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PII: S0032-3861(97)00294-2

Polymer Vol. 39 No. 4, pp. 933–941, 1998
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0032-3861/97/$17.00+0.00

Synthesis of addition polymers derived from enantiomerically pure amino acids

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(Received 6 November 1996; revised 24 March 1997)

The synthesis of fully and partially protected serine derived monomers suitable for addition polymerization is reported, along with the homo- and copolymerization of these enantiomerically pure monomers. The monomers are all derived from (*S*)-serine methyl ester, by the introduction of an acryloyl or methacryloyl group onto the serine alcohol functionality. The fully protected monomers also contain a triphenylmethyl group on the serine amino group. The characterization of the resulting polymers using gel permeation chromatography, polarimetry, circular dichroism, elemental analysis and nuclear magnetic resonance is described. All of the polymers are atactic and optically active. The specific rotation of the polymers was found to vary in a non-linear manner with the proportion of chiral monomer incorporated into the polymers. © 1997 Elsevier Science Ltd.

(Keywords: serine; chiral; addition polymer)

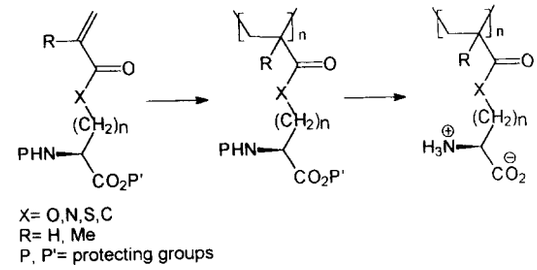
INTRODUCTION

The synthesis of condensation polymers derived from amino acids by the ring opening polymerization of Leuch's anhydrides is a well established process for the synthesis of biomimetic polyamides[1–6]. However, this type of polymerization process destroys the amino and acid functional groups which were present in the amino acid starting materials. Therefore, we have undertaken a project aimed at the synthesis of a different type of polymer derived from amino acids; by the radical induced addition polymerization of amino acid derivatives bearing alkene functionalities in their side chain, as outlined in *Scheme 1*. The synthesis of condensation polymers utilising amino acid sidechains has previously been reported[7,8]. This approach will have the advantage of retaining the amine and acid functional groups within the polymer, and as a result of this, the polymers would be expected to possess a number of useful properties including: optical activity, solubility in aqueous and highly polar solvents, electrical conductivity through ion movement, and applications to templated polymers[9,10]. These properties will also be expected to be pH dependent. In this paper, we report our first results on the synthesis of monomers, polymers and copolymers of the type shown in *Scheme 1* using serine as the chiral monomer precursor. A preliminary account of some of the work reported in this paper has been published[11].

MONOMER SYNTHESIS

(*S*)-Serine **1** was chosen as the starting material for this study, as its three functional groups can be easily differentiated. Thus esterification of (*S*)-serine with methanol/HCl gave the corresponding methyl ester as shown in *Scheme 2*. For amine protection, the triphenylmethyl group was chosen as it was anticipated that the steric bulk of this group may confer desirable conformational properties on the final polymers[12–16]. In addition, the triphenylmethyl group is easily removed under a variety of mild conditions, and does not enhance the acidity or hydrogen bonding ability of the remaining NH a factor which will be important in the later preparation of templated polymers. Hence treatment of (*S*)-serine methyl ester with triphenylmethyl chloride and triethylamine gave the desired derivative[17] with both amine and acid groups protected. Reaction of the doubly protected serine derivative with acryloyl chloride or methacryloyl chloride in the presence of triethylamine gave the desired monomers **2** and **3**. Finally, deprotection of the triphenylmethyl groups using trifluoroacetic acid gave the partially deprotected monomers **4** and **5**.

O,N-Diacryloyl monomer **6** was also prepared by treatment of (*S*)-serine methyl ester with excess acryloyl chloride. Monomer **6** is a potential crosslinking agent, but was primarily prepared to show that no *O*-*N*-acyl migration had occurred during the synthesis of monomers **4** and **5**. In the ^{1}H nuclear magnetic resonance (n.m.r.) spectrum of compound **6** (see experimental section), the N*H* resonance occurs as a doublet, and the resonances for the *N*-acryloyl unit occur at different chemical shifts for those of the *O*-acryloyl group. These results indicated that the (meth)-acryloyl groups of monomers **4** and **5** were still attached to the oxygen atom.



Scheme 1

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Table 1 Analysis of polymers derived from monomer **3**

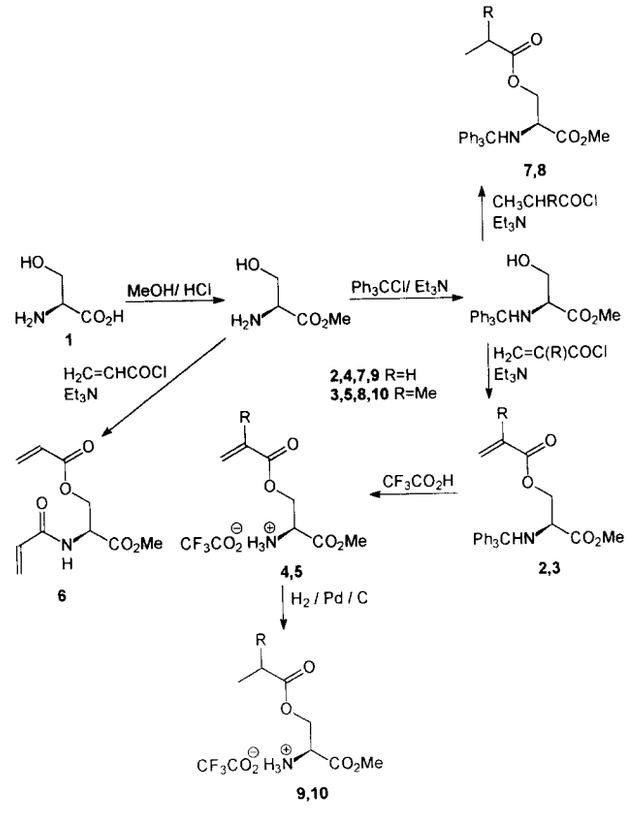
Monomer	MMA added	MMA[a](inc)	M_n^b	M_w^b	M_w/M_n	$[\alpha]_D^{20}$	Found (C,H,N%)	Requires (C,H,N%)
3[c]	0	0	16100[f]	127500	7.9	+ 54.1	75.7,6.3,3.3	75.5,6.3,3.3
3[d]	0	0	1400	1700	1.3	+ 48.0	not analysed	
3[d]	1	2.7	3100	6400	2.1	+ 24.9	not analysed	
3[d]	2	4.5	3900	9200	2.4	+ 24.9	not analysed	
3[d]	3	6	5100	12400	2.4	+ 23.2	not analysed	
3[e]	0.1	0.27	22300	164000	7.4	+ 49.0	74.4,6.8,3.1	74.6,6.4,3.1
3[e]	0.25	0.5	17000	124000	7.3	+ 45.5	74.3,6.6,3.1	73.9,6.5,2.9
3[e]	1	2	22400[f]	299000	13.3	+ 33.0	70.1,6.5,2.3	70.6,6.9,2.2
3[e]	2	3	18400[f]	226000	12.3	+ 28.4	69.5,7.4,2.2	69.1,7.0,1.9
3[e]	5	11	14500[f]	95550	6.6	+ 18.0	63.9,7.1,1.4	64.3,7.6,0.9
3[e]	10	15	27050	250000	9.2	+ 14.8	63.1,7.6,0.7	63.4,7.7,0.7
3[e]	15	24	20500	122500	6.0	+ 7.6	62.3,8.0,0.4	62.3,7.8,0.5
3[e]	25	37	28200	157000	5.6	+ 6.2	61.2,8.4,0.3	61.6,7.9,0.3
3[e]	50	65	16550	190500	11.5	+ 3.9	60.4,8.2,0.2	60.9,7.9,0.2
3[e]	100	127	29850	177500	6.0	+ 2.5	60.8,8.5,0.2	60.6,8.0,0.1

