J. Org. Chem. 1987, 52, 2662-2665

Polymer-Bound Mixed Carboxylic Dithiocarbamic Anhydrides. A New Class of Selective and Recyclable Solid-Phase Acylating Reagents

V. K. Haridasan, A. Ajayaghosh, and V. N. Rajasekharan Pillai*

Department of Chemistry, University of Calicut, Kerala 673 635, India

Received September 15, 1986

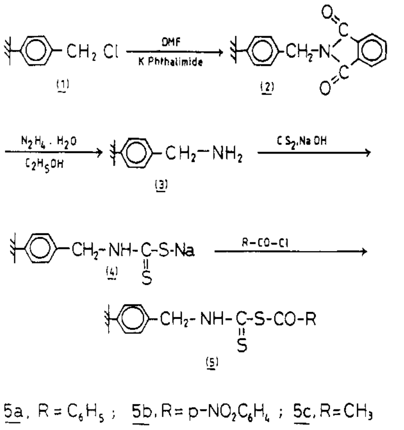
Polymer-supported mixed carboxylic dithiocarbamic anhydrides are a new class of regenerable solid-phase reagents for acylating amino groups specifically. The resins were prepared by a four-step synthesis from cross-linked poly(chloromethylstyrene) (Merrifield's resin). The chloromethyl groups were converted to aminomethyl groups by the Gabriel synthesis, and reaction of the aminomethyl resin with carbon disulfide and aqueous sodium hydroxide gave a dithiocarbamate resin. Treatment of this resin with an acyl chloride gave the mixed carboxylic dithiocarbamic anhydride resin. These insoluble anhydrides transfer the acyl group to amines or amino acids in solution at room temperature, yielding a solution of the corresponding amide or peptide. The spent polymeric reagent can be regenerated to the carboxylic dithiocarbamic anhydride by treatment with carbon disulfide and sodium hydroxide followed by acylation.

A large number of polymeric reagents that contain a reactive function attached to a polymeric backbone have been developed since the introduction of the polymer-supported solid-phase organic synthesis by R. B. Merrifield in 1963.[1-4] These insoluble reagents have the advantages over their soluble counterparts of easy separation from the reaction mixture and regenerability. In addition, the polymer matrix can provide selectivity in a reaction because of steric effects, cross-link density, pore size, or a dilute distribution of reactive functions on the polymer chain.[5,6]

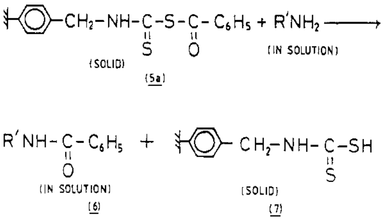
Polymeric active esters have been used as acylating reagents in peptide synthesis,[7,8] in the preparation of semisynthetic penicillins and cephalosporins,[9] in studying intrapolymer interactions,[10] and in polymer reactions with carbanions.[11] Polymeric benzoic anhydrides have been used to benzoylate alcohols and amines,[12] and *N*-trifluoroacetyl nylons have been employed for the trifluoroacetylation of alcohols and amines.[13]

It has been reported that mixed anhydrides of benzoic or *p*-nitrobenzoic acid with N-substituted dithiocarbamic acids are selective reagents for the benzoylation or p-nitrobenzoylation of amino groups.[14,15] We report here on the preparation of polymeric reagents that contain this mixed anhydride function and on their use in the selective acylation of amino groups.

Scheme I. Synthesis of Mixed Carboxylic *N*-Methylpolystyrene Dithiocarbamic Anhydrides



Scheme II. Benzoylation of Amines Using Resin 5a



Results and Discussion

Synthesis of Polymer-Bound Mixed Carboxylic Dithiocarbamic Anhydrides. We selected cross-linked poly(styrene–divinylbenzene) as the polymeric matrix because of its easy functionalization and its commercial availability in different cross-link densities.[16] Cross-linked poly(chloromethylstyrene) (Merrifield resins, **1**) with different degrees of substitution and cross-link density were converted to poly(aminomethylenestyrene) resins (**3**) through the poly(phthalimidomethylstyrene) (**2**), following the literature procedures.[17] The amino group capacity of the aminomethyl resins was determined by the colorimetric method employing picric acid.[18] Treatment of the aminomethyl resin with a fivefold molar excess (based on the amino group capacity) of an equimolar mixture of carbon disulfide and sodium hydroxide in aqueous solution gave the sodium dithiocarbamate resin (**4**). The completion of the reaction was tested by a semiquantitative ninhydrin

---

(1) (a) Merrifield, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 2149. (b) Merrifield, R. B. *Science (Washington, D.C.)* **1986**, *232*, 341.

