The use of polymer supports in organic synthesis. XII. The total stereoselective synthesis of cis insect sex attractants on solid phases

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A 2% cross-linked divinylbenzene-styrene copolymer, incorporating trityl chloride groups (2) was used in the synthesis of insect sex attractants of Lepidoptera by a two-step alkyne coupling route. Polymer 2 reacted with the symmetrical diols, 1,8-octanediol and 1,10-decanediol, to give the monoblocked polymer-bound diols 5 and 6 respectively. Mesylation of 5 and 6 gave the polymer-bound monomesylates 7 and 8 which on coupling with lithiumacetylide gave the polymer-bound terminal alkynes 9 and 10 respectively. Acid cleavage of 9 and 10 provided 9-decyn-1-ol and 11-dodecyn-1-ol respectively. A second coupling step was performed by lithiation of 9 and 10 with n-butyllithium or tert-butyllithium followed by treatment with n-butyl bromide or ethyl bromide to give polymer-bound internal alkynes, which on acid hydrolysis gave 9-tetradecyn-1-ol (22), 11-hexadecyn-1-ol (23), and 11-tetradecyn-1-ol (24). If 10 had been lithiated with n-butylithium and coupled with ethyl bromide, some translithiation occurred to liberate n-butyl bromide which entered into the coupling reaction eventually giving a mixture of 23 and 24. This problem was resolved by the use of tert-butyllithium in the lithiation step. Attempts were made to reduce polymer-bound internal alkynes stereoselectively to cis-alkenes with 9-borabicyclononane, disisobutylaluminium hydride, and catechol borane but all these reagents proved inadequate due to incomplete reduction, overreduction, hydrogenolysis of the alkyne from the polymer, and non-selectivity. Polymer-bound internal alkynes were quantitatively reduced exclusively to cis insect sex attractants using disiamylborane without concurrent overreduction or hydrogenolysis.


On a utilisé un copolymère divinylbenzène-styrène réticulé à 2% et incorporant des groupes chlorure de trityle (2) pour réaliser la synthèse de l’attirant sexuel du Lepidoptera en faisant appel à un schéma de couplage d’alkynes impliquant deux étapes. Le polymère 2 réagit avec les diols symétriques octanediol-1,8 et dodecanediol-1,10 pour conduire suivant le cas diols monoblockés 5 et 6 liés au polymère. La mesylation de 5 et 6 fournit les monomesylates 7 et 8 liés au polymère qui, par couplage avec l’acétylurée de lithium, conduisent respectivement aux alcynes terminales 9 et 10 liés au polymère. Une scission acide de 9 et 10 conduit respectivement aux décyn-9-ol-1 et dodécyne-11 ol-1. Une nouvelle étape de couplage, effectuée par la lithiation de 9 et 10 avec le n-butyllithium ou le tert-butyllithium, suit par un traitement avec le bromure de n-butyle ou le bromure d’éthyle conduit aux alcynes internes liés au polymère qui par hydrolyse acide fournissent le tétradécyn-9 ol-1 (23), l’hexadécyn-11 ol-1 (23) et le tétradécyn-11 ol-1 (24). Si l’on avait effectué la lithiation de 10 avec du n-butyllithium et si l’on avait coupé avec du bromure d’éthyle, il se serait produit un peu de translithiation pour libérer du bromure de n-butyle qui peut entrer éventuellement dans la réaction de couplage pour conduire à un mélange de 23 et 24. On a résolu ce problème par l’utilisation du tert-butyllithium dans l’étape de lithiation. On a effectué des essais pour réduire d’une façon stéréoselective les alcynes internes liés au polymère afin d’obtenir des alcynes cis ; à cette fin on a fait appel au 9-borabicyclononane, à l’hydrure de disisobutylaluminium et au catechol-borane mais tous ces réactifs s’avèrent inadéquats à cause soit d’une réduction incomplète, d’une réduction trop grande, d’une hydrogénolysè de l’alkyne du polymère ou à cause de la non-sélectivité. On a pu réduire quantitativement les alcynes internes liés au polymère et obtenir exclusivement les attractants sexuels des insectes cis en faisant appel au disiamylborane sans obtenir de réduction supplémentaire ou d’hydrogénolysè. [Traduit par le journal]

