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SYNTHESIS AND POLYMERIZATION OF SOME CHIRAL VINYL MONOMERS. PART I. PREPARATION OF VINYLBENZYL ESTERS OF AMINO ACIDS

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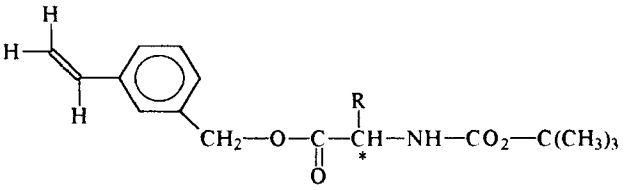
ABSTRACT

In this study we are interested in the synthesis of vinylbenzyl esters of amino acids. A method previously described in the literature has some disadvantages. We tried to find a better one. Three methods were tested and four amino acids were used. The best one consists of alkylation with an alkyl halide. The yield for this synthesis reached 96%. In all the case the products obtained were characterized by IR, NMR, and mass spectroscopies. The optical purity of the products was determined by polarimetry or by an NMR shift study. The ability of this type of monomer to polymerize and copolymerize was tested.

INTRODUCTION

The aim of this paper is to prepare vinylbenzyl esters of *N-tert*-butyloxycarbonyl (N-tBOC) amino acids. The vinylbenzyl esters prepared in this study are listed in Scheme 1. Those monomers were polymerized to give polymer-supported chiral amino acids, and those bearing amino alcohol functions (obtained by loading threonine or serine) were used in various application (chiral separation, supported chiral reagents or catalysts, etc.).

There is only one paper dealing with this synthesis in the literature [1]. In Ref. 1, amino acid was reacted with vinylbenzylchloride (VBC) in an equimolar amount



R=H	monomer 1	(Gly)
R=CH_3	monomer 2	(Ala)
R=ϕCH_2	monomer 3	(Phe)
R=$CH(CH_3)OCH_2\phi$	monomer 4	(Thr)

SCHEME 1. Vinylbenzyl esters prepared in this study.

for 90 hours at ambient temperature; the synthesis proceeded to 78% yield. We wanted to improve the yield and decrease the reaction time, and so we applied the method used to prepare benzylesters of tBOC amino acids.

The preparation of esters of *N*-protected α-amino acids could be achieved in two different ways. It is possible to realize *esterification from an alcohol.* Only a few simple processes allow this esterification under mild conditions [2, 3]. Furthermore, it is often necessary to activate the acid function to obtain good yields [4]. We applied the classical method [2] to prepare one monomer: this is method 1 which is described in Scheme 2.

However, the preparation of esters of *N*-protected α-amino acids is often more effective by *alkylation with an alkyl halide* of the triethylammonium [5] or cesium [6] salt of the corresponding carboxylate ion.

In 1973 a method for the total esterification of Merrifield resin with the cesium salt of *N*-tBOC amino acids was investigated [7]. The reaction proceeds rapidly and quantitatively under mild conditions. This reaction was applied a few years later [6] to the synthesis of protected amino acids and protected peptide esters in solution. We used this method (method 2, Scheme 2) with VBC as the starting material.

To improve this reaction, we tried to reduce the reaction time. Use of a three-phase catalyst allowed us to obtain such an improvement. This is method 3 (see Scheme 2).

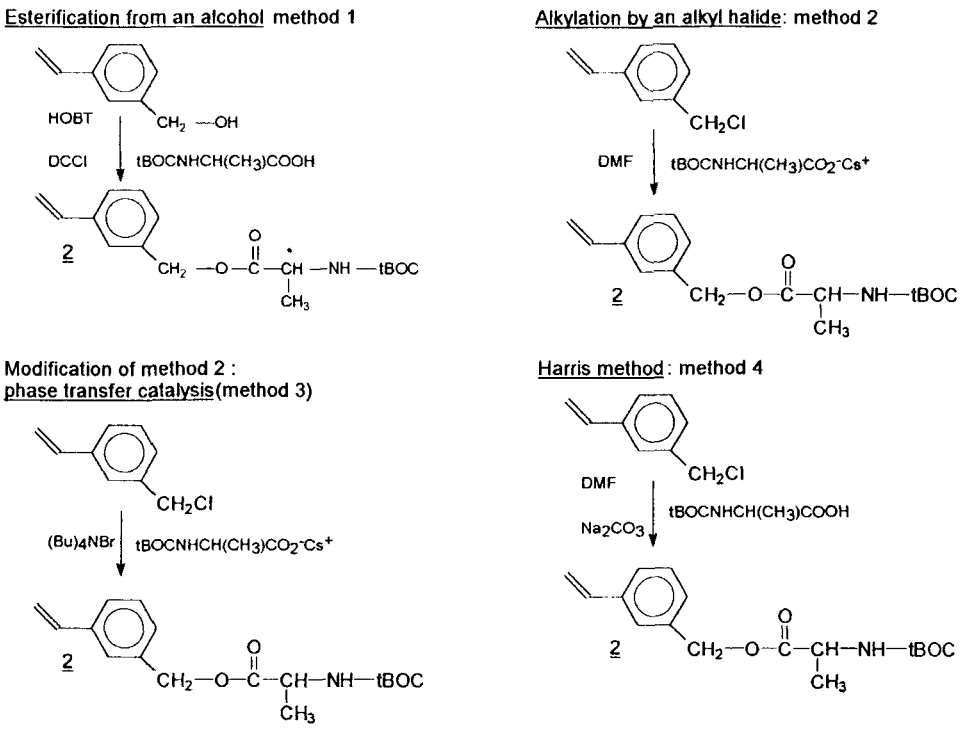
The method described in a patent [1] was called method 4, and it is also reported in Scheme 2.