(2) (a) Frechet, J. M. J. *Tetrahedron* **1981**, *37*, 663. (b) Hodge, P., Sherrington, D. C., Eds. *Polymer-Supported Reactions in Organic Synthesis*; Willey: London, 1980. (c) Mathur, N. K.; Narang, C. K.; Williams, R. E. *Polymers as Aids in Organic Chemistry*; Academic: New York, 1980. (d) Akelah, A.; Sherrington, D. C. *Chem. Rev.* **1981**, *81*, 557.

(3) Rebek, J., Jr. *Tetrahedron* **1979**, *35*, 723.

(4) Pillai, V. N. R.; Mutter, M. *Top. Curr. Chem.* **1982**, *106*, 119.

(5) Leznoff, C. C. *Acc. Chem. Res.* **1978**, *11*, 327.

(6) Patchornik, A. In *Macromolecules*; Benoit, H., Rempp, P., Eds.; Pergamon: New York, 1982; pp 113–123.

(7) Patchornik, A.; Cohen, B. J. In *Perspectives in Peptide Chemistry*; Eberle, A., Weiland, T., Geiger, B., Eds.; Karger: Basal, 1980; pp 118–128.

(8) Fridkin, M. In *The Peptides*; Gross, E., Meienhofer, J., Eds.; Academic: New York, 1979; pp 333–363.

(9) Patchornik, A.; Fridkin, M.; Katchalsky, E. German Patent 1913486; *Chem. Abstr.* **1970**, *72*, 66932y.

(10) Rebek, J.; Trend, F. E. *J. Am. Chem. Soc.* **1979**, *101*, 737.

(11) Cohen, B. J.; Kraus, M. A.; Patchornik, A. *J. Am. Chem. Soc.* **1981**, *103*, 7620.

(12) Shambhu, M. B.; Digenis, G. A. *Tetrahedron Lett.* **1973**, *18*, 1627.

(13) Schulz, R. C.; Schuttenberg, H. *Angew. Chem.* **1976**, *88*, 848; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 777.

(14) Nair, P. G.; Joshua, C. P. *Tetrahedron Lett.* **1972**, *47*, 4785.

(15) Nair, P. G.; Joshua, C. P. *Ind. J. Chem.* **1975**, *13*, 35.

(16) Frechet, J. M. J.; Farral, M. J. In *Chemistry and Properties of Cross-Linked Polymers*; Labana, S. S., Ed.; Academic: New York, 1977; p 59.

(17) Mitchell, A. R.; Merrifield, R. B. *J. Org. Chem.* **1976**, *41*, 2015.

(18) Gisin, B. F. *Anal. Chim. Acta* **1972**, *58*, 248.

0022-3263/87/1952-2662$01.50/0

Table I. Benzoylation of Amines with Polymer-Bound Mixed Benzoic Dithiocarbamic Anhydride 5a

no.	amine	concn of amine, mmol	amt resin with benzoyl gp, mmol	yield of amide, %	mp, °C
1	ammonia	0.30	0.45	88	130
2	methylamine	0.30	0.45	94	81
3	ethylamine	0.30	0.45	92	68
4	dimethylamine	0.30	0.45	92	oil
5	isopropylamine	0.50	0.70	84	76
6	aniline	0.30	0.45	95	163
7	*p*-toluidine	0.30	0.45	87	158
8	*o*-toluidine	0.30	0.45	85	137
9	*m*-toluidine	0.50	0.70	86	141
10	*m*-aminophenol	0.60	0.90	80	173
11	glycine	0.5	0.70	80	184
12	glycine ethyl ester	0.30	0.45	65	66

reaction, which is sensitive to 0.1 μmol of amino groups.[19] Even though the aminomethyl resin swells in such solvents as dioxane and dimethylformamide, the reaction with carbon disulfide was not facilitated in these solvents. Treatment of resin 4 with an excess of benzoyl chloride, *p*-nitrobenzoyl chloride, or acetyl chloride in acetonitrile or chloroform afforded the corresponding mixed carboxylic–dithiocarbamic anhydride resins **5a–c**, respectively (Scheme I).