MMA, methyl methacrylate
[a]Ratio of MMA to amino acid in polymer determined by integration of the ^{1}H n.m.r. signals for the methyl esters
[b]Measured by g.p.c. using chloroform as eluent
[c]Polymerization carried out in toluene using benzoyl peroxide as initiator
[d]Polymerization carried out in toluene using AIBN as initiator
[e]Polymerization carried out with no solvent and benzoyl peroxide as initiator
[f]G.p.c. results are calculated on all material in the sample with a molecular weight greater than 1000

SYNTHESIS AND CHARACTERIZATION OF POLYMERS DERIVED FROM MONOMERS 3 AND 2

Initially, the radical initiated homopolymerization of monomer **3** was attempted in toluene solution, using AIBN as the radical initiator. The synthesis of copolymers between monomer **3** and methyl methacrylate was also attempted using this methodology. Selected analytical data for all of these polymers are reported in *Table 1*, and as the results indicate, only relative low molecular weight materials were obtained using this methodolgy. All of the gel permeation chromatography (g.p.c.) results are referenced to polystyrene, so the molecular weight data given in *Table 1* are actually polystyrene equivalent molecular weights. As the structure of the polymers prepared in this work differ significantly from that of polystyrene, it was felt prudent to check the appropriateness of these polystyrene equivalent molecular weight values. Thus, a combined g.p.c./viscosity measurement was carried out on the copolymer containing a 6/1 ratio of methyl methacrylate to monomer **3**, and this indicated that the polystyrene equivalent molecular weights were underestimating the true molecular weight values by a factor of about two. Even with this correction however, the polymerizations using this procedure were still giving only relatively low molecular weight polymers. In addition, the data in *Table 1* show that the M_n and M_w values for the polymers increase as the proportion of methyl methacrylate in the polymer increases, which would suggest that compound **3** is a less efficient monomer than methyl methacrylate.

To optimize the homopolymerization of monomer **3**, the effect of the monomer concentration in toluene upon polymer molecular weight was investigated using benzoyl peroxide as an initiator. The optimum concentration was found to be 3 M, with lower concentrations producing low molecular weight material and higher concentrations causing solubility problems. Under these optimized conditions, homopolymer with M_n = 16100 and M_w = 127500 was obtained.



Scheme 2

To increase the molecular weight of the copolymers, bulk polymerization effectively using methyl methacrylate as the solvent was undertaken, using benzoyl peroxide as the initiator. As can be seen from the results in *Table 1*, this had the desired result of dramatically increasing the molecular weight of the various polymers. *Table 1* also shows that there appears to be no correlation between the proportion

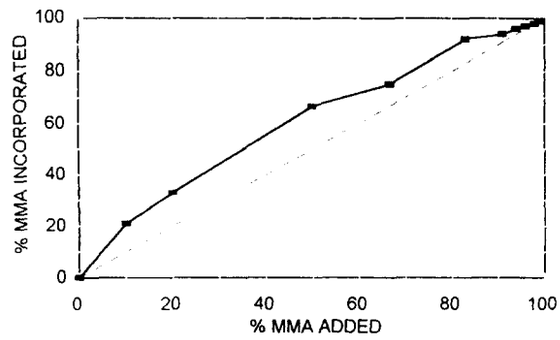


Figure 1 Incorporation of methyl methacrylate (MMA) into copolymers with monomer **3**

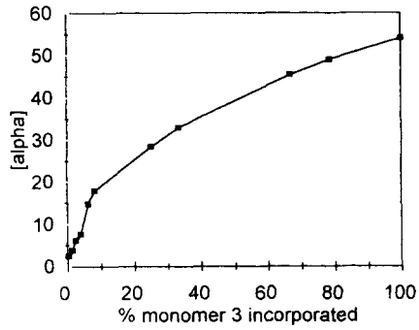


Figure 2 Variation of [α] with % incorporation of monomer **3**

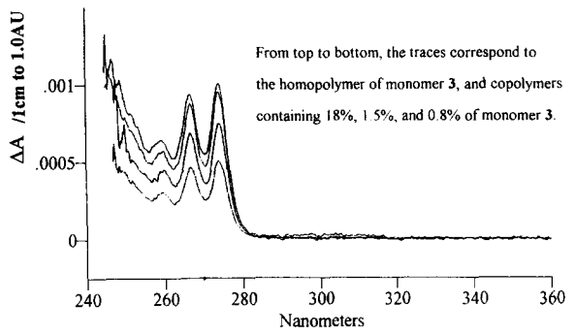


Figure 3 CD spectra of homo- and copolymers of monomer **3** and methyl methacrylate

of monomer **3** incorporated into the polymer, and the molecular weight of the polymer, in contrast to the results obtained for solution polymerization. The polydispersities of the polymers are highly variable, though these are usually in the range of 4–15, values which are typical for polymerizations carried under conditions where autoacceleration can occur[18]. Consistent with this, a rapid rise in the viscosity of the polymerization mixture was observed soon after polymerization commenced.

In all cases, the ratio of methyl methacrylate to monomer **3** in the polymer was greater than the corresponding ratio in the monomer mix as determined by ^{1}H n.m.r. integration of the two methyl ester signals in the polymers (*Table 1*, *Figure 1*). This analysis was facilitated by the triphenylmethyl group present in monomer **3**, which has a strongly shielding effect[19–22] on the methyl ester of monomer **3**, shifting its ^{1}H n.m.r. resonance upfield by about 0.5 ppm, compared to the methyl ester of methyl methacrylate. The preferential incorporation of methyl methacrylate into the polymers, again suggests that monomer **3** has a relatively lower propensity for radical polymerization. A doubling of the ^{1}H and ^{13}C n.m.r. resonances due to the methyl methacrylate residue peaks was observed in all of the polymerizations, indicating that the polymers are atactic with signals being seen for both syndiotactic and isotactic regions of the polymer chains, as well as for changeover regions in some cases.

All of the polymers derived from monomer **3** were optically active, the specific rotations being given in *Table 1*. However, as shown in *Figure 2*, the specific rotation of the polymers does not vary linearly with the %-incorporation of chiral monomer. Rather, the specific rotation initially increases rapidly as the % of chiral monomer incorporated increases from 0 to 10%, then the rate of increase of specific rotation slows down and continues to rise approximately linearly to 100% incorporation. This non-linear variation is not due to differences in the molecular weight or polydispersities of the polymers, as the same effect is observed for the specific rotation of the low molecular weight polymers obtained by solution polymerization (*Table 1*, entries 2–5). There appear to be two possible reasons for this non-linear dependence of specific rotation to % composition of the polymer: asymmetric induction from the enatiomericaly pure serine α-centre to the new chiral centres within the polymer backbone which are created during the polymerization; or a change in the conformation of the polymer from random coil to ordered, a process which would be essentially complete once the polymer contains about 10% of the chiral monomer.

A similar non-linear variation of specific rotation has been reported for copolymers (radically or anionically initiated) derived from *N*-substituted maleimides and other monomers such as other maleimides[23], styrenes, or methacrylate in which one of the components was enantiomerically pure, with both positive[24–27] and negative[28–32] deviations from linearity having been observed, as well as more complex cases in which the specific rotation increases linearly for a period followed by a deviation from linearity[33,34]. Similar non-linear effects have also been reported for polymers derived from a chiral styrene unit and a variety of styrene or methacrylate based comonomers[35]. In these cases asymmetric induction into the polymer backbone was reported to be the cause. However, a non-linear relationship between polymer composition and specific rotation is not always observed, as the radical copolymerization of an enantiomerically pure norbornyl ester of methacrylate with either methyl methacrylate or styrene gave a series of copolymers in which the specific rotation was directly proportional to the % of chiral monomer incorporated into the polymer[36,37].