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Introduction

Recently, we have reported the preparation of insect sex attractants (shown below) of Lepidop-
\[ \text{CH}_2(\text{CH}_3)_2\text{CH}=\text{CH(\text{CH}_3)}_2\text{OAc} \]
cis
where \( m = 1-3 \) and \( n = 6, 8-10 \)
tera on solid phases by an alkyne coupling route and by two different Wittig sequences (1, 2). The yields of reactions on solid phases, the use of symmetrical starting materials (3), the simplicity of solid phase reactions (4, 5), and the potential for synthesis in an automated procedure (6) showed distinct promise over solution phase methods, but several problems remained to be solved for the complete stereoselective synthesis of insect sex attractants (7) on solid phases. The use of expensive terminal alkynes in the coupling step can be construed as a disadvantage in both solid phase and solution methods of synthesis. Furthermore, in our previous syntheses on solid phases via the alkyne coupling route, the polymer-bound alkyne was cleaved from the polymer before stereoselective reduction to cis insect sex attractants was attempted. The stereoselective reduction was then achieved using 9-borabicyclononane (9-BBN) in solution (2, 8). A complete solid phase synthesis of cis insect sex attractants would require that the stereoselective cis reduction of an internal alkyne be accomplished directly on the polymer support. In this report we describe the synthesis of insect sex attractants on solid phases by a two-step alkyne coupling route using only acetylene and alkyl halides (9, 10). In addition, the stereoselective reduction of a polymer-bound alkyne to a polymer-bound cis-alkene by an examination of a variety of soluble reducing agents is described.

Results and Discussion

The Two-step Alkyne Route

A 2% crosslinked divinylbenzene (DVB)-styrene copolymer, incorporating trityl alcohol functional groups (1) (11, 12), was prepared by our direct lithiation method (12) and converted to a polymer-bound trityl chloride (2) (11, 12). Polymer 2 was treated with 1,8-octanediol (3) and 1,10-decanediol (4) for 48 h in pyridine at room temperature to give the monoprotected polymer-bound diols 5 and 6 respectively. Mesylation of 5 and 6 in benzene-pyridine (3:1) gave the polymer-bound symmetrical diol monomesylates 7 and 8 respectively. The amounts of diols bound to 5 and 6 and the yields of monomesylates derived from 7 and 8 were determined by acid cleavage as previously described (2) and are recorded in Table 1.

Monolithioacetylide can now be readily prepared in large quantities (13). Treatment of 7 and 8 with monolithioacetylide in tetrahydrofuran–hexamethylphosphoramide (THF–HMPT) (14) gave the polymer-bound terminal alkynes 9 and 10 respectively. Cleavage of 9 and 10 with HCl in dioxane as usual (2) gave 9-decyn-1-ol (11) and 11-dodecyn-1-ol (12) respectively in high conversion (Table 1) and some recovered 3 and 4 respectively. Lithiation of 9 with n-butyllithium (13) and 10 with 13 or tert-butyllithium (14) yielded the polymer-bound lithioalkynes 15 and 16 respectively. Coupling in THF–HMPT (14) of 15 with n-butyl bromide (17) and 16 with 17 or ethyl bromide (18) yielded the polymer-bound alkynes 19–21 respectively as shown in Scheme 1. Polymer-bound alkynes 19 and 21 had been previously prepared by a one-step alkyne coupling route from 7 and 1-lithio-1-hexyne and from 8 using 1-lithio-1-butylene respectively. Acid cleavage of 19–21 gave 9-tetradecyn-1-ol (22), 11-hexadecyn-1-ol (23), and 11-tetradeceyn-1-ol (24) in high conversion from the symmetrical diols 3 and 4 (Table 1). All yields in Table 1 are calculated on products purified by preparative thin layer chromatography (tlc).