The IR spectrum of the dithiocarbamate resin 4 shows characteristic IR peaks at 3400 (NH), 1445 (C=N), 1415 (CH_2), 1345 and 1270 (CN), 1210 (NCS_2), and 1005 (C=S) cm^{-1}. The conversion of resin 4 to 5 could be followed by the appearance of a carbonyl peak around 1700 cm^{-1}. The loading of the acyl groups on the polymer support was determined by elemental analysis or by the increase in weight in the acylation step. In the mixed benzoic dithiocarbamic anhydride resin, an average capacity of about 50 mg of benzoyl group/g of resin could be obtained. Presumably the capacity of the resins could be increased by starting with more highly substituted Merrifield resins.

Acylation of Amino Groups with Resins 5. The insoluble resin **5a** reacted with amines or amino acids dissolved in dioxane, chloroform, ethyl acetate, or methylene chloride, transferring the benzoyl group to yield a solution of the benzamide or benzoyl peptide (Scheme II). A solution of the amino compound was stirred with 1.5 equiv of **5a** for 30–60 min. The reaction mixture was filtered through a sintered glass filter, and the resin was washed with 20–30 mL of the solvent. Evaporation of the solvent from the combined filtrate and washings followed by crystallization of the residue afforded the products **6** in high yields (Table I).

In similar experiments using a molar excess of the amino substrate based on the resin benzoyl groups, all of the benzoyl groups in the resin were transferred, as shown by the absence of any carbonyl absorption band around 1700 cm^{-1} in the IR spectrum of the spent resin. The reaction conditions for benzoylation with this resin are much less severe than those needed with polymeric benzoic anhydride,[12] which had to be refluxed with aniline or ethanol in toluene for 1 h to afford benzanilide or ethyl benzoate.

Resin **5a** is selective for benzoylating an amino group in the presence of a hydroxyl group. The resin did not react with ethanol to give ethyl benzoate, and prolonged reaction with *m*-aminophenol produced only *m*-hydroxybenzanilide (Table I). Similar selectivity for N-acylation has been observed with mixed anhydrides of benzoic or *p*-nitrobenzoic acid with N-substituted dithiocarbamic acids.[14,15]

Table II. *p*-Nitrobenzoylation of Amines Using Polymer-Bound Mixed *p*-Nitrobenzoic Dithiocarbamic Anhydride 5b

no.	amine	concn of amine, mmol	amt resin with *p*-nitrobenzoyl gp, mmol	yield of amide, %	mp, °C
1	aniline	0.30	0.40	97	211
2	methylamine	0.30	0.40	95	216
3	*m*-toluidine	0.30	0.40	85	186
4	*o*-toluidine	0.30	0.40	86	184

Table III. Acetylation Using Polymer-Bound Acetic Dithiocarbamic Anhydride 5c

no.	amine	concn of amine, mmol	amt resin with acetyl gp, mmol	yield of amide, %	mp, °C
1	aniline	0.35	0.55	80	113
2	methylamine	0.35	0.55	75	oil
3	*m*-toluidine	0.35	0.55	77	64
4	*p*-toluidine	0.35	0.55	74	154
5	glycine	0.35	0.55	65	205

The *p*-nitrobenzoyl resin **5b** and the acetyl resin **5c** also reacted with amines or amino acids dissolved in chloroform or methylene chloride to give the corresponding N-acylated products in solution (Tables II and III). The degree of incorporation of the *p*-nitrobenzoyl group from resin **5b** could be followed by the presence or absence of the IR nitro group peaks at 1350 and 1530 cm^{-1}. In reactions of **5c**, the weight increase was too small to be used as an analytical procedure.

Peptide Synthesis. Since polymeric active esters are widely used in the synthesis of peptides,[8] we investigated methods for the incorporation of amino acid residues into the dithiocarbamate resins as acyl components. We first tried to prepare a polymeric mixed dithiocarbamic–aminoacyl anhydride by condensing an N-protected amino acid in the presence of dicyclohexylcarbodiimide (DCC) with the polymer-bound dithiocarbamic acid **7** obtained by acidification of **4**. This procedure did not work well because of the instability of **7**. A second method involved reaction of the symmetric N-protected amino acid anhydride with 0.5 equiv of DCC at 0 °C for 30 min followed by treatment of the filtered solution with an equivalent amount of triethylamine or pyridine. With both of these methods, too little amino acid function (<0.1 mmol/g) was incorporated into the polymer to provide a polymeric acyl transfer agent.