Sterically hindered esters of methacrylates such as triphenylmethyl methacrylate are known to form helically chiral polymers which can be separated into left and right handed forms[12–16], and this could provide the alternative explanation for the non-linear variation of specific rotation. In these cases no asymmetric induction into the polymer backbone is observed, as removal of the triphenylmethyl esters gives an optically inactive polymer. Rather, the optical activity of the polymer is due solely to its conformation which is maintained by the bulky triphenylmethyl groups. A similar effect has also been observed in the copolymerization of amino acid derived and other chiral isocyanates[38,39]. In this case, the specific rotation decreased as the amount of chiral monomer incorporated into the polymer increased.

None of the polymers described in this paper exhibited

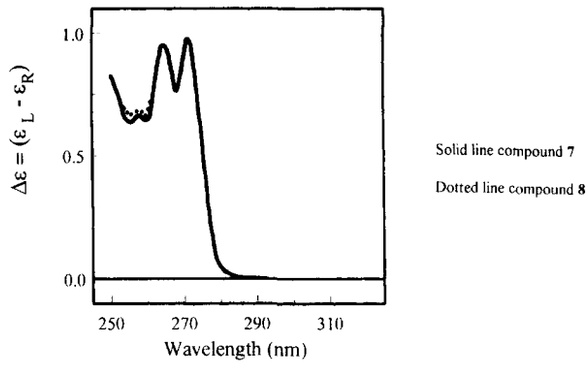


Figure 4 CD spectra of monomers **7** and **8**

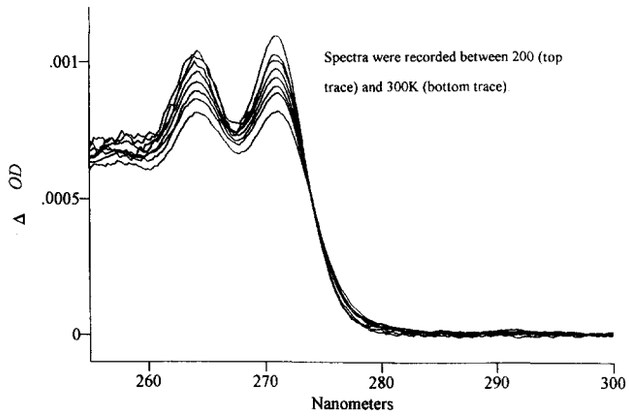


Figure 5 Temperature dependence of the CD of the homopolymer of monomer **3**

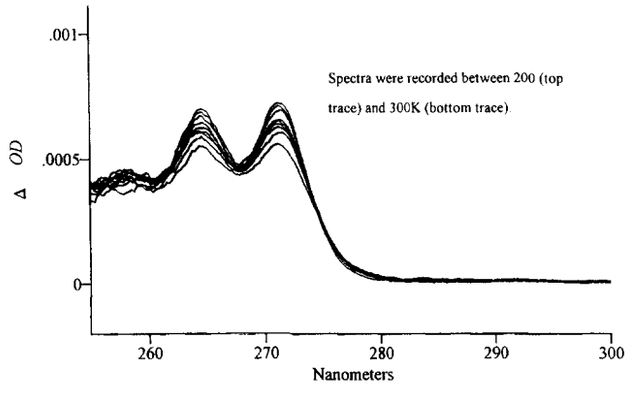


Figure 6 Temperature dependence of the CD of the copolymer of monomer **3** and methyl methacrylate containing 1.5% of monomer **3**

mutarotation, a property which has been observed for other polymethacrylates whose chirality is due to conformational effects[40], and for other helical polymers[38,39]. Also, the specific rotation of the polymer samples was unchanged after a solution of the polymer had been heated at 50°C for 1 h and allowed to re-cool to ambient temperature, and the specific rotation of the polymers was independent of the concentration of the sample solution. The specific rotations of the polymers measured in tetrahydrofuran (THF) showed the same non-linear variation seen in chloroform though with different numerical values. The change to a more polar solvent would be expected to diminish any ordered conformation and hence to reduce

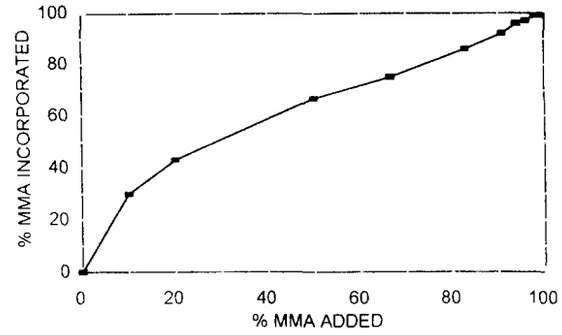


Figure 7 Incorporation of monomer **2** into copolymers

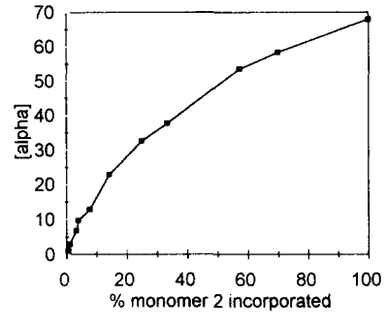


Figure 8 Variation of [α] with % incorporation of monomer **2**

any non-linear effects due to helicity. This has been previously observed[24–27,36,37], though using solvents more polar than THF. In the present work this was not feasible due to the solubility characteristics of the polymers. It has also previously been suggested[23] that the saturated analogues of monomers can serve as model compounds for studying the chiro-optical properties of addition polymers. Thus serine derivates **7–8** were prepared as shown in *Scheme 2*. The specific rotations of compounds **7–8** are 10.9 and 1.7° lower than the specific rotations of the corresponding homopolymers as detailed in the experimental section. The difference in specific rotation between the model compounds **7–8** and the homopolymers may provide a measure of the amount of asymmetric induction or helicity in the polymers.

In order to further investigate the origin of this non-linear variation of specific rotation, a selection of the polymers (containing 100, 18, 1.5 and 0.8% of monomer **3** were investigated by circular dichroism (CD) spectrophotometry. The polymers show a characteristic CD spectrum (in dichloromethane), with maxima at 267 and 275 nm (*Figure 3*). The intensity of these CD bands increases linearly as the %-compound **3** in the polymer increases, with the homopolymer showing the most intense CD. The CD spectra of model compounds **7** and **8** with absorbance normalized to one at 275 nm were also obtained (*Figure 4*), and these were found to be virtually identical to those of the homopolymer. Finally, a variable temperature (200–300 K) CD study was undertaken on the polymers containing 100 and 1.5% of monomer **3** (*Figures 5 and 6*, respectively) as well as on the model compound 8. In each case, the intensity of the CD is seen to decrease as the temperature increases.