Finally, we show the ability of this type of monomers to polymerize and copolymerize (with styrene as comonomer).

EXPERIMENTAL PART

Products

The vinylbenzyl esters prepared in this study are listed in Scheme 1. All amino acids used (except from glycine) were of the L-configuration. We also tried D-alanine once. The protected amino acids were purchased from Fluka, except for threonine which was obtained from Senn Chemicals. VBC was purchased from Aldrich; it consists of 75% meta isomer and 25% para isomer.



SCHEME 2. Synthesis of monomer **2** via four different methods.

Synthesis

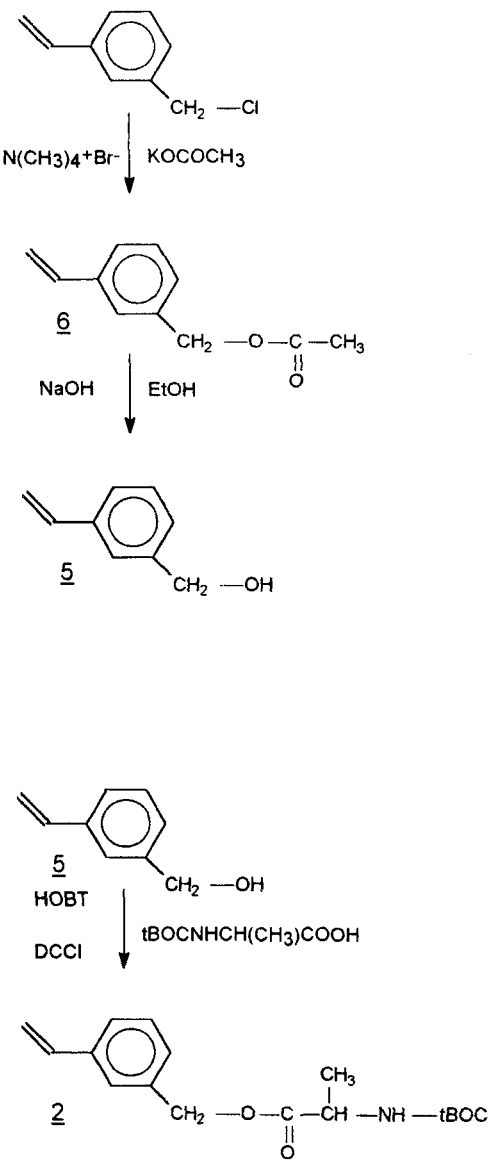
Four methods have been used to prepare monomers *1* to *4*. The results obtained with these methods are compared in the Results and Discussion Section. Since the procedures utilized to make the esters listed in Scheme 1 are very similar, only the synthesis of alanine esters will be described. The characterization of all the monomers is reported following the descriptions of the syntheses.

Preparation via Method 1

The synthesis was performed according to Scheme 3.

Synthesis of m-Hydroxymethylstyrene **5.** The alcohol was prepared from VBC in two steps. The first step was the substitution of Cl by an acetoxy group via phase-transfer catalysis [8]. To optimize the yield, some modifications of the original method were developed. Then the acetate derivative **6** was saponified to give the alcohol [9].

Synthesis of **6**: To a solution of 39.4 g (402 mmol) potassium acetate in 100 mL water was added 7.4 g tetrabutylammoniumbromide ($(Bu)_4NBr$) and then 20 ml (141 mmol) VBC in 100 mL $(CH_2)_2Cl_2$. The solution was stirred at 85°C for 24 hours. The organic layer was separated and the aqueous layer was extracted with five 30-mL portions $(CH_2)_2Cl_2$. The extracts were washed with 40 mL water until



SCHEME 3. Synthesis of monomer **2** via method 1.

the water was clear (to remove the excess potassium acetate). After drying ($MgSO_4$), the solvent was removed by evaporation, giving the pure product **6**.

IR (liquid): 1739 and 1228 (ester C=O) and 990 cm^{-1} (vinyl group). NMR: Centered at δ 2.06 (3H, ester CH_3), δ 5.07 (2H, benzyl CH_2), δ 5.50 (2H, vinyl CH_2), δ 6.69 (1H, vinyl CH), and δ 7.30 (5H, ring protons).

Synthesis of **5**: A mixture of *m*-vinylbenzylacetate **6** (26 g, 170 mmol), sodium hydroxyde (12.7 g, 318 mmol) in water (40 mL) and ethanol (120 mL) was refluxed for 2.5 hours. The mixture was diluted with water (200 mL) and extracted with four

40-mL portions $CHCl_3$. The extracts were dried ($MgSO_4$), and the solvent was removed by evaporation to give **5**, a pale yellow oil, in 82% yield.

IR (liquid): 990 and 1630 (vinyl group) and 3340 cm^{-1} (OH) (complete absence of carbonyl bands). NMR: Centered at δ 4.59 (2H, benzyl CH_2), δ 3.70 (1H, hydroxyl), δ 5.51 (2H, vinyl CH_2), δ 6.71 (1H, vinyl CH) and δ 7.24 (5H, ring protons).