A better method for incorporating the amino acid residue into the polymer involved treating resin **4** with the acid chloride of the N-protected amino acid. Although this method is not applicable to acid-sensitive amino acids or to amino acids with acid-cleavable N-protecting groups, it works with the acid-stable, photoremovable 2-nitrobenzyloxycarbonyl (NBOC) N-protecting group.[20-22] Thus, *N*-(2-nitrobenzyloxycarbonyl)phenylalanine (**8**) was reacted with thionyl chloride to give the acid chloride **9**, which reacted with resin **4** to give the mixed N-protected aminoacyl dithiocarbamic anhydride **10**. This resin was treated with a solution of glycine ethyl ester hydrochloride in dioxane containing a few drops of triethylamine for 1 h. The reaction mixture was filtered to remove the spent

---

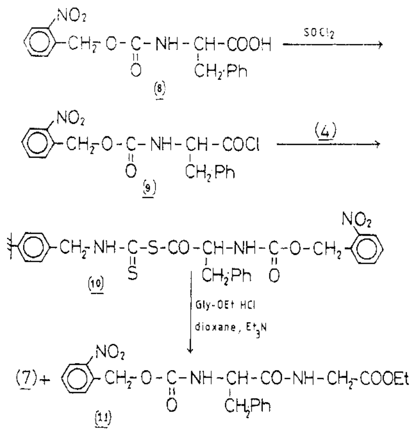
(19) Spackmann, D. H.; Stein, W. H.; Moore, S. *Anal. Chem.* **1958**, *30*, 1190.

(20) Pillai, V. N. R. *Synthesis* **1980**, 1–26.

(21) Patchornik, A.; Amit, B.; Woodward, R. B. *J. Am. Chem. Soc.* **1970**, *92*, 6333.

(22) Amit, B.; Zehavi, U.; Patchornik, A. *J. Org. Chem.* **1974**, *39*, 192.

Scheme III. Peptide Synthesis Using Polymeric Mixed Dithiocarbamic Aminoacyl Anhydrides



polymeric reagent, and the resin was washed with dioxane. Evaporation of the filtrate and crystallization of the residue afforded the dipeptide NBOC-Phe-Gly-OEt (11).

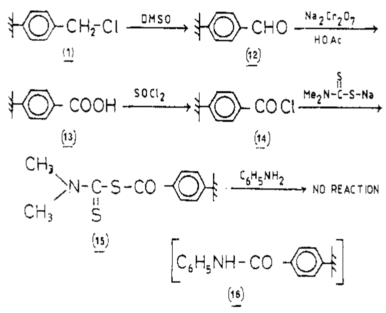
Regeneration of the Spent Polymeric Reagent. Two methods were investigated to check the regenerability of the spent polymeric reagent from the acylation step. The spent resin 7 from the acylation step was treated with a dilute solution of sodium hydroxide to convert it to the sodium dithiocarbamate resin 4, and the product from this step was treated with benzoyl chloride. The resultant resin was treated with excess aniline. The low yield of benzanilide indicated that the benzoyl capacity of the regenerated resin was very low, probably because of the instability of the dithiocarbamic acid resin 7.[23] Accordingly, the spent resin 7 from the acylation step was treated with an equimolar mixture of CS_2 and NaOH to form the dithiocarbamate resin, which on subsequent benzoylation gave the original polymeric benzoylating reagent. After two such regeneration cycles, this resin was as effective a benzoylating agent as the original resin.

All steps starting from the poly(aminomethylstyrene) resin, as well as the regeneration process, proceed readily at room temperature. Accordingly, these reactions were also carried out by passing solutions of the substrates through a small chromatographic column filled with the polymeric reagents. Pure acylated products were obtained by evaporation of the solvent from the solution percolated through the column. Thus, it should be possible to automate the resin synthesis and acylation steps.

Structure Requirements for a Polymeric Acyl Group Transfer Reagent. We wanted to determine whether a resin with the acyl group attached directly to the polymer chain would be a polymeric acylating agent. The polymeric mixed *N*,*N*-dimethyldithiocarbamic benzoic anhydride 15 was prepared from Merrifield resin 1 as depicted in Scheme IV.[24] Prolonged treatment of 15 with aniline did not produce any reaction, as indicated by lack of change in the IR spectrum of 15. If acyl group transfer had occurred, the product would have been the polymeric benzanilide 16.