The above specific rotation, CD and ultra-violet (u.v.) results are consistent with asymmetric induction into the polymer backbone during the polymerization process, but not with the formation of a polymer with an ordered

Table 2 Analysis of polymers derived from monomer **2**

Monomer	MMA added	MMA[a] (inc)	M_n[b]	M_w[b]	M_w/M_n	$[\alpha]_D^{20}$	Found (C,H,N%)	Requires (C,H,N%)
2[c]	0	0	4980	20250	4.1	+ 68.0	75.0,6.5,3.5	75.2,6.1,3.4
2[d]	0.1	0.4	5610	15900	2.8	+ 58.3	74.9,6.6,3.6	74.5,6.2,3.2
2[d]	0.2	0.75	9170	21000	2.3	+ 53.5	73.5,6.6,3.1	73.8,6.2,3.1
2[d]	1	2	6330	73550	11.6	+ 37.7	70.0,7.2,2.3	70.2,6.7,2.3
2[d]	2	3	7965	59600	7.5	+ 32.6	69.2,7.4,2.2	68.8,6.9,2.0
2[d]	5	6	3900	46700	12.0	+ 21.1	66.1,7.6,1.5	66.2,7.2,1.4
2[d]	10	12	15350	142500	9.3	+ 12.9	64.2,7.3,0.9	63.9,7.5,0.9
2[d]	15	25	16300	245000	15.0	+ 9.7	62.7,7.5,0.4	62.2,7.7,0.5
2[d]	25	30	18700	113000	6.0	+ 6.8	62.1,8.0,0.6	61.8,7.8,0.4
2[d]	50	98	29400	149000	5.1	+ 3.0	60.7,8.1,0.4	60.6,7.8,0.1
2[d]	100	not detected	25950	120500	4.8	+ 1.0	60.2,8.0,0.2	60.6,8.0,.1

MMA, methyl metacrylate
[a]Ratio of MMA to amino acid in polymer determined by integration of the ^{1}H n.m.r. signals for the methyl esters
[b]Measured by g.p.c. using chloroform as eluent
[c]Polymerization carried out in toluene using benzoyl peroxide as initiator
[d]Polymerization carried out with no solvent and benzoyl peroxide as initiator

Table 3 Specific rotations of polymers derived from monomers **4** and **5**

Monomer[a]	MMA[b]	$[\alpha]_D^{20c}$	Monomer[a]	MMA[b]	$[\alpha]_D^{20c}$
4	100	+ 0.3	**5**	127	0
4	98	+ 0.8	**5**	65	+ 0.4
4	35	+ 2.0	**5**	37	+ 0.6
4	25	+ 2.4	**5**	24	+ 1.4
4	21	+ 3.0	**5**	15	+ 2.0
4	6	+ 4.5	**5**	11	+ 4.2
4	3	+ 5.3	**5**	3	+ 8.0
4	2	+ 7.0	**5**	2	+ 11.5
4	0.75	+ 9.0	**5**	0.5	+ 15.4
4	0.4	+ 10.5	**5**	0.27	+ 15.9
4	0	+ 14.0	**5**	0	+ 16.0

MMA, methyl methacrylate
[a]The polymer was prepared by deprotection of the appropriate copolymer prepared from monomer **2** or **3** and methyl methacrylate
[b]Ratio of MMA to monomer **2**/**3** in the precursor polymer
[c]All specific rotations were recorded in 1/1 DMSO/MeCN at a concentration of 1.0 g per 100 ml

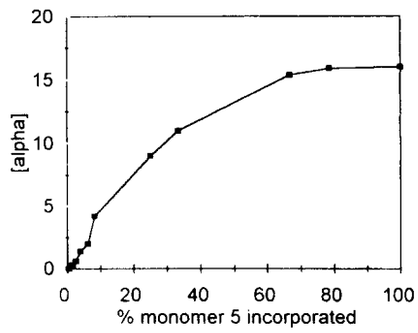


Figure 9 Variation of [α] with % incorporation of monomer **5**

conformation. The CD spectra are dominated by the absorbance of the triphenylmethyl group with no discernible contribution from any secondary structure, and the intensity of the CD is directly proportional to the amount of monomer **3** in the polymer. As such they do not mirror the non-linear variation seen in the specific rotation measurements. Furthermore, since the CD spectra of the polymers and compound **7** show the same temperature dependence, this temperature dependence must be related to conformational changes within the monomer unit and not to changes in the conformation of the polymer backbone.

Having optimized the polymerization of monomer 3, the homo- and copolymerization (with methyl methacrylate) of the acrylate derived monomer 2 was investigated. For this monomer, only bulk copolymerization and homopolymerization in toluene were investigated, and the results shown in *Table 2* are very similar to the results obtained using monomer **3**. As shown in *Figure 7*, monomer **2** also has a lower propensity for polymerization than methyl methacrylate, and the same non-linear dependence of specific rotation on %-monomer 2 incorporated into the polymers was observed (*Figure 8*).

SYNTHESIS AND CHARACTERIZATION OF POLYMERS DERIVED FROM MONOMERS 4 AND 5

Since a triphenylmethyl group is known to stabilize chiral, helical conformations in polymers[12–16], it was decided to investigate the role of the triphenylmethyl group in the non-linear specific rotation variation observed for the above polymers by preparing a series of polymers in which this group had been removed. These polymers were formally derived from monomers **4** and **5**, and two separate routes for their preparation were investigated, radical induced polymerization of monomers **4** and **5**, or acidolysis of the polymers derived from monomers **2** and **3**. Only the latter route was successful however, since monomers **4** and **5** were insoluble in methyl methacrylate (and most organic solvents) and could not be induced to homopolymerize or copolymerize with methyl methacrylate. The relative incorporation of methyl methacrylate and chiral monomers **4** and **5** in the detritylated polymers could not be determined due to signal overlap in the n.m.r. spectra in the absence of the shielding effect of the *N*-triphenylmethyl group, but is assumed to be unchanged from the triphenylmethyl containing polymers from which they are derived.

As can be seen from the data in *Table 3* and *Figures 9* and *10*, these polymers exhibit the same pronounced non-linear variation of specific rotation to that observed for the corresponding polymers which do contain a triphenylmethyl protecting group. Hence it could be concluded that the chirality of the amino acid was solely responsible for the non-linear effect, and that the *N*-triphenylmethyl group was not involved in causing this effect. The model compounds **9** and **10** were prepared (*Scheme 2*), and the specific rotation of these compounds again compared with

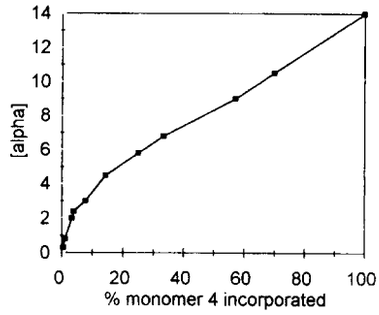


Figure 10 Variation of [α] with % incorporation of monomer **4**

the specific rotation of the homopolymers derived from monomers **4** and **5**. The specific rotations of the model compounds were found to be lower (by 10.5 and 17.7° respectively) than the specific rotations of the homopolymers, again similar to the results obtained for polymers derived from compounds **2** and **3**.

CONCLUSIONS

In this work we have shown that amino acid derived acrylate and methacrylate derivatives can be prepared, and that these compounds are suitable monomers for radical induced addition polymerization and copolymerization reactions. Conditions for the polymerization have been optimized, and the resulting polymers have been shown to be optically active and atactic. A non-linear variation of specific rotation against proportion of chiral monomer incorporated was observed for all of the copolymers. CD results suggest that this non-linear effect is due to asymmetric induction into the polymer backbone during the polymerization process, since no evidence for the presence of an ordered conformation was apparent. The applications of these polymers are currently being investigated, and will be reported in due course.