Synthesis of Monomer **2.** To an ice-cooled solution of N-tBOC-Ala-OH (1.89 g, 10 mmol) and *m*-hydroxymethylstyrene **5** (2 g, 14.9 mmol) in dried CH_2Cl_2 (10 mL) was added hydroxybenzotriazole (HOBT) (1.53 g, 10 mmol) and dicyclohexylcarbodiimide (DCCI) (2.61 g, 12 mmol). The mixture was then allowed to stand at room temperature and stirred overnight; a precipitate of dicyclohexylurea (DCU) appeared. The mixture was then filtered through a Büchner funnel and washed with CH_2Cl_2. After evaporation of the solvent, the residue was tritrated with ether. The organic layer was then washed with a 4% Na_2CO_3 solution to eliminate the unreacted HOBT, with a NaCl solution, a 1% HCl solution, and finally another time with the NaCl solution. After drying the organic layer over $MgSO_4$ and removal of ether, a crude product consisting of monomer, alcohol, and secondary products was obtained. Flash chromatography [10] can be used to purify this product (solvent petroleum ether/ethyl acetate 80/20; silica gel 230–400 mesh). The yield reached then 30%.

$$[\alpha]_{589} = -33.1°(c = 1.20, \text{MeOH})$$

IR (liquid): 3400 (NH), 1700 (C=O tBOC) and 1745 cm^{-1} (C=O ester linkage). NMR: Centered at δ 5.16 (2H, benzyl CH_2), δ 4.37 (1H, CH bearing branched chain), for other attributions see Table 1.

Preparation via Method 2

Cesium Salt of N-tBOC-Ala-OH. N-tBOC-Ala-OH (2 g, 10.6 mmol) was dissolved in 12 mL EtOH, and 5 mL water was added. The solution was titrated to pH 7.0 (pH paper) with a 20% aqueous solution of Cs_2CO_3 (about 5 mL). The mixture was evaporated to dryness, and the residue was reevaporated from toluene (5 mL).

Esterification Procedure. The reaction was monitored by thin-layer chromatography (TLC). TLC analyses were performed on 0.2 mm thick, precoated silica plates (Merck DC-Alufolien Kieselgel F254). Spots were visualized by inspection under UV light at 254 nm. The reaction was complete after 15 hours.

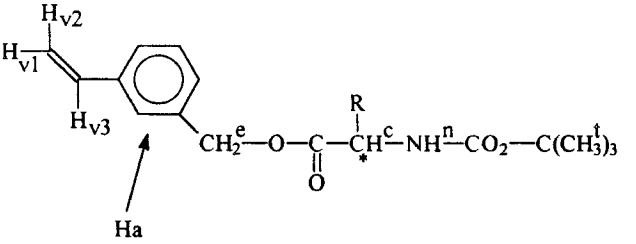
The white cesium salt (2.5 g, 7.8 mmol) obtained was stirred with 1 mL (7 mmol) of VBC in DMF (20 mL) at 50°C for 15 hours. At the end of the reaction, 20 mL toluene was added to the mixture. It was washed with water (20 mL, five times). The organic layer was dried over $MgSO_4$ and the solvent was removed by evaporation. The structure of **2** was confirmed by its NMR spectrum, as was its purity. The yield of the reaction was 95%. $[\alpha]_{589}$ is reported in Table 2.

IR and ^{1}H-NMR spectra were identical to those obtained for monomer **2** prepared by method 1. Calculated: For $C_{17}H_{23}NO_4$: C, 66.86; H, 7.59; N, 4.59. Found: C, 67.00; H, 7.42; N, 4.35.

TABLE 1. δ in ppm for the NMR Spectra of the Monomers[a]

R	H	CH_3	$CH_2\phi$	$CH(CH_3)(OCH_2\phi)$
Hv1	6.69	6.70	6.74	6.68
Hv2	5.76	5.76	5.80	5.76
Hv3	5.26	5.27	5.31	5.27
Ha	7.25	7.28	7.26	7.27
He	5.15	5.16	5.17	5.13
Hc	3.94	4.37	4.67	4.41
Hn	5.15	5.21	5.10	5.38
Ht	1.44	1.44	1.46	1.48
HR	—	1.39	A	B

[a]The protons are indexed as described in the scheme below:



HR are the protons in the R radical. A: CH_2 at 3.11 ppm; ϕ at 7.28 ppm. B: CH at 4.16 ppm; CH_3 at 1.28 ppm; CH_2 at 4.39 ppm; ϕ at 7.27 ppm.

TABLE 2. Yields and Value of [α] for Methods 2, 3, and 4*

M	Y (2)	[α] (2)	Y (3)	[α] (3)	Y (4)	[α] (4)
1	96	0	51	0	NT	0
2	96	$-33.5°$[a]	46	$-33.2°$[b]	76	$-33.5°$[c]
3	94	$-9.1°$[d]	40	$-9.0°$[e]	NT	—
4	94	$-20.5°$[f]	40	$-20.2°$[g]	NT	—

*M = monomer; NT = the product synthesis was not tried; Y = yield. (2), (3), and (4) refer to method 2, method 3, and method 4, respectively. [α] = specific rotation at 589 nm (Na) and T (°C) = 20.

[a]c = 1.16, MeOH.
[b]c = 1.1, MeOH.
[c]c = 1.19, MeOH.
[d]d = 0.99, MeOH.
[e]c = 1.0, MeOH.
[f]c = 1.55, $CHCl_3$.
[g]c = 1.56, $CHCl_3$.