Experimental Section

Scheme IV. Synthesis of Mixed *N*,*N*-Dimethyldithiocarbamic Polymeric Benzoic Anhydride



Melting points were determined on a hot-stage melting point apparatus and are uncorrected. Solvents were reagent grade and were distilled and purified by literature procedures. Microanalyses were performed by Regional Sophisticated Instrumentation Centre, CDRI, Lucknow. IR spectra were recorded on a PyeUnican Sp-300 spectrophotometer.

Phthalimidomethyl Resin 2. Poly(chloromethylstyrene) (1; 2% cross-linked, 2.3 mmol Cl/g, 20.0 g, Fluka), potassium phthalimide (22.2 g, 120 mmol), and dimethylformamide (400 mL) were stirred at 120 °C for 6 h. The resin was collected by filtration on a sintered glass filter (G3), washed successively with hot DMF, DMF–H_2O, H_2O–dioxane (1:1), dioxane, ethanol, and methanol (30 mL × 2 min, three times), and dried under vacuum to afford resin 2: yield 25.3 g; Anal. N, 2.74% (1.95 mmol N/g); IR (KBr) 1780 and 1720 cm^{-1} (C=O).

Aminomethyl Resin 3. A suspension of resin 2 (20 g, 39 mmol) in a solution of hydrazine hydrate (95%, 16 mL, 480 mmol) in ethanol (400 mL) was heated under reflux for 3 h. The resin was collected by filtration, washed with hot ethanol, DMF, DMF–H_2O, H_2O–dioxane (1:1), dioxane, ethanol, and methanol (30 mL × 2 min, three times), and vacuum-dried to give the resin 3 (16.2 g), which contained 3.49% N (2.5 mmol N/g) by elemental analysis and 2.0 mmol NH_2/g by picric acid titration.[18] The IR spectrum showed no peak due to the carbonyl group, indicating complete hydrolysis of the phthalimidomethyl group to the amino group.

Sodium Dithiocarbamate Resin 4. A mixture of resin 3 (10.0 g), sodium hydroxide (10.0 g, 250 mmol in 50 mL H_2O), and carbon disulfide (19.0 g, 250 mmol) was shaken on a mechanical shaker for 6 h. The mixture turned dark red. The resin was collected by filtration washed several times with water, ethanol, and methanol, and dried under vacuum to provide the dithiocarbamate resin 4: yield 11.0 g; Anal. N, 2.87% (2.05 mmol N/g); IR (KBr) 3400 (NH), 1445 ($C\rightharpoondown N$), 1415 (CH_2), 1345 and 1270 (CN), 1210 (NCS_2), 1005 cm^{-1} (C=S).

Mixed Benzoic *N*-Methylpolystyrene Dithiocarbamate Anhydride 5a. A mixture of resin 4 (5.0 g), acetonitrile (25 mL), chloroform (25 mL), and benzoyl chloride (5.8 mL, 50 mmol) was shaken for 3 h. The resin was collected by filtration, washed with acetonitrile, water, ethanol, and methanol (25 mL × 2 min, three times), and dried under vacuum: yield 5.3 %; Anal. found N, 2.76% (1.97 mmol N/g); IR (KBr) 3400 (NH), 1715 (C=O), 1451 ($C\rightharpoondown N$), 1420 (CH_2), 1370, 1333, 1275 (CN), 1205 (NCS_2), 1005 cm^{-1} (C=S). Determination of loading by reaction with excess aniline and weighing the resulting amide shoowed 46 mg PhCO/g.

Mixed *p*-Nitrobenzoic *N*-Methylpolystyrene Dithiocarbamic Anhydride 5b. Resin 4 (3.0 g), acetonitrile (20 mL), chloroform (20 mL), and *p*-nitrobenzoyl chloride (3.0 g) were shaken for 3 h. The product was collected by filtration, washed as was 5a, and dried under vacuum to afford resin 5b: yield 3.08 g; IR (KBr) 3400 (NH), 1350, 1530 (NO_2), 1710 (C=O), 1450 ($C\rightharpoondown N$), 1370, 1275 (CN), 1205 (NCS_2), 1000 cm^{-1} (C=S). Determination of loading with excess aniline and weighing the resulting amide showed 60 mg of $p\text{-}O_2NC_6H_4CO$/g.