When a terminal alkyne is lithiated in a normal solution reaction (9, 10), equivalent amounts of n-butyllithium can be used to effect the lithiation. On polymer supports it is usually necessary to use excess reagents to drive reactions to completion and hence in our experiments on polymer 10, excess 13 was used. Thus, in the coupling reaction of 16 with ethyl bromide (18), some excess 13 was present, which could and did exchange with 18 to give ethyllithium and some n-butyl bromide (17). The coupling of 16 prepared from n-butyllithium (13) with 18 thus led to a mixture of 20 and 21, which on acid cleavage gave a mixture of the alkynols 23 and 24. Analysis of this mixture, as their acetates, by high pressure liquid chromatography (hplc) showed that 24 was contaminated by about 15% of 23 (Table 2). The problem of translithiation was overcome by using tert-butyllithium (14) for the lithiation step and 24 could be prepared free of 23 (Table 2).

Conditions necessary for the conversion of 9
and 10 to 22-24 according to Scheme 1 could be readily monitored by hplc analysis of crude 22-24 prepared via solid phases. In practice, the alkyne fraction, containing internal and sometimes terminal alkyne, was separated by preparative tlc from recovered diol and the alkyne fraction and converted to their acetates which were analyzed by hplc. By this method, the amounts of terminal alkyne in 22-24 could be accurately determined (Table 2).

**cis Reductions of Polymer-bound Alkynes**

Although we had previously reduced internal alkynes to cis-alkenes in solution by catalytic hydrogenation over a Lindlar-type catalyst (2), the results were not completely stereoselective in that less than 85% of the pure cis isomers were produced. In addition, the use of an insoluble palladium oxide catalyst would be incompatible with insoluble polymer supports in any attempt to reduce polymer-bound alkynes to cis-alkenes. It had been shown (2, 8) that internal alkynes can be reduced stereoselectively to cis-alkenes with soluble 9-BBN. After experimenting with a variety of soluble reducing agents (see below), disiamylborane (15) was found to be ideal for the job of reducing polymer-bound alkynes stereoselectively to polymer-bound cis-alkenes. Thus, the polymer-bound internal alkynes, 19 and 21, that had been prepared, in fact, by the one-step alkyne coupling route (2), were treated with a large excess of 0.5 M disiamylborane ((Sia)_2BH) in THF at 0°C for 4 h. Protonolysis with acetic acid yielded the polymer-bound cis-alkenes 25 and 26, which on acid cleavage and acetylation yielded, according to Scheme 2, cis-9-tetradecen-1-yl acetate (27) (10), the sex attractant of Spodoptera frugiperda (J. E. Smith), and cis-11-tetradecen-1-yl acetate (28) (16), the sex attractant of Argyrotaenia velutinana (Walker), in high...
Table 1. Yields of alkynols and intermediates prepared on solid phases via the two-step alkyne route

<table>
<thead>
<tr>
<th>Internal alkynol</th>
<th>Quantity of diol initially bound to polymers 5 and 6 (mmol/g)</th>
<th>Quantity of diol monomesylate bound to polymers 7 and 8 (mmol/g)</th>
<th>Quantity of terminal alkynol bound to polymers 9 and 10 (mmol/g)</th>
<th>Quantity of recovered diol (mmol/g)</th>
<th>Quantity of internal alkynol bound to polymers 19-21 (mmol/g)</th>
<th>Quantity of recovered diol (mmol/g)</th>
<th>Overall yield of internal alkynols (%)</th>
<th>Overall conversion to internal alkynols (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>0.58</td>
<td>0.29</td>
<td>0.23</td>
<td>0.30</td>
<td>0.21</td>
<td>0.29</td>
<td>36f</td>
<td>73</td>
</tr>
<tr>
<td>23</td>
<td>0.69</td>
<td>0.35</td>
<td>0.32</td>
<td>0.35</td>
<td>0.29</td>
<td>0.34</td>
<td>42f</td>
<td>83</td>
</tr>
<tr>
<td>24</td>
<td>0.69</td>
<td>0.35</td>
<td>0.32</td>
<td>0.35</td>
<td>0.28</td>
<td>0.31</td>
<td>41f</td>
<td>74</td>
</tr>
</tbody>
</table>