Preparation via Method 3

The cesium salt of N-tBOC-Ala-OH was prepared as described above. The cesium salt (2.5 g, 7.8 mmol) was dissolved in the smallest possible quantity of water (2.5 mL). Then 0.4 g $(Bu)_4NBr$ was added and finally 2 mL (14.1 mmol) VBC. The temperature reaction was 80°C. The use of $(CH_2)_2Cl_2$ (3 mL) as organic solvent induced a longer reaction time (24 hours instead of 4 hours). At the end of the reaction the two phases were separated. The aqueous layer was washed 5 times with 5 mL $(CH_2)_2Cl_2$. The organic layers were mixed and washed several times with 10 mL water until the aqueous layer become clear.

The organic layer was then dried over $MgSO_4$ and evaporated to give 2.55 g of a crude product. By NMR analysis we show that there is 94% of **2** and 6% of **5**. Moreover, all VBC had reacted. Both products can be separated by flash chromatography [10] on silica gel, using ethyl acetate 20%/petroleum ether 80% as eluant. Monomer **2** was finally obtained in 47% isolated yield.

$[\alpha]_{589}$ is reported in Table 2.

IR and ^{1}H-NMR spectra were identical to those obtained for monomer **2** as prepared by method 1.

Preparation via Method 4

A mixture of 6.4 g (0.034 mol) N-tBOC-Ala-OH, 1.8 g (17 mmol) sodium carbonate, 5.3 g (34 mmol) VBC, and 150 mL dimethylformamide was stirred at room temperature for 90 hours.

Water (150 mL) was added to the slurry and an oil which precipitated was extracted with toluene. The toluene extract was washed with water and dried over anhydrous sodium sulfate and distilled under vacuum.

A 75% yield of product was obtained.

$[\alpha]_{589}$ is reported in Table 2.

IR and ^{1}H-NMR spectra were identical to those obtained for monomer **2** as prepared by method 1.

Analysis: Characterization of Monomers 1 to 4

The four monomers have been characterized by IR, NMR, spectrometric mass, and polarimetric methods. Elemental analyses were also performed.

NMR spectra were measured at room temperature in $CDCl_3$ with tetramethylsilane as an internal standard using a Brückner 300 MHz apparatus. IR spectra were recorded on a Perkin-Elmer IR 882 spectrophotometer. Optical rotation was measured using a 1-dm cell in a Perkin-Elmer 141 polarimeter at 25°C. Elemental analyses were performed by the CNRS VERNAISON. When oxygen was titrated, the quoted results take the quantity of oxygen from potential water into account.

IR Spectra. For all the monomers we noticed the presence of two bands between 1700 and 1800 cm^{-1} which can be attribuated to the C=O in the N-protecting group (1720 cm^{-1}) and in the ester linkage (1745 cm^{-1}). The NH stretching is characterized by a large band at around 3400 cm^{-1}. The bands at 1390 and 1305 cm^{-1} are due to the stretching of the $C(CH_3)_3$ group. No band at 1264 cm^{-1} (characteristic of C—Cl) is present, which confirmed total esterification.

H^1-NMR Spectra. An example of the spectrum obtained for monomer **2** is shown in Fig. 1. The attributions were made by comparison with the spectrum of the starting material. In all cases the appearance of a peak at around 5.2 ppm is characteristic of the coupling reaction; it is attributed to the methylene protons from the benzyl group. The other attributions are reported in Table 1.

SM Spectra. For all the monomer we noticed the $M^{+\cdot}$ peak. In the four cases a peak appeared for the cleavage of the $C(CH_3)_3$ group at ($M^{+\cdot} = 56$) and one at 57 for $C(CH_3)_3$.

The vinylbenzyl fragment at $M^{+\cdot} = 117$ gives another fragment at $M^{+\cdot} = 57$.

The appearance of a peak at $M^{+\cdot} = 91$ in the case of monomers **3** and **4** is characteristic of the CH_2O fragment in the branched chain.

Optical Purity. Several methods to determine the optical purity of a product can be used. The most usually used is polarimetry. The values of $[\alpha]$ as determined by polarimetry for all the monomers are reported in Table 2. A discussion about the values obtained is given in the next section.

Another method is to use a chiral shift reagent in NMR spectroscopy which allows the separation of the enantiomers. The percentage of each enantiometer can easily be determined by this method. ^{1}H-NMR shift study analysis involved sequential treatment of a solution of 15 mg monomer **2** in 0.5 mL $CHCl_3$ with 50–100 μL portions of a filtered solution of 250 mg $Eu(hfc)_3$ (europium(III) tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorate]) in 1 mL $CHCl_3$ and observation of the CH_3 in the tBOC group. A typical spectrum is given in Fig. 2, for a mixture of 35% of D-monomer **2** and 65% of L-monomer **2**.

Elemental Analyses. Results are reported in Table 3. We see that the values found agreed well with the calculated values.

Polymerization and Characterization of the Polymers

The ability of this type of monomer to polymerize and copolymerize was tested on monomer **2**. Polymers were synthesized by suspension radical polymerization [11] using benzoyl peroxide as initiator for 24 hours at 90°C. The polymers were purified by precipitation [for P1 and P2 (see Table 4 for the definition of polymers), solvent $CHCl_3$, precipitant CH_3OH; for P3 to P5, solvent CH_3OH, precipitant H_2O] and dried under vacuum at 60°C for 24 hours.