EXPERIMENTAL

2,2'-Azobis(isobutyronitrile) was recrystallized from methanol, and benzoyl peroxide was purified by precipitation with distilled water from an acetone solution. Methyl methacrylate was distilled in an atmosphere of nitrogen. Toluene was purified by distillation from sodium metal. All glassware was oven dried at 150°C for 24 h. ^{1}H n.m.r. spectra were recorded at 250 MHz on a Brucker AM250 spectrometer fitted with a ^{1}H–^{13}C dual probe, and were recorded at 293 K in $CDCl_3$ unless otherwise stated. Spectra were internally referenced either to TMS or to the residual solvent peak, and peaks are reported in ppm downfield of TMS. Multiplicities are reported as singlet (*s*), doublet (*d*), triplet (*t*), quartet (*q*), some combination of these, broad (*br*), or multiplet (*m*). ^{13}C n.m.r. spectra were recorded at 62.9 MHz on the same spectrometer as the ^{1}H n.m.r. spectra, at 293 K and in $CDCl_3$, unless otherwise stated. Spectra were referenced to the solvent peak and are reported in ppm downfield of TMS. Peak assignments were made by DEPT editing of the spectra. Infra-red (i.r.) spectra were recorded on a Perkin Elmer 1600 series Fourier transform (*FT*) i.r. spectrometer, only characteristic absorptions are recorded, and peaks are reported as strong (*s*), moderate (*m*), weak (*w*), or broad (*br*). U.v. spectra were recorded in dichloromethane on an ATI Unicam UV4 spectrophotometer. CD spectra were recorded in dichloromethane on Jasco J720 or Jasco J600 spectrophotometers. Mass spectra (MS) were recorded using the fast atom bombardment (FAB) technique (Cs^+ ion bombardment at 25kV) on a VG Autospec spectrometer, or by electron ionization (EI) or chemical ionization (CI) on either a VG model 12-253 quadrupole spectrometer or a VG Quattro II triple quadrupole spectrometer. Only significant fragment ions are reported, and only molecular ions are assigned. High resolution mass measurements were made on a VG ZAB-E spectrometer. Optical rotations were recorded on an Optical Activity Ltd. Polar 2001 polarimeter, at a concentration of 1.0 g per 100 ml in chloroform unless otherwise stated. Melting points are uncorrected. Elemental analyses were performed within the Chemistry Department on a Carlo Erba Model 1106 or Model 1108 analyser. G.p.c. analyses were carried out at a concentration of 2.0 g l^{-1} in $CHCl_3$, on two PLgel mixed bed B, 10 μm, 30 cm columns. Each analysis was conducted in duplicate, and the reported values are the average of the two sets of results.

O-acryloyl-N-triphenylmethyl-(S)-serine methyl ester (2)

To a solution of *N*-triphenylmethyl-(*S*)-serine methyl ester (16.0 g, 44.3 mmol) in dichloromethane (300 ml), cooled to 0°C was added first triethylamine (30.6 ml, 221.5 mmol), then acryloyl chloride (7.2 ml, 88.6 mmol). After stirring at 0°C for 1 h, the reaction was allowed to warm to room temperature. Stirring was continued for a further 24 h, after which a white precipitate was filtered off under suction and the filtrate evaporated *in vacuo* to leave a brown oil which was dissolved in ethyl acetate (200 ml), filtered again under suction, and washed with 1 M $NaHCO_3$ (3 × 100 ml), 2 M HCl (5 × 150ml), and water (2 × 150 ml). The organic layer was dried ($MgSO_4$) and evaporated *in vacuo* to leave a pale yellow oil. Dry column chromatography[41] (dichloromethane/petrol 1/1) gave compound **2** as a colourless oil, which crystallized when washed with hexane to leave a white solid. Yield 13.1 g (71%); R_f (30% ether/hexane) 0.69; mp 99–100°C; $[\alpha]_D$ + 51.6°; Found C 75.4, H 6.4, N 3.2%, $C_{26}H_{25}NO_4$ requires C 75.2, H 6.1, N 3.4%; ν_{max} ($CHCl_3$) 3325 (*w*), 3020 (*m*), 2953 (*w*), and 1730 cm^{-1} (*s*); δ_H 2.90 (1H, *brs*, NH), 3.24 (3H, *s*, OCH_3), 3.7–3.8 (1H, *m*, α-CH), 4.30 (1H, *dd J* 10.9, 6.6 Hz, β-CH_2), 4.51 (1H, *dd J* 10.8, 5.2 Hz, β-CH_2), 5.89 (1H, *dd*, *J* 1.5, 10.5 Hz, CH=CH_2), 6.17 (1H, *dd J* 11.5, 17.5 Hz, CH=CH_2), 6.46 (1H, *dd J* 1.5, 17.5 Hz, CH=CH_2), 7.3–7.5 (15H, *m*, ArCH); δ_C 51.9 (OCH_3) 55.5 (α-CH), 66.2 (β-CH_2), 71.0 (CPh_3), 126.6, 128.0, and 128.7 (ArCH), 128.0 (=CH), 131.3 (=CH_2), 145.6 (ArC), 165.7 (=CHCO), 173.0 (CO_2CH_3); *m/z* (FAB) 416 (MH^+, 2), 243 (100), 165 (10).

O-methacryloyl-N-triphenylmethyl-(S)-serine methyl ester (3)

To a solution of *N*-triphenylmethyl-(*S*)-serine methyl ester (16.0 g, 44.3 mmol) in dichloromethane (300 ml), cooled to 0°C was added first triethylamine (30.6 ml, 221.5 mmol), then methacryloyl chloride (7.2 ml, 88.6 mmol). After stirring at 0°C for 1 h, the reaction was allowed to warm to room temperature. Stirring was continued for a further 24 h, after which a white precipitate was filtered off under suction and the filtrate evaporated *in vacuo* to leave a brown oil which was dissolved in ethyl acetate (200 ml), filtered again under suction, and washed with 1 M $NaHCO_3$ (3 × 100 ml), 2 M HCl (5 × 150ml), and water (2 × 150 ml). The organic layer was dried ($MgSO_4$) and evaporated *in vacuo* to leave a pale yellow oil. Dry column chromatography (dichloromethane/petrol 1/1)

gave compound **3** as a colourless oil, which crystallized when washed with hexane to leave a white solid. Yield 13.1 g (71%); R_f (30% ether/hexane) 0.86; mp 100–101°C; $[\alpha]_D$ + 45.1°; Found C 75.5, H 6.0, N 2.9%, $C_{27}H_{27}NO_4$ requires C 75.5, H 6.3, N 3.3%; ν_{max} ($CHCl_3$) 3032 (*m*), 2952 (*w*), 1721 (*s*), and 1159cm^{-1} (*s*); δ_H 1.98 (3H, *d J* 2.5 Hz, CH_3), 2.87 (1H, *brs*, NH), 3.23 (3H, *s*, OCH_3), 3.72 (1H, *t J* 6.8 Hz, α-CH), 4.27 (1H, *dd J* 10.7, 7.0 Hz, β-CH_2), 4.52 (1H, *dd J* 10.8, 5.3 Hz, β-CH_2), 5.62 (1H, pentet, *J* 1.5 Hz, =CH_2), 6.12 (1H, *s*, =CH_2), 7.39 (15H, *m*, ArCH); δ_C 18.2 (CH_3), 51.9 (OCH_3), 55.4 (α-CH), 66.4 (β-CH_2), 70.9 (CPh_3), 126.1 (=CH_2), 126.6, 128.0, and 128.7 (ArCH), 135.9 (=CCH_3), 145.6 (ArC), 166.9 (=CCO), 173.1 (CO_2CH_3); *m/z* (FAB) 430 (MH^+, 6%), 243 (100), 165 (10).