* Determined by acid cleavage of 5 and 6.
1 Determined by acid cleavage of 7 and 8.
2 Determined by acid cleavage of 9 and 10.
3 Yield if diol recovered from acid cleavage of 19-21 is recycled.
4 Solution yield from ref. 10 is 90% based on 8-chloro-l-tyrosine.
5 Prepared using 14 as the lithiating agent (Scheme 1).
identical to their solution analogs in all respects. We make this observation because for this particular reduction a possible explanation is available. In the solution reaction the vinyl borane intermediate, hydrolyzed by protonolysis with acetic acid, yields boron-containing impurities which must be removed by treatment with hydrogen peroxide (15). In the analogous reductions of 19 and 21 leading to 25 and 26, the boron-containing impurities are removed by simple filtration, as the desired products are bound to the insoluble support, and the products 27 and 28 are thus not subjected to treatment with hydrogen peroxide.

**Elemental Analysis as a Diagnostic Tool for the Determination of Polymer-bound Products**

We had previously stated that elemental analyses of polymer-bound products are unreliable guides to the purity of polymer-bound products (2), because, as in all reactions, side products are often obtained along with the desired product and hence polymer-bound products are unlikely to be pure. We prefer to base our yields of reactions on pure products isolated after cleavage from the polymer. Relles and Schluenz partially addressed this problem in discussing polymer-bound phoshine dichlorides (19). Firstly, they mention that elemental analysis of polymer-bound phosphorous is unreliable and irreproducible and, secondly, they quantify the amount of reagent bound to the polymer by the job it does and not by the phosphorous content of the polymer, which we feel is reasonable. In our own work in this paper, for example, elemental analysis of one batch of 8 for S (1.65%) shows a sulfur content corresponding to 0.52 mmol of 1,10-decanediol monomethylate/g, but acid cleavage yields only 0.29 mmol of 1,10-decanediol.

![Scheme 2](image-url)
Table 3. Yields of sex attractants prepared by reduction of polymer-bound aldehydes using various soluble reducing agents

<table>
<thead>
<tr>
<th>Quantity of diol</th>
<th>Quantity of mesylate bound to polymers</th>
<th>Quantity of aldehydes bound to polymers</th>
<th>Quantity of recovered aldehydes</th>
<th>Overall yield (%)</th>
<th>Overall conversion (%)</th>
<th>Reducing agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>(mmol)</td>
<td>(mmol)</td>
<td>(mmol)</td>
<td>(mmol)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27.45</td>
<td>0.22</td>
<td>0.21</td>
<td>0.30</td>
<td>40.0</td>
<td></td>
<td>DBAH</td>
</tr>
<tr>
<td>28.65</td>
<td>0.65</td>
<td>0.30</td>
<td>0.25</td>
<td>35.7</td>
<td></td>
<td>DBABH</td>
</tr>
<tr>
<td>28.65</td>
<td>0.65</td>
<td>0.30</td>
<td>0.25</td>
<td>35.7</td>
<td></td>
<td>DBAH</td>
</tr>
<tr>
<td>28.65</td>
<td>0.65</td>
<td>0.30</td>
<td>0.25</td>
<td>35.7</td>
<td></td>
<td>DBABH</td>
</tr>
</tbody>
</table>