The polymers were characterized by ^{1}H-NMR, IR, and elementary analyses and by a polarimetric method (the values of $[\alpha]_{589}$ obtained from $CHCl_3$ solution ($c = 1.5$ g in 100 mL) at 20°C are reported in Table 4).

Elemental Analyses. The ratio of **2** incorporated in the polymers and calculated from the microanalysis results are reported in Table 4. We see that the values are in good agreement with those determined from NMR analysis.

H^1-NMR Spectra. An example of the spectrum obtained for polymer P1 is shown in Fig. 3: δ at 1.40 (CH_3), 1.44 (tBOC), 4.31 (CH), 4.92 (NH), and 5.05

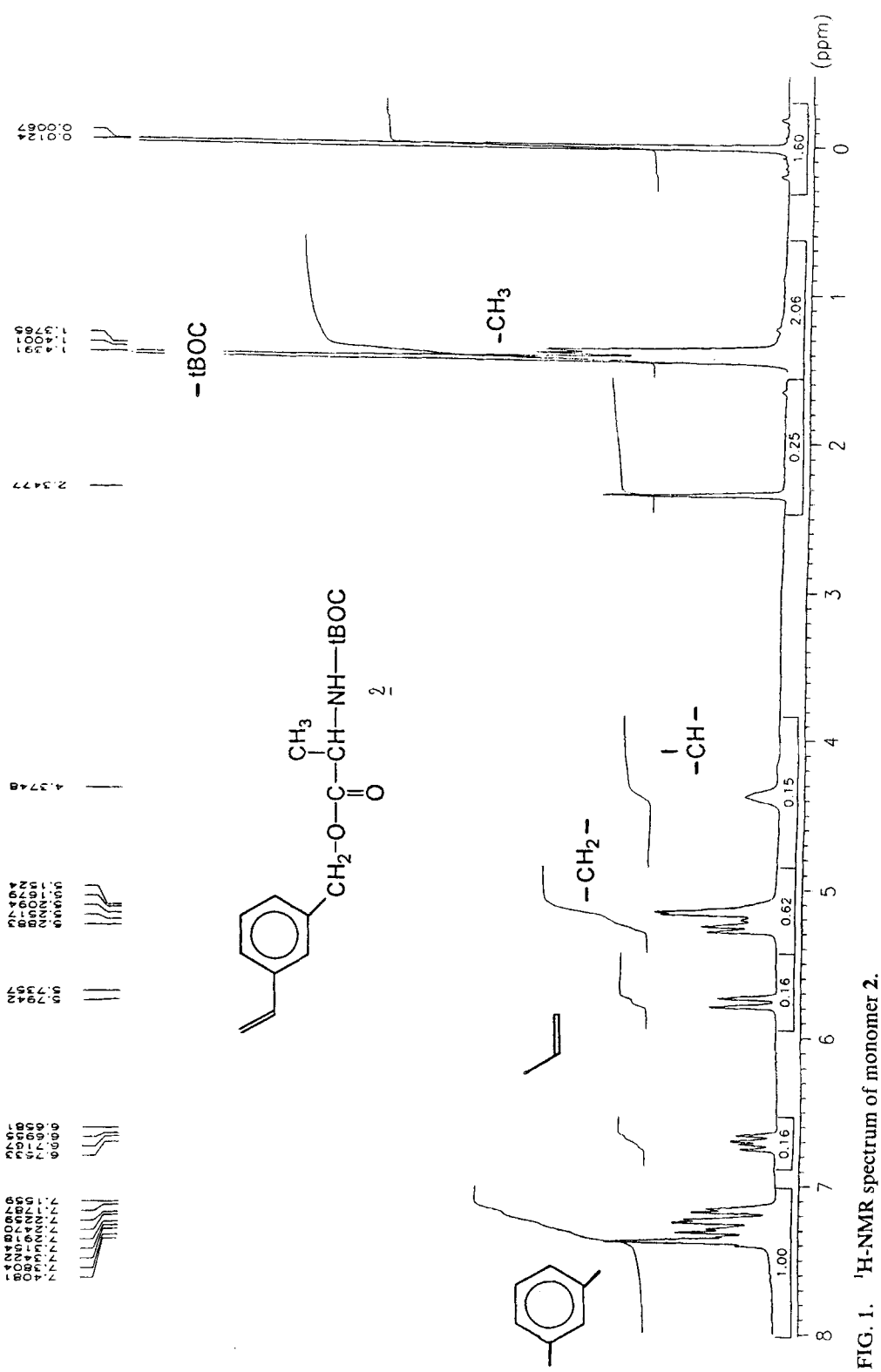


FIG. 1. ^{1}H-NMR spectrum of monomer **2**.