Mixed Acetic *N*-Methylpolystyrene Dithiocarbamic Anhydride 5c. A mixture of resin 4 (2.0 g), acetonitrile (20 mL), and chloroform (20 mL) was cooled in an ice bath. Acetyl chloride (4 mL) was added to this mixture with constant stirring. After 0.5 h the mixture was shaken for 2 h, filtered, washed as was 5a, and dried to give resin 5c: yield 2.03 g; IR (KBr) 3400 (NH), 1690 (C=O), 1450 ($C\rightharpoondown N$), 1370, 1275 (CN), 1205 (NCS_2), 1000 cm^{-1} (C=S). Determination of loading of acetyl group on this resin as in 5a showed 12 mg of CH_3CO/g.

Benzoylation of Amines Using Resin 5a. A mixture of resin 5a (1.0 g), aniline (0.03 g), and chloroform (20 mL) was shaken for 1 h. The residual resin was filtered off and washed with

---

[23] Karchmer, J. H., Ed. In *The Analytical Chemistry of Sulfur and Its Compounds*, Part II; Wiley-Interscience: New York, 1972; p 620.

[24] Frechet, J. M. J.; Haque, K. E. *Macromolecules* 1975, *8*, 130.

chloroform (15 mL × 2). The filtrate together with the washings was washed with HCl (1 N, 10 mL) to remove excess aniline, followed by washing with water and drying over anhydrous $CaCl_2$. Evaporation of the solvent affoded benzanilide, mp and mixed mp 163 °C. Results of similar reactions are shown in Table I.

***p*-Nitrobenzoylation of Amines Using Resin 5b.** A mixture of resin **5b** (1.0 g), aniline (0.03 g), and chloroform (20 mL) was shaken for 1 h. The residual resin was filtered off and washed with chloroform (15 mL × 2). Workup as for **5a** afforded *p*-nitrobenzanilide, mp 211 °C. Results of similar reactions are shown in Table II.

Acetylation of Amines Using Resin 5c. A mixture of resin **5c** (2.0 g), aniline (0.03 g), and chloroform (20 mL) was shaken for 1 h. Workup as for **5a** afforded acetanilide, mp 113 °C. Results of similar reactions are shown in Table III.

Peptide Synthesis. A. Incorporation of the Protected Amino Acid in Resin 7. Polymer-Bound Boc-Ala. A mixture of resin 7 (2.0 g), Boc-Ala (0.945 g, 5 mmol), DCC (1.03 g, 5 mmol), and methylene chloride (25 mL) was shaken for 6 h, filtered, washed successively with chloroform, methylene chloride–methanol (2:1), and methanol (20 mL × 2 min, three times), and dried under vacuum to afford 2.01 g of the Boc-Ala-incorporated resin.

Polymer-Bound NBOC-Phe. A mixture of NBOC-Phe (**8**; 0.750 g) and thionyl chloride (4 mL) was stirred for 1 h. The residue was boiled with charcoal and chloroform and filtered to get the corresponding acid chloride **9**. To this solution of NBOC-Phe-OCl was added resin **4** (2.0 g) and the resultant mixture shaken for 6 h, filtered, washed, and dried to afford resin **10**, yield 2.025 g.

Formation of the Peptide Bond: NBOC-Phe-Gly-OEt (11). A mixture of the mixed N-protected aminoacyl dithiocarbamic anhydride resin (**10**; 2.0 g), glycine ethyl ester hydrochloride (0.695 g, 5 mmol), triethylamine (0.4 mL), and dioxane (20 mL) was shaken for 6 h and filtered. The residue was washed with dioxane (15 mL × 2). The combined filtrate and washings on evaporation followed by crystallization gave the dipeptide NBOC-Phe-Gly-OEt (**11**): 70%; mp 164 °C; IR (KBr) 1530 and 1340 (NO_2); 1710 (urethane), 3310 (amide-A); 1650 (amide-I); 1750 cm^{-1} (ester); ^1H NMR (60 MHz, $CDCl_3$) δ 1.3 (d, CH_3), 2.6 (m, NH), 3.6 (m, CH_2), 5.3 (s, $ArCH_2$), 7.8–8.2 (m, aromatic). Anal. Calcd for $C_{21}H_{23}N_3O_7$: C, 58.7, H, 5.4, N, 9.8. Found: C, 58.2, H, 5.3, N, 9.6.