Monomesylate/g of 8. Indeed recycled polymer 1 contained 0.06 mmol S (0.2%)/g which indicates that a small amount of sulfur-containing product or impurities become permanently bound to the polymer, while a larger fraction of sulfur-containing impurities are washed out during the acid cleavage step or during the procedure used for cleaning recycled 1. Thus elemental analysis of 8 is an unreliable guide to the quantity of 1,10-decanediol monomesylate bound to 8, but does, of course, give a maximum possible value. On the other hand elemental analysis for N, of freshly prepared 1 exhibited 0.78 mmol N (1.1%)/g of 1, while recycled 1 still showed 0.29 mmol N (0.41%)/g. Undoubtedly, the nitrogen comes from the N,N,N',N'-tetramethylethylenediamine used in the preparation of 1 (12), but the nature and consequences of these irreversibly bound polymer-bound nitrogen-containing impurities is unclear at this time. Recycled 1 also contains 0.42 mmol Cl (1.49%)/g of 1, probably derived from the conversion of 1 to 2 with acetyl chloride, but possibly due to multiple cleavages with HCl in dioxane. Since we can separately analyze for benzyl chloride and trityl chloride by the Volhard method (20) and for aliphatic chloride (2) using a palladium tetrabutoxide, and these methods show no residual chloride for recycled 1, we feel that the residual chloride in recycled 1 results from chloride bound to the phenyl rings of 1. Perhaps the surprising aspect of these analytical results lies in the fact that these irreversibly bound impurities do not appear to affect the success of polymer-bound syntheses, although an understanding of these processes will make polymer-bound syntheses even more attractive.

Conclusions

A total stereoselective synthesis of cis insect sex attractants on solid phases has been achieved by a two-step alkyne coupling route using very inexpensive symmetrical diols, acetylene, and alkyl halides. Disamylborane proved to be the

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3Bios-Bead SX-2 were used in all reactions. Chemical analysis of the beads as purchased showed 0.91% CI, 0.68% N, and 0.84% S, while washed beads still showed 0.73% CI, 0.36% N, and 0.41% S. Thus, non-exhaustive washing procedures do not reduce all of the CI, N, and S content of the initial polymer, which contribute to unreliable analyses at a later stage.

4Polymer 1 has been recycled over 25 times without degradation or significant loss of capacity to bind symmetrical diols.
only effective reagent capable of converting a polymer-bound alkyne to a cis polymer-bound alkene in almost quantitative yield and high stereoselectivity. The polymer-bound products proved to be easier to purify and provided higher yields than reductions performed in solution. Elemental analysis cannot be used to provide quantitative information about polymer-bound products but can provide useful clues to possible side reactions and the presence of polymer-carried impurities.

**Experimental**

A Bausch and Lomb Abbé 3L refractometer was used to record the refractive indices. Infrared spectra were recorded on a Unicam SP1000 ir spectrophotometer as neat films between NaCl discs unless otherwise specified. Nuclear magnetic resonance spectra were recorded on a Varian EM360 spectrometer using deuteriochloroform as solvent and tetramethylsilane as internal standard. Mass spectra were recorded on a Perkin-Elmer-Hitachi RMU6E mass spectrometer. Silica gel was used for all thin and preparative layer chromatography. Fractions were extracted with ether in a Soxhlet extractor. Filtration was done under vacuum through sintered glass Buchner funnels. Filtration under an inert atmosphere was done as previously described (2). Microanalyses were performed by G. Gygi of Toronto.

Vapour phase chromatograms were run with a Perkin Elmer 990 instrument using a 15 ft x 1/4 in. column of 10% Silur C on Gaschrom Q(60/80) at a temperature of 170°C and a nitrogen flow rate of 15 ml/min. High pressure liquid chromatograms were run with a Waters Associates Model 440 instrument, with an R-400 refractive index detector. A 30 x 0.4 cm reverse phase μ Bondapak C-18 column using water-acetonitrile mixtures as solvent was used at a flow rate of 1.0 ml/min. Spectral and analytical data are given for all new compounds and for known compounds where data are unreported.

**Preparation of Polymer-bound Dial Monomesylates 7 and 8**

The polymer-bound monomesylates 7 and 8 were prepared as previously described (2) except that benzene-pyridine, 3:1, was used as solvent instead of pure pyridine in the mesylation steps. This change gives a cleaner, less brown, polymer than previously described.