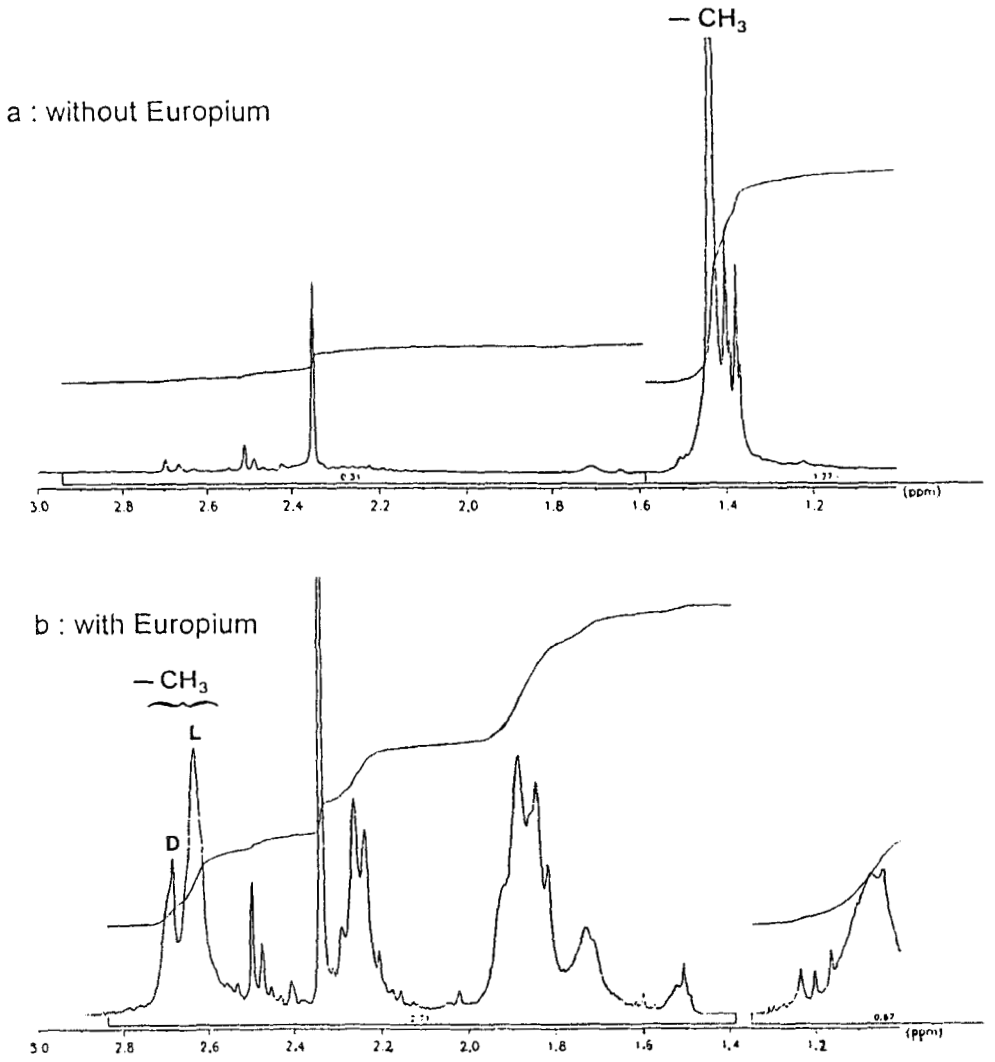


FIG. 2. NMR analysis with shift reagent (europium). (a) NMR spectrum of monomer **2** (range 1–3 ppm). (b) NMR spectrum of monomer **2** with 300 μL of europium solution (range 1–3 ppm).

(benzyl CH_2); NMR centered at 6.5 and 7 ppm (aryl group) and at 1.3, 1.6, and 1.8 ppm (proton from the chain).

IR Spectra. For all polymers we noticed two bands between 1700 and 1800 cm^{-1} which can be attributed to the C=O in the N-protecting group (1720 cm^{-1}) and in the ester linkage (1750 cm^{-1}). The NH stretching is characterized by a large band at around 3400 cm^{-1}. The bands at 1390 and 1305 cm^{-1} are due to stretching of the $C(CH_3)_3$ group. We note the disappearance of the weak band at 1620 cm^{-1}, characteristic of the vinyl group.

TABLE 3. Results from Elemental Analysis in %

		C	H	N	O
1	Calculated	65.96	7.26	4.81	21.97
1	Found	66.85	7.36	4.76	20.5
2	Calculated	66.86	7.59	4.59	20.96
2	Found	67.00	7.42	4.35	19.82
3	Calculated	72.42	7.13	3.67	16.78
3	Found	72.47	7.20	3.60	16.25
4	Calculated	70.57	7.34	3.29	18.80
4	Found	70.49	7.38	3.25	18.33

RESULTS AND DISCUSSION

Yields and Reaction Time

Four methods have been used to prepare amino acid esters. The results obtained for the synthesized monomers are reported in Table 2.

We compared the new methods used to prepare the vinylbenzyl esters of amino acids (methods 1, 2, and 3) to the one described in the literature (method 4).

Method 1

This method is esterification from an alcohol.

This very long method requires three steps. The monomer obtained from the last step is not pure (yield = 25%) and is quite difficult to isolate, so it was eliminated.

Method 2

This method consists of alkylation with an alkyl halide.