O-acryloyl-(S)-serine methyl ester trifluoroacetate (4)

To a solution of *O*-acryloyl-*N*-triphenylmethyl-(*S*)-serine methyl ester (**2**) (9.1 g, 22.0 mmol) in dichloromethane (30 ml) was added dropwise trifluoroacetic acid (5.1 ml, 66.0 mmol). After stirring the solution for 1 h at room temperature, the solvent was evaporated *in vacuo* to leave a yellow solid. Trituration with ether/petrol (1/5) gave compound **4** as a white solid, which was collected by filtration and dried *in vacuo*. Yield 3.3 g (66%); $[\alpha]_D$ + 61.0°; ν_{max} 3015 (*m*), 2866 (*m*), 1753 (*s*), 1734 (*s*), and 1205 cm^{-1} (*s*); Found C 37.9, H 4.4, N 4.8%, $C_9H_{12}NO_6F_3$ requires C 37.6, H 4.2, N 4.9%; δ_H 3.76 (3H, *s*, OCH_3), 4.49 (2H, *d J* 4.0 Hz, β-CH_2), 4.55 (1H, *t J* 4.0 Hz, α-CH), 6.02 (1H, *dd J* 1.5, 10.0 Hz, =CH_2), 6.15 (1H, *dd J* 10.5, 17.0 Hz, H_2C=CH), 6.43 (1H, *dd J* 2.0, 17.0 Hz, =CH_2), 8.80 (3H, *brs*, NH_3^+); δ_C 51.4 (OCH_3), 53.3 (α-CH), 61.7 (β-CH_2), 117.1 (CF_3), 127.5 (=CH), 133.0 (=CH_2), 158.7 (CF_3CO_2), 164.9 (=CCO_2), 167.6 (CO_2CH_3); *m/z* (EI) 174 (M^+, 40), 114 (98), 55 (80); Found 174.0766 ($C_7H_{12}NO_4$ requires 174.0766).

O-methacryloyl-(S)-serine methyl ester trifluoroacetate (5)

To a solution of *O*-methacryloyl-*N*-triphenylmethyl-(*S*)-serine methyl ester (**3**) (9.1 g, 22.0 mmol) in dichloromethane (30 ml) was added dropwise trifluoroacetic acid (5.1 ml, 66.0 mmol). After stirring the solution for 1 h at room temperature, the solvent was evaporated *in vacuo* to leave a yellow solid. Trituration with ether/petrol (1/5) gave compound **5** as a white solid, which was collected by filtration and dried *in vacuo*. Yield 1.5 g (58%); $[\alpha]_D$ + 59.0°; ν_{max} 3187 (*m*), 3019 (*m*), 2854 (*m*), 1750 (*s*), 1720 (*s*), and 1210 cm^{-1} (*s*); Found C 40.3, H 4.4, N 5.1%, $C_{10}H_{14}NO_6F_3$ requires C 39.9, H 4.7, N 4.6%; δ_H 1.13 (3H, *s*, CH_3), 3.06 (3H, *s*, OCH_3), 3.7–3.8 (1H, *m*, α-CH), 3.79 (2H, *d J* 4.0 Hz, β-CH_2), 4.08 (3H, *brs*, NH_3^+), 4.91 (1H, *d J* 1.5 Hz, =CH_2), 5.37 (1H, *s*, =CH_2); δ_C 17.9 (CH_3), 51.4 (OCH_3), 53.2 (α-CH), 62.1 (β-CH_2), 117.2 (CF_3), 127.4 (=CCH_3), 135.0 (=CH_2), 158.6 (CF_3CO_2), 166.0 (=CCO_2), 167.6 (CO_2CH_3); *m/z* (EI) 188 (M^+, 15), 128 (95), 69 (100); Found 188.0923 ($C_8H_{14}NO_4$ requires 188.0923).

O,N-diacryloyl-(S)-serine methyl ester (6)

To (*S*)-serine methyl ester (4.0 g, 26 mmol) suspended in dichloromethane (250 ml) at 0°C, triethylamine (17.8 ml, 128 mmol, 5.0 eq.) was added dropwise. Acryloyl chloride (2.2 ml, 26 mmol, 1.0 eq.) was then added dropwise to the mixture over a period of 2 min. The mixture was stirred at 0°C for 30 min then at room temperature for 24 h. A white precipitate (triethylamine hydrochloride) was removed by filtration, then the filtrate was washed with saturated Na_2CO_3 solution (2 × 100 ml), water (100 ml), dilute HCl (3 × 80 ml), and finally with water (3 × 80 ml). The organic layer was dried over $MgSO_4$, filtered, and evaporated *in vacuo*. Chromatography on silica gel eluting with ethyl acetate/petrol (3/2) gave compound **6** as a colourless oil. Yield 0.41 g (7%); R_f (3/2 ethyl acetate/petrol) 0.39; $[\alpha]_D$ + 35.5°; ν_{max} 3305 (*m*), 3029 (*m*), 2956 (*m*), 1734 (*s*) and 1670 cm^{-1} (*s*); δ_H 3.81 (3H, *s*, CO_2CH_3), 4.51 (1H, *dd J* 3.5, 11.5 Hz, β-CH_2), 4.61 (1H, *dd J* 3.8, 11.5 Hz, β-CH_2), 5.00 (1H, *dt J* 3.5, 7.5 Hz, α-CH), 5.74 (1H, *dd J* 1.7, 10.1 Hz, *N*-acryloyl =CH_2), 5.89 (1H, *dd J* 1.4, 10.4 Hz, *N*-acryloyl =CH_2), 6.0–6.4 (3H, *m*, 2 × =CH + O–acryloyl =CH_2), 6.50 (1H, *brs*, NH); δ_C 51.5 (CO_2CH_3), 52.6 (α-CH), 63.9 (β-CH_2), 127.3 (=CH_2), 127.4 (=CH), 130.0 (=CH), 131.7 (=CH_2), 165.2, and 169.9 (C=O); *m/z* (CI) 245 ($M + NH_4^+$, 15) 228 (MH^+, 100); Found 228.0872 ($C_{10}H_{14}NO_5$ requires 228.0872).

O-propanoyl-N-triphenylmethyl-(S)-serine methyl ester (7)

To a solution of *N*-triphenylmethyl-(*S*)-serine methyl ester (1.0 g, 2.8 mmol) in dichloromethane (40 ml) cooled to 0°C was added triethylamine (0.42 g, 4.2 mmol, 15 eq.), followed by propionyl chloride (0.26 g, 4.2 mmol, 1.0 eq.) added dropwise. The resulting mixture was stirred at 0°C for 10 min, then at room temperature for 4 h. The solvent was removed *in vacuo* to leave a white solid to which ethyl acetate (20 ml) was added. The mixture was filtered to remove the white solid (triethylamine hydrochloride) and then the solvent was removed *in vacuo* to leave a yellow oil from which compound (**7**) was recovered as a white solid by washing the oil with cold hexane. Yield 0.36 g, (31%); mp 74°C, $[\alpha]_D$ + 57.1°; N_{max} 3326 (*w*), 3029 (*m*), 2943 (*m*), and 1739 cm^{-1} (*s*); δ_H 1.14 (3H, *t*, *J* 7.6 Hz, CH_3), 2.35 (2H, *q*, *J* 7.6 Hz, CH_2CO), 2.80 (1H, *d J* 10.5 Hz, NH), 3.20 (3H, *s*, CO_2CH_3), 3.6–3.7 (1H, *m*, α-CH), 4.19 (1H, *dd J* 6.8, 10.8 Hz, β-CH_2), 4.45 (1H, *dd J* 5.1, 10.8 Hz, β-CH_2), 7.3–7.4 (15H, *m*, ArCH); δ_C 9.03 (CH_3), 27.47 (CH_2CO), 51.88 (CO_2CH_3), 55.45 (α-CH), 66.01 (β-CH_2), 70.92 (CPh_3), 126.57, 127.94, and 128.74 (ArCH), 145.62 (ArC), 173.07, and 174.00 (CO_2); *m/z* (CI) 418 (MH^+, 5%); Found 418.2018 ($C_{26}H_{28}NO_4$ requires 418.2018).