**Preparation of Polymer-bound Terminal Alkynes 9 and 10**

In a typical experiment, 10.8 ml (25 mmol) of a 2-3 M solution of n-butyllithium in 100 ml of dry THF was cooled in a Dry Ice – acetone bath under argon. Dry, acetone free, acetylene was bubbled into the solution for 0.5 h and the solution was stirred for a further 20 min at the Dry Ice bath temperature. To this solution 5 g of 7 or 8, containing 0.25–0.35 mmol of dial monomesylate/g of polymer was added followed by the further addition of 100 ml of HMPT. The mixture was warmed to room temperature and stirred overnight. The black mixture was hydrolyzed with 20 ml of water. The polymer was filtered and washed with three 50 ml portions of ethanol, five 50 ml portions of water, three 25 ml portions of ethanol, and two 50 ml portions of benzene. The polymer, wet with benzene, was transferred to a thimble in a Soxhlet extractor in which molecular sieves (3Å) had been placed in a second thimble or in the round bottom flask of the extractor, and the polymer was extracted with benzene for 4 h under reflux conditions. The polymer was washed

<table>
<thead>
<tr>
<th>Polymer bound alkyne</th>
<th>Reducing agent</th>
<th>T (°C)</th>
<th>Relative yield of unreduced alkyne (%)</th>
<th>Relative yield of attractant (%)</th>
<th>cis:trans ratio of attractant</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>(Si)₃BH</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>99:1</td>
</tr>
<tr>
<td>21</td>
<td>(Si)₃BH</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>90:10</td>
</tr>
<tr>
<td>21</td>
<td>9-BBN</td>
<td>20–30</td>
<td>99.5</td>
<td>0.5</td>
<td>100:0</td>
</tr>
<tr>
<td>21</td>
<td>9-BBN</td>
<td>20–30</td>
<td>17</td>
<td>83</td>
<td>73:27</td>
</tr>
<tr>
<td>21</td>
<td>9-BBN</td>
<td>50</td>
<td>0</td>
<td>100</td>
<td>67:33</td>
</tr>
<tr>
<td>21</td>
<td>Catechol borane</td>
<td>100</td>
<td>0</td>
<td>0.5</td>
<td>100:0</td>
</tr>
<tr>
<td>21</td>
<td>Catechol borane</td>
<td>65</td>
<td>0</td>
<td>63</td>
<td>100:0</td>
</tr>
<tr>
<td>21</td>
<td>DIBAH</td>
<td>20–30</td>
<td>96</td>
<td>6</td>
<td>80:20</td>
</tr>
<tr>
<td>21</td>
<td>DIBAH</td>
<td>60</td>
<td>74</td>
<td>75</td>
<td>85:15</td>
</tr>
</tbody>
</table>

Note: 1. Solvent B is used (see Table 2, footnote d).
2. Obtained by cleavage of 25 or 26, separated from starting dial and acetylated for hplc or vpc analysis.
3. This entry refers to 25.
4. These ratios were determined by vpc and hplc analysis. The retention volume (Vₜ) of cis-27 is 24.2 ml, trans-27 26.2 ml, cis-28 26.9 ml, and trans-28, 27.4 ml.
5. This and all lower entries in this column refer to 28.
6. Only a small excess of reducing agent was used.
7. This reduction was done in dioxane.
8. The remaining product was tetradecan-1-yl acetate produced by overreduction.
9. Complete hydrogenolysis from the polymer occurred and the product was isolated from the filtrate.