In the initial paper [6] the reaction was performed at room temperature with benzylbromide (BB) and not with VBC. Because we used VBC as the starting

TABLE 4. Incorporation Ratio of VBA in the Copolymers and Values of $[\alpha]$

	2 ratio in the mixture of monomers	2 ratio in the polymers			
		Molar ratio			
		NMR	Microanalysis	Weight ratio	$[\alpha]$
P1	10	14	17	35	−5.99
P2	30	41	41.7	67.5	−10.86
P3	50	70	75.6	88.5	−13.84
P4	75	100	—	100	−15.6
P5	100	100	—	100	−17.4

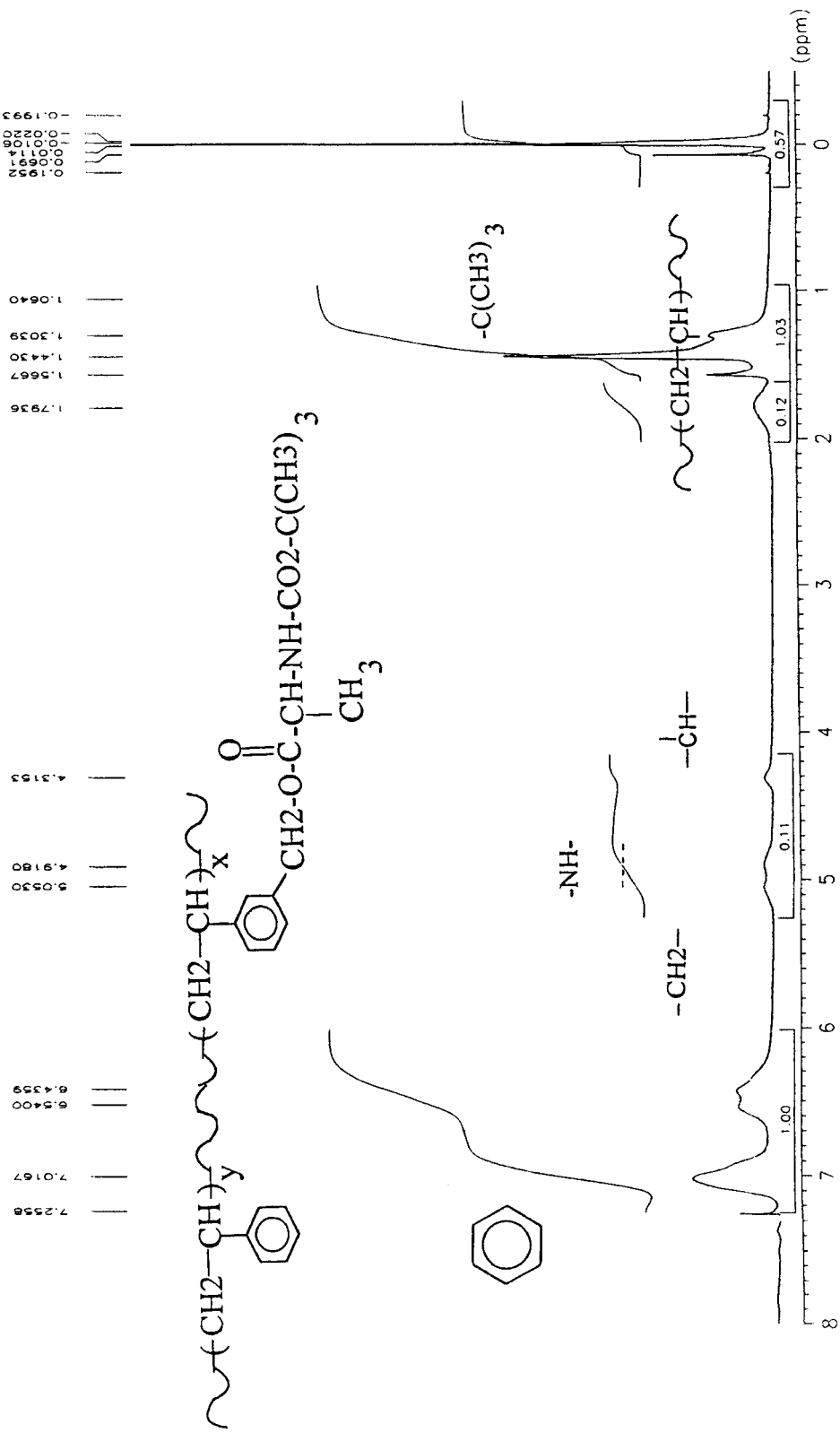


FIG. 3. ^{1}H-NMR spectrum of polymer P1.

material (less reactive than BB), the temperature should be increased to 50°C to improve the yield. The yield obtained was often higher with our system than with the system described in the literature.

The monomers were obtained in very high purity (more than 99%) and in a very good yield. No secondary reactions were detected.

According to Table 2, the yields were independent on the amino acid used.

Moreover, the yields were higher than the ones obtained using method 4 (96% instead of 78%). In addition, method 2 has the advantage of a reduced reaction time (15 hours for monomers **1** and **2** or 24 hours for monomers **3** and **4** instead of 90 hours).

Method 3

According to Table 2, the yield is lower with this method than for method 2. In fact, a secondary reaction which occurs during synthesis produces *m*-hydroxymethylstyrene **5**. There is competition between esterification and hydrolysis reactions. We can assume that there is hydrolysis of the ester group of the monomer during the reaction. Another assumption is hydrolysis of the phase-transfer catalyst, which is explained by Scheme 4. This hypothesis can be confirmed by a short experiment. When we mixed VBC, $(Bu)_4NBr$, and distilled water at 85°C under stirring for 24 hours and did the workup as described for method 3, the crude product obtained consisted essentially of alcohol **5**.