Recycling Methods. The spent resin from the acylation step (2.0 g) was shaken with sodium hydroxide solution (2 N, 25 mL) for 1 h. The resin was filtered, washed with water several times, then with ethanol and methanol (20 mL × 2 min, three times), and dried under vacuum. No noticeable increase in weight was observed. This resin was converted to the corresponding benzoic anhydride by shaking with benzoyl chloride (4.0 mL) in chloroform. One gram of the resulting resin was shaken with aniline (0.03 g) in chloroform for 1 h. The residue was filtered off, and the product benzanilide (yield 20 mg) was collected as in the previous case.

In another experiment the spent resin (2.0 g) was shaken with CS_2 (6.3 mL, 100 mmol) and NaOH (4.0 g, 100 mmol in 25 mL of H_2O). The product was collected by filtration, washed several times successively with water, ethanol, and methanol, and dried. The dried resin was treated with benzoyl chloride (4.0 mL) in chloroform for 3 h. The resin was filtered, washed with chloroform, ethanol, and methanol (20 mL × 2 min three times), and dried: yield 2.09 g; IR (KBr) 3400 (NH), 1715 (C=O), 1451 ($\mathrm{C\overset{\cdot\,\cdot}{-}N}$), 1420 ($CH_2$), 1370, 1333, 1275 (CN), 1205 (NCS_2), 1005 cm^{-1} (C=S). This resin (1.0 g) was treated with aniline (0.3 mL) in chloroform (15 mL). Workup as in the previous cases afforded benzanilide, 0.090 g. Capacity of the resin: 47 mg of PhCO/g.

Synthesis of Polymer-Bound Benzaldehyde 12.[24] A mixture of Merrifield resin (**1**; 20.0 g, 3.7 mmol of Cl/g), dimethyl sulfoxide (300 ml), and sodium bicarbonate (19.0 g) was stirred at 138–140 °C for 10 h. The resultant resin was filtered, washed with hot water several times and then with dioxane–H_2O (1:1), dioxane, ethanol, methylene chloride, and benzene (50 mL × 2 min, three times), and dried under vacuum: yield 18.67 g; IR (KBr) 2715, 1685 cm^{-1}.

Synthesis of Polymeric Benzoic Acid 13. Resin **12** (10.0 g) was stirred with a saturated solution of $Na_2Cr_2O_7$ in glacial acetic acid (200 mL) and concentrated H_2SO_4 (3.0 mL). The mixture was heated at 70 °C for 4 days. The reaction mixture was cooled, and the polymer was collected by filtration. After being washed with hot acetic acid, hot water, acetone, and methanol, the resin acid **13** was obtained as a light green powder: yield 10 g; IR (KBr) 3450 (COOH), 1700 cm^{-1} (C=O).

Synthesis of Polymeric Benzoyl Chloride 14. To a suspension of resin **13** (6.0 g) in a mixture of benzene–dimethylformamide (5:1) was added thionyl chloride (10 mL) slowly. The reaction mixture was stirred for 3 h at 75 °C. After cooling, the resin was collected and washed repeatedly with dimethylformamide, benzene, dry dioxane, and finally methylene chloride: yield 6.02 g; IR (KBr) 1710 cm^{-1} (C=O).

Coupling of Polymeric Benzoyl Chloride with *N*,*N*-Dimethyldithiocarbamate: Formation of Resin 15. Resin **14** (1.0 g) was shaken with *N*,*N*-dimethyldithiocarbamate (15 mL) (obtained by treating dimethylamine with an equimolecular mixture of carbon disulfide and aqueous sodium hydroxide solution) for 3 h in acetonitrile, filtered, washed with water, acetonitrile, chloroform, and methanol, and dried to afford resin **15**: yield 1.08 g; IR (KBr) 1710, 1590, 1545, 1390 cm^{-1}.

Attempted Reaction of Resin 15 with Aniline. Polymeric mixed benzoic *N*,*N*-dimethyldithiocarbamic anhydride (**15**; 1.0 g) was shaken with aniline (0.3 mL) in chloroform (15 mL) for 3 h. The resin was removed by filtration, washed, and dried. The filtrate on evaporation gave only unchanged aniline. The IR spectrum of the resin was identical with that of the starting resin **15**.

Acknowledgment. We thank the University Grants Commission, Government of India, for the award of a fellowship under the Faculty Improvement Programme (to V.K.H.) and the Council of Scientific and Industrial research, New Delhi, for the award of a Junior Research Fellowship (to A.A.).