O-2-methylpropanoyl-N-triphenylmethyl-(S)-serine methyl ester (8)

To a solution of *N*-triphenylmethyl-(*S*)-serine methyl ester (1.5 g, 4.2 mmol) in dichloromethane (40 ml) cooled to 0°C was added triethylamine (1.73 ml, 12.5 mmol, 3.0 eq.) followed by isobutyryl chloride (0.43 ml, 4.2 mmol, 1.0 eq.) added dropwise. The mixture was stirred at 0°C for 10 min, then at room temperature for 2 h. The solvent was removed *in vacuo* to leave a pink solid to which ethyl acetate (20 ml) was added. The mixture was filtered to remove the white solid (triethylamine hydrochloride) and the filtrate washed with saturated Na_2CO_3 solution (3 × 30 ml), water (1 × 20 ml), dilute HCl (3 × 20 ml) and finally with water (3 × 30 ml). The organic layer was dried ($MgSO_4$) and filtered, then the solvent was removed *in vacuo* to leave compound **8** as a white solid. Yield 1.30 g, (73%); mp 92°C; $[\alpha]_D$ + 52.4°; ν_{max} 3400 (*w*), 3031 (*m*), 2975 (*m*), and 1728 cm^{-1} (*s*); δ_H 1.15 (3H, *d J* 7.0 Hz, CH_3), 1.16 (3H, *d J* 7.0 Hz, CH_3), 2.56 (1H, septet, $CHMe_2$), 2.79 (1H, *d J* 10.5 Hz, NH), 3.19 (3H, *s*, CO_2CH_3), 3.6–3.7 (1H, *m*, α-CH), 4.19 (1H, *dd J* 6.3, 11.0 Hz, β-CH_2), 4.44 (1H, *dd J* 5.0, 10.8 Hz, β-CH_2), 7.2–7.5 (15H, *m*, ArCH); δ_C 18.91 (CH_3), 33.97 ($CHMe_2$), 51.85 (CO_2CH_3), 55.40 (α-CH),

66.00 (β-CH_2), 70.96 (CPh_3), 126.58, 127.95, and 128.75 (ArCH), 145.64 (ArC), 173.11 and 176.59 (CO_2); *m/z* (CI) 432 (MH^+, 1%); Found 432.2175 ($C_{27}H_{30}NO_4$ requires 432.2175).

*O-propanoyl-(S)-serine methyl ester trifluoroacetate (**9**)*

To a solution of *O*-acryloyl-(*S*)-serine methyl ester trifluoroacetate (100 mg, 0.35 mmol) in methanol (10 ml) was added palladium on charcoal (10 mg, 10% w/w). Hydrogen was passed over the solution until the required volume (7.8 ml) had been absorbed. The solution was then filtered through celite and the solvent was removed *in vacuo* to leave compound **9** as a colourless oil. Yield 95 mg (93%); $[\alpha]_D$ + 5.0° (*c* = 1.0, DMSO), + 3.5° (*c* = 1.0, 1/1 CH_3CN/DMSO); ν_{max} 3420 (*s*), 2962 (*s*), 1751 (*s*) and 1677 cm^{-1} (*s*); δ_H 1.02 (3H, *t J* 7.5 Hz, CH_3), 2.34 (2H, *q J* 7.5 Hz, CH_2CO), 3.77 (3H, *s*, CO_2CH_3), 4.3–4.45 (2H, *m*, β-CH_2), 4.45–4.6 (1H, *m*, α-CH), 8.64 (3H, *brs*, NH_3^+); δ_C 8.72 (CH_3), 26.58 (CH_2CO), 50.11 (CO_2CH_3), 52.82 (α-CH), 61.29 (β-CH_2), 118.00 (CF_3), 158.42 ($\overline{C}F_3\overline{C}O_2$), 167.61 and 173.33 ($\overline{C}O_2$); *m/z* (EI) 176 ($M^+$; 100); Found 176.0923 ($C_7H_{14}N\overline{O}_4$ requires 176.0923).

*O-2-methylpropanoyl-(S)-serine methyl ester trifluoroacetate (**10**)*

To a solution of *O*-methacryloyl-(*S*)-serine methyl ester trifluoroacetate (110 mg, 0.37 mmol) in methanol (10 ml) was added palladium on charcoal (10 mg, 10% w/w). Hydrogen was passed over the solution until the required volume (8.3 ml) had been absorbed. The solution was then filtered through celite and the solvent was removed *in vacuo* to leave compound **10** as a colourless oil. Yield 110 mg (98%); $[\alpha]_D$ + 10.3° (*c* = 1.0, DMSO), + 2.3° (*c* = 1.0, 1/1 CH_3CN/DMSO); ν_{max} 3413 (*s*), 2976 (*s*), and 1678 cm^{-1} (*s*); δ_H 1.07 (3H, *d J* 7.0 Hz, CH_3), 1.08 (3H, *d J* 7.0 Hz, CH_3), 2.52 (1H, septet *J* 7.0 Hz, $CHMe_2$), 3.76 (3H, *s*, CO_2CH_3), 4.2–4.4 (2H, *m*, β-CH_2), 4.4–4.5 (1H, *m*, α-CH), 8.59 (3H, *brs*, NH_3^+); δ_C 18.43, and 18.69 (2 × CH_3), 33.29 ($CHMe_2$), 51.42 (CO_2CH_3), 52.80 (α-CH), 61.47 (β-CH_2), 117.00 (CF_3), 158.00 ($CF_3\overline{C}O_2$), 167.61 and 175.69 (2 × CO_2); *m/z* (CI) 190 (MH^+, ~73%); Found 190.1097 ($C_8H_{16}NO_4$ requires 190.1097).

*General method for bulk copolymerizations of monomer **2** and methyl methacrylate*

To a round bottomed flask was added *O*-acryloyl-*N*-triphenylmethyl-(*S*)-serine methyl ester (**2**) (100 mg, 0.24 mmol for experiments with 50 and 100 equivalents of methyl methacrylate, 200 mg, 0.48 mmol for 10–25 equivalents, or 1.0 g, 2.41 mmol for 1–5 equivalents), methyl methacrylate (1–100 equivalents), and benzoyl peroxide (1 mol%). The solution was thoroughly degassed with nitrogen for 1 h, then immersed in an oil bath and heated at 100°C for 30 min under a nitrogen atmosphere. After cooling to room temperature, the solid crude polymer was dissolved in $CHCl_3$ (15 ml), and a white powder was precipitated with petrol (200 ml), and collected by filtration. The polymer was dried *in vacuo* for 72 h at 60°C. The polymers were obtained in 62–92% yield, and showed the following spectral characteristics: ν_{max} ($CHCl_3$) 3325 (*w*), 3024 (*s*), 2952 (*w*), 1733 (*s*), and 1218 cm^{-1} (*s*); δ_H 0.7–1.4 (*m*, CH_3 + CH_2), 1.4–2.3 (*m*, CH_2 + CH), 2.83 (*brs*, NH), 3.23 (*s*, OCH_3), 3.63 (*s*, OCH_3), 41.5 (*br d*, CH_2O), 7.4–7.5 (*m*, ArCH); δ_C 17.7 (CH_3), 19.4 (CH_3), 44.5 ($\overline{C}CH_3$), 51.8 (OCH_3), 51.9 (OCH_3), 55.1 (α-CH), 66.6 ($\beta\overline{-C}H_2$), 71.0 (CPh_3), 126.6, 127.9, and 128.7 (ArCH), 145.6 (ArC), 172.8 (CO_2). Other data for the polymers is given in *Table 2*.