**Table 4. High pressure liquid chromatographic analysis of insect attractants, obtained by reduction of polymer-bound alkynes in THF overnight with an excess of various reducing agents at different temperatures**
Preparation of Polymer-bound Internal Alkynes 19-21

A suspension of 1.0 g of 9 in 40 ml of a 0.35 M HCl dioxane solution was stirred at room temperature for 48 h. The polymer residue was washed as previously described (12) and the filtrate diluted with water. As the product was somewhat soluble in water it was necessary to isolate the product from the aqueous solution in a liquid-liquid extractor using ether as the organic phase. The ether phase was dried over MgSO₄ and evaporated to yield 95 mg of crude material. Purification by preparative tlc (eluant, ether-benzene 2:3) afforded, from the slowest moving band (Rₛ 0.15), 47 mg of recovered 3 and, from the faster moving band (Rₛ 0.55), 34 mg of pure 9-deceny-1-ol (11), in 38% yield, as an oil; ν (d4) 1658, 1628 cm⁻¹; ν (CH₂O), 1.7-1.2 (m, 2, (CH₂)₃H); m (2, 2, CH₂=CH₂), 1.9 (t, 1, J = 1.5 Hz, C=CH₂-H), and 1.7-1.2 (m, 12, (CH₂)₃H). Anal. calcd. for C₁₉H₃₈O: C 77.87, H 11.76; found: C 76.98, H 11.88.

Acetylation of 11 with acetic anhydride in pyridine yielded 9-deceny-1-yl acetate as an oil; ν: 1740, 1250 cm⁻¹ (ester C-O); ν (C-O), 3.6 (t, 2, J = 7 Hz, CH₂O), 2.0 (m, 2, CH₂=CH₂), 1.9 (t, 1, J = 1.5 Hz, C=CH₂-H), and 1.8-1.2 (m, 12, (CH₂)₃H); ms (70 eV) m/e (relative intensity): 196 (2.6) (M⁺), 136 (10) (M⁺ - CH₃CO₂H), 47 (100). Anal. calcd. for C₂₁H₄₀O₂: C 73.43, H 10.27; found: C 73.23, H 10.19.

Similarly (except that liquid-liquid extraction need not be used in this example), 10 yielded 61 mg of recovered 4 and 56 mg of 11-dodecyne-1-ol (12), in 43% yield, as an oil (lit. (21) bp 0.033 83-86°C; νₕ 1.4899 (lit. (21) νₕ 1.4898); ν: 3500 (C=O), 3400 (C=H), 2100 (C=C), 1740 (ester C=O) and 1520 cm⁻¹ (C=O); ν (C-O), 3.6 (t, 2, J = 7 Hz, CH₂O), 2.2 (m, 2, CH₂=CH₂), 1.9 (t, 1, J = 1.5 Hz, C=CH₂-H), and 1.8-1.2 (m, 12, (CH₂)₃H). Acetylation of 12 as before yielded 11-dodeceny-1-yl acetate as an oil; ν: 1740 (C=O), 1740 (ester C=O), 1740 (C=C), 1740 (C=O); ν (C-O), 3.6 (t, 2, J = 7 Hz, CH₂O), 2.2 (m, 2, CH₂=CH₂), 2.0 (s, 3, CH₃CO₂), 1.8 (t, 1, J = 1.5 Hz, C=CH₂-H), and 1.8-1.2 (m, 16, (CH₂)₃H); ms (70 eV) m/e (relative intensity): 224 (1) (M⁺), 164 (9) (M⁺ - CH₃CO₂H), and 43 (100). Anal. calcd. for C₁₉H₃₈O₂: C 74.95, H 10.78; found: C 74.61, H 10.75.

Preparation of Polymer-bound Internal Alkynes 19-21

In a typical experiment, 1.25 g of 10, containing 0.4 mmol of 12 was suspended in 20 ml of dry THF at 60-70°C under argon. The mixture was treated with n-butyllithium (13) (3.5 ml of a 0.5 M solution in hexane, 8 mmol) and stirred at 60-70°C for 0.5 h. To the suspension was added 5 ml of n-butyl bromide (17) and 20 ml of HMPT and the mixture was stirred for 4 h at 60-70°C. The polymer was filtered, washed successively with 10 ml portions of ethanol (three times), water (three times), ethanol (three times), dioxane (three times), and ether (three times), and air dried to give the polymer-bound internal alkyne 20.