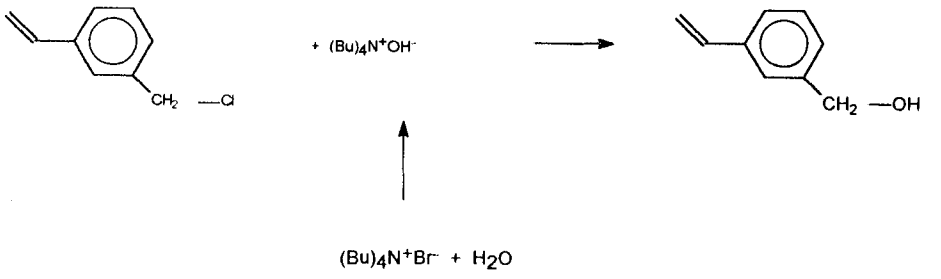
The monomer could be separated from **5** by flash chromatography, leading to a loss of monomer and consequently a lower yield.

In comparison with method 4, method 3 has only the advantage of a shorter reaction time (4 hours).

Optical Purity

The value of $[\alpha]$ obtained for monomer **2** is the same for all the methods used, which confirms that monomer **2** as prepared by those methods are identical. The literature [1] gives a value of $[\alpha]$ of $-36°$ (c = 1.1, MeOH). The small difference can be due to a shifting in the wavelengths.

Monomer **2** was prepared from L-alanine. We also synthesized it from D-alanine. The value of $[\alpha]$ was $+31.5°$ (c = 1.08, MeOH).



SCHEME 4. Secondary reaction in method 3.

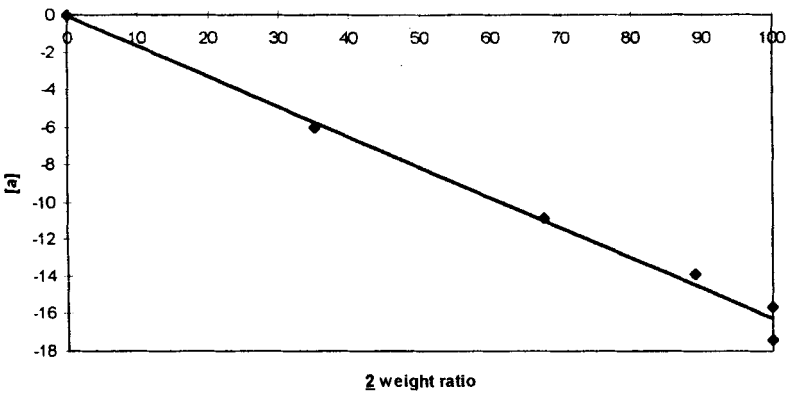


FIG. 4. Evolution of $[\alpha]_{589}$ vs the weight ratio of monomer **2** in copolymer P1.

To be sure that no racemization occurred during synthesis, we determined the optical purity by NMR as described in the previous part. The NMR spectrum of monomer **2** (synthesized by method 2) revealed that no D-monomer was present.

In the case of monomer **4** prepared from threonine, racemization would result in the preparation of diastereoisomers which could be detected in the NMR spectra. This was not the case.

Polymerization

It is possible to polymerize and copolymerize vinylbenzyl esters of amino acids easily (polymerization tested with monomer **2**). We polymerized these monomers via the suspension radical polymerization technique, and the yield of the polymerization was about 40%. It can be seen in Table 4 that the ratio of monomer **2** incorporated in the copolymers is always greater than the ratio of monomer **2** in the initial mixture of monomers.

Figure 4 shows the evolution of $[\alpha]_{589}$ vs the weight ratio of monomer **2** in the copolymer. A linear relationship is observed, showing that there is not an important interaction between the chiral groups. Our objective for our next paper is to determine the copolymerization parameters for these types of monomers and to study the solution properties.

CONCLUSION

Four methods have been tested to prepare vinylbenzyl esters of different amino acids. The best method consists in treating vinylbenzylchloride with the cesium salt of the amino acid, using dimethylformamide as solvent. A yield of 96% was obtained. Moreover, the optical purity (determined by polarimetry or NMR shift study) of the synthesized monomers was 100%, and we have showed the ability of this type of monomer to polymerize.

REFERENCES

[1] N. D. Harris, US Patent 736,403 (1976), Morton-Norwich Products; *Chem. Abstr., 87*, 102656g (1977).
[2] (a) J. C. Sheehan and G. P. Hess, *J. Am. Chem. Soc., 77*, 1067 (1955). (b) W. König and R. Geiger, *Chem. Ber., 103*, 788 (1970).
[3] M. K. Dhaon, R. K. Olsen, and K. Ramasamy, *J. Org. Chem., 47*, 1962 (1982).
[4] P. Jouin, B. Castro, C. Zeggaf, A. Pantaloni, J. P. Senet, S. Lecolier, and G. Sennyey, *Tetrahedron Lett., 28*(15), 1661 (1987).
[5] R. Schwyzer and P. Sieber, *Helv. Chim. Acta, 42*, 972 (1959).
[6] S. S. Wang, B. F. Gisin, D. P. Winter, R. Makofske, I. D. Kulesha, C. Tzougraki, and J. Meienhofer, *J. Org. Chem., 42*, 1286 (1977).
[7] B. F. Gisin, *Helv. Chim. Acta, 56*, 1476 (1973).
[8] J. M. J. Fréchet, M. D. de Smet, and M. J. Farrall, *Polymer, 20*, 675 (1979).
[9] C. H. Bamford and H. Lindsay, *Ibid., 14*, 330 (1973).
[10] W. C. Still, M. Kahn, and A. Mitra, *J. Org. Chem., 43*(14), 2923 (1978).
[11] H. Jacobelli, M. Bartholin, and A. Guyot, *J. Appl. Polym. Sci., 23*, 927 (1979).

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