*General method for bulk copolymerizations of compound **3** and methyl methacrylate*

To a round bottomed flask was added *O*-methacryloyl-*N*-triphenylmethyl-(*S*)-serine methyl ester (**3**) (40 mg, 0.09 mmol for polymerizations with 100 or 50 equivalents, 80 mg for 25 equivalents, 135 mg for 15 equivalents, 140 mg for 10 equivalents, 0.75 g for 5 equivalents, 1.0 g for other ratios of methyl methacrylate), methyl methacrylate (1–100 equivalents), and benzoyl peroxide (1 mol%). The solution was thoroughly degassed with nitrogen for 1 h, then the flask was then immersed in an oil bath and heated to 100°C for 30 min under nitrogen. After cooling to room temperature, the solid crude polymer was dissolved in $CHCl_3$ (5 ml), and a white powder was precipitated by the addition of petrol (150 ml), and collected by filtration. The polymer was dried *in vacuo* for 72 h at 60°C. The polymers were obtained in 53–97% yield, and showed the following spectral characteristics: ν_{max} ($CHCl_3$) 3325 (*w*), 3019 (*s*), 2952 (*s*), 1731 (*s*) and 1211 cm^{-1} (*s*); δ_H 0.6–1.2 (*m*, CH_3), 1.2–2.15 (*m*, CH_2), 2.94 (*brs*, NH), 3.20 (*s*, OCH_3), 3.58 (*s*, OCH_3), 4.08 (*brd*, CH_2O), 7.3–7.5 (*m*, ArCH); δ_C 16.6, and 19.5 (CH_3), 44.6 ($\overline{C}CH_3$), 51.8, and 52.0 (OCH_3), 53.6 (CH_2), 55.0 (NCH), 67.3 (CH_2), 71.1 (CH_2O), 126.6, 127.9, and 128.7 (ArCH), 145.6 (ArC), 172.6 (CO_2). Other data for the polymers is given in *Table 1*.

Homopolymerization of compound 2

To a round bottomed flask was added *O*-acryloyl-*N*-triphenylmethyl-(*S*)-serine methyl ester (**2**) (1.00 g, 2.41 mmol), benzoyl peroxide (5.8 mg, 0.024 mmol, 1 mol%), and toluene (0.80 ml). The solution was thoroughly degassed with nitrogen for 1hr, then the flask was then immersed in an oil bath and heated to 111°C for 3 h. After cooling to room temperature, the solid crude polymer was dissolved in $CHCl_3$ (10 ml), and a white powder was precipitated twice by the addition of petrol (150 ml), and collected by filtration. The polymer was dried in vacuo for 72 h at 60°C. Yield 0.76 g (76%); ν_{max} ($CHCl_3$) 3321 (*w*), 3059 (*w*), 2952 (*w*), 1739 (*s*), and 1207 cm^{-1} (*w*); δ_H 1.0–1.9 (2H, *m*, CH_2), 1.95–2.4 (1H, *br s*, CH), 2.77 (1H, *br s*, NH), 3.06 (3H, *s*, OCH_3), 3.55 (1H, *brs*, NCH), 4.22 (2H, *brd*, CH_2O), 7.3–7.5 (15H, *m*, ArCH); δ_C 41.0 (CH), 52.0 (OCH_3), 55.0 (NCH), 66.3 (CH_2), 70.9 (CH_2O), 126.5, 127.9 and 128.7 (ArCH), 145.6 (ArC), 173.0, and 173.7 (CO_2). Other data is given in *Table 2*.

Homopolymerization of compound 3

To a round bottomed flask was added *O*-methacryloyl-*N*-triphenylmethyl-(*S*)-serine methyl ester (**3**) (1.00 g, 2.33 mmol), benzoyl peroxide (5.6 mg, 0.023 mmol), 1 mol%) and toluene (0.78 ml). The solution was thoroughly degassed with nitrogen for 1 h, then immersed in an oil bath and heated to 110°C for 3 h. After cooling to room temperature, the solid crude polymer was dissolved in $CHCl_3$ (10 ml), and a white powder was precipitated from a tenfold excess of petrol and collected by filtration. The polymer was dried *in vacuo* for 72 h at 60°C. Yield 0.62 g (62%); ν_{max} ($CHCl_3$) 3323 (*w*), 3059 (*w*), 2951 (*w*), 1734 (*s*) and 1207 cm^{-1} (*m*); δ_H 0.5–1.1 (3H, *brd*, CH_3), 1.5–2.0 (2H, *brs*, CH_2), 2.79 (1H, *brs*, NH), 3.08 (3H, *brs*, OCH_3), 3.54 (1H, *br*, NCH), 4.03 (2H, *brd*, CH_2O), 7.3–7.5 (15H, *m*, ArCH); δ_C 16.6 (CH_3), 44.64 ($\overline{C}CH_3$), 52.0 (OCH_3), 54.8 (NCH), 67.5 (CH_2), 71.1 ($C\overline{H}_2O$), 126.6, 128.0, and 128.7 (ArCH), 145.6 (ArC), 172.8 (CO_2). Other data is given in *Table 1*.

General method for removing the N-triphenylmethyl group from the homo- or copolymers of monomer 2 and methyl methacrylate

The homo- or copolymer of monomer **2** and methyl methacrylate (150 mg) was dissolved in dichloromethane (2 ml) and trifluoroacetic acid (5 ml) was added. The solution was stirred at room temperature for 2 h, after which time a yellow coloured solution remained. Addition of ether (20 ml) caused the precipitation of a white solid, which was filtered and washed copiously with ether (500 ml) and dried *in vacuo* to leave the *N*-deprotected polymer as its trifluoroacetate salt in 66–93% yield. The polymers exhibited the following spectral characteristics: ν_{max} (KBr) 2952 (*m*), 1734 (*s*), and 1458 cm^{-1} (*s*); δ_H (DMSO-d_6) 0.8–1.0 (*m*, CH_3), 1.0–2.4 (*m*, CH_2CH_2CO + $CHCH_2CO$), 3.0–3.5 (*br*, NH_3^+ + OCH_3), 3.8 (*s*, OCH_3), 4.2–4.5 (*br s*, NCH + OCH_2); δ_C (DMSO-d_6) 17.1 (CH_3), 19.7 (CH_3), 43.2 (CMe), 51.8 (CH_2), 52.2 (α-CH), 53.6 (OCH_3), 61.3 (β-CH_2), 117.2 (CF_3), 158.3 (CF_3CO_2), 167.5 (CO_2), 172.8 (CO_2), 175.4 (CO_2). Specific rotations for the polymers are given in *Table 3*.

General method for removing the N-triphenylmethyl group from the homo- or copolymers of monomer 3 and methyl methacrylate

The homo- or copolymer of monomer **3** and methyl methacrylate (190 mg) was dissolved in dichloromethane (5 ml) and trifluooacetic acid (5 ml) was added. The solution was stirred at room temperature for 2 h, after which time a yellow coloured solution remained. Addition of ether (20 ml) caused the precipitation of a white solid, which was filtered and washed copiously with ether (500 ml) and dried *in vacuo* to leave the *N*-deprotected polymer at its trifluoroacetate salt in 76–94% yield. The polymers exhibited the following spectral characteristics: ν_{max} (KBr) 2952 (*m*), 1742 (*s*), and 1448 cm^{-1} (*s*); δ_H (DMSO-d_6) 0.5–1.0 (*m*, CH_3), 1.5–2.2 (*m*, $CHCH_2CO$), 3.8 (*s*, OCH_3), 3.9–4.7 (*m*, NCH + OCH_2); δ_C (DMSO-d_6) 16.3 (CH_3), 19.4 (CH_3); 44.2 (CMe), 51.3 (CH_2 + α-CH), 53.1 (OCH_3), 63.2 (β-CH_2), 116.5 (CF_3), 160.0 (CF_3CO_2), 167.4 (CO_2), 177.2 (CO_2). Specific rotations for the polymers are given in *Table 3*.

ACKNOWLEDGEMENTS

The authors thank the EPSRC Innovative Polymer Synthesis Initiative for a studentship (to SMB). G.p.c. analyses were conducted by the EPSRC service at RAPRA, CD spectra were recorded by the EPSRC service at King's college London, and mass spectra were measured by the EPSRC service at Swansea. The authors thank the staff of these facilities (especially Dr G. Siligardi and Ms T.T. Bui of the CD service) for their efforts in connection with this project.

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