n, M_w and M_w/M_n data (Table 1) rise systematically with the level of brancher, EGDMA, and this is consistent with branching increasing in this series. Remarkably however the EGDMA/MTS mole ratios for GTP2–4 are in the range ~2.3/1 to ~4.3/1 and it is difficult to rationalize why these polymerizations do not gel, especially when the ^{1}H NMR spectra indicate that the consumption of both vinyl groups in the EGDMA is essentially quantitative. One likely explanation is that the extremely reactive enolate chain ends in these GTP syntheses give rise to a significant level of cyclopolymerisation of EGDMA or at least an increase in cyclised structures (*i.e.* intramolecular reaction rather intermolecular branching). Indeed the contribution from cyclisation reactions in conventional free radical copolymerization of MMA/EGDMA was investigated some time ago.[9]

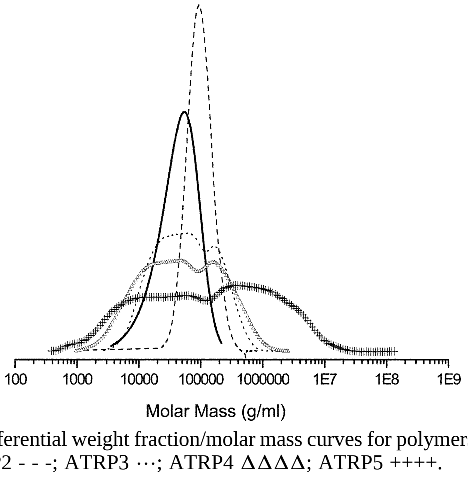

Fig. 1 Differential weight fraction/molar mass curves for polymers: ATRP1 —; ATRP2 - - -; ATRP3 ···; ATRP4 ΔΔΔΔ; ATRP5 ++++.

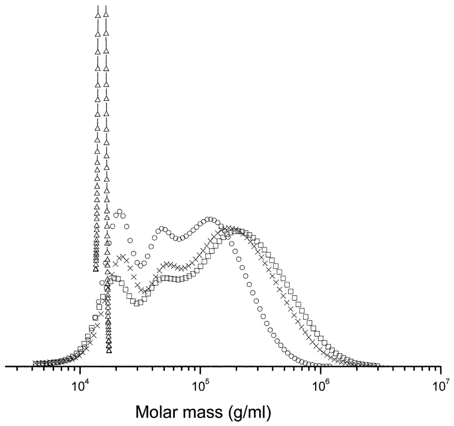

Fig. 2 Differential weight fraction/molar mass curves for polymers: GTP1 ΔΔΔΔ; GTP2 oooo; GTP3 xxxx; GTP4 □□□□.

We believe that the results reported here constitute examples of a generic methodology for the synthesis of branched vinyl polymers which simply involves appropriate manipulation of *existing* polymerisation procedures. Indeed very recently Baskaran[10] reported on a so-called self-condensing[11] anionic polymerisation involving divinyl and diisopropenyl benzene. In fact his work is just one example of the principle which we have generalised in this manuscript, and, together with the conventional free radical polymerisation methodology we have disclosed,[2] these now provide facile methods not only for producing branched vinyl polymers, but potentially also linear–branched and branched–branched block copolymers. The scene is now set for a step-change in the availability, at only modest cost, of polymeric materials with these complex architectures.

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