Synthesis of *S*-Alkyl Thiobenzoates from Alkyl Halides Mediated by Poly(4-vinylpyridine) Supported Sodium Thiobenzoate at Room Temperature Under Heterogeneous Conditions

Mohammad Ali Karimi Zarchi, Mojgan Nejabat

Department of Chemistry, College of Sciences, Yazd University, Yazd 89195-741, Iran

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ABSTRACT: We describe the use of readily available crosslinked poly(4-vinylpyridine) supported sodium thiobenzoate, [P_4VP]SCOPh, in the suspended solution phase synthesis of *S*-alkyl thiobenzoate at room temperature in high yields. The spent polymeric reagent can be removed quantitatively by filtration and pure products can be obtained by evaporation of the solvent. The spent polymeric reagent can be regenerated and reused for several times. J Appl Polym Sci 125: 1041–1048, 2012

Key words: S-alkyl thiobenzoate; alkyl halide; polymeric reagent; Thioester

INTRODUCTION

Thioesters are activated carboxylic acid derivatives which exhibit acylating properties similar to those of acid anhydrides.[1,2] Thioesters show higher reactivity and selectivity toward nucleophiles than their oxygen analogues, and they play important roles in biological systems such as acyl coenzyme A, and S-acetyl dihydrolipolic acid.[3,4]

Thioesters are important intermediates in organic synthesis. They have been used as mild acyl transfer reagents,[5] as intermediates in the synthesis of aldehydes,[6–8] ketones,[9–11] acids,[12–15] esters,[16,17] lactones,[18–20] amides,[21–23] lactams and related heterocycles,[24–27] and utilized as a protecting group of thiols.[28]

Until the mid-1980s, Thioesters were prepared by conventional methods, that is, condensational of thiols with the parent carboxylic acids in the presence of an activating agent or substitution of acid chlorides or acid anhydrides with metal thiolates.[5,29–31] However, in proportion with growing interests in organic transformation of thioesters, the following synthetic methods are now available: transition metal catalyzed carbonylation,[32–35] reaction of acyllithiums with disulfides,[36] hydration of thioacetylenes,[37,38] Tishchenko-type reaction[39] and coupling of thiol chloroformate with organotin compounds.[40] However, these methods implicate toxic and hazardous reagents, harsh conditions, or uncommon starting materials.

Although polymer-supported reagents especially anion exchange resins have been widely applied in organic synthesis,[41–60] there is only a few report in the literature for the synthesis of organic thioesters based on polymeric reagents.[59,60]

Cainelli et al. reported the synthesis of alkyl thioesters from alkyl halides or tosylates by using amberlyst A-26 thioacetate form.[59] Using polymeric quaternary ammonium thiocarboxylate, the reaction time is very long (many hours), and some products remain adsorbed on the polymer.

Another report in the literature based on polymeric reagent is the synthesis of thioacetates from alkyl halides and sodium thioacetates catalyzed by polyethylene glycol, (PEG 400).[60]

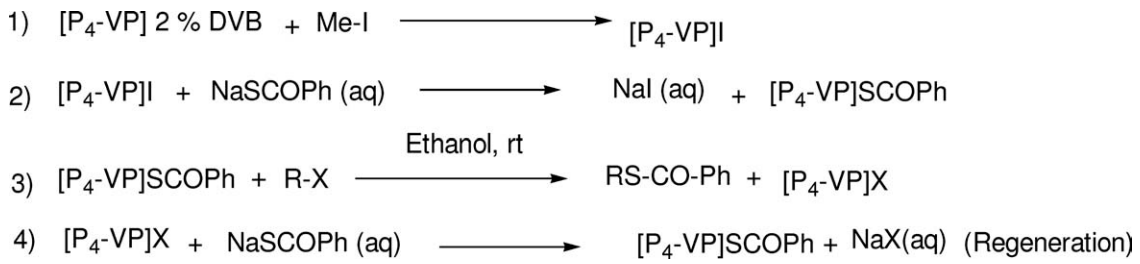
In this strategy, displacement of the leaving group with thioacetate ion afforded the thioesters. In connection with our previous work on crosslinked poly(4-vinylpyridine),[47–58] now we wish to report an improved and general method for preparation of alkyl thioesters from alkyl halides by using a polymer supported sodium thiobenzoate under mild, nonaqueous and heterogeneous conditions in a green solvent (ethanol) and at room temperature in high yields.

EXPERIMENTAL

General

Chemicals were either prepared in our laboratory or were purchased from Fluka Chemical Co. (Buchs,

Correspondence to: M. A. K. Zarchi (makarimi@yazdun.ac.ir).



Scheme 1 Mechanism of the reaction and regeneration of polymeric reagent.

Switzerland), Aldrich Chemical Co. (Milwaukee, WI), Riedel-deHaen AG (Seelze, Germany), and Merck Chemical Co.

Crosslinked poly (N-methyl-4-vinylpyridinium) iodide, [P_4-VP]I, was synthesized according to our procedure (Scheme 1)[49–51] and sodium thiobenzoate were prepared by treatment of thiobenzoic S-acid with sodium hydroxide in dry Et_2O. Progress of the reaction was followed by thin layer chromatography (TLC) using silica gel Poly Gram SIL G/UV 254 plates. All products were characterized by comparison of their melting point, FTIR, ^{1}H-NMR, and ^{13}C-NMR spectral data, with those of known samples and all yields refer to the isolated pure products. Melting points were determined with a Buchi melting point B-540 B.V. CHI apparatus. FTIR spectra were obtained by using a Bruker, Equinox (model 55) and NMR spectra were recorded on a Bruker AC 500, Aveance DPX spectrophotometer at 500 MHz for ^{1}H and at 125 MHz for ^{13}C NMR in $CDCl_3$ solutions.

Preparation of crosslinked poly(4-vinylpyridine) supported sodium thiobenzoate, [P_4-VP] SCOPh

Crosslinked poly (N-methyl-4-vinylpyridinium) iodide (1.00 g) was added to 10 mL of 3 M solution of aqueous sodium thiobenzoate (In a 100 mL of a round-bottomed flask), and slowly was stirred for 24 h at room temperature. The mixture was filtered and was washed with distilled water (2 × 10 mL). It was then dried under vacuum at 40°C to produce polymeric reagent, [P_4-VP] SCOPh (0.95 g). The capacity of the polymeric reagent was determined by potetiometric titration with a 0.10 *M* solution of silver nitrate and was obtained 2.02 mmol of thiobenzoate ion per gram of polymer.

General procedure for conversion of alkyl halides to the corresponding *S*-alkyl thioesters by using [P_4-VP] SCOPh

To a mixture of alkyl halide (1 mmol) and ethanol (5 mL) in a round-bottomed flask (50 mL), 1.49 g (3 mmol) of crosslinked poly(4-vinylpyridine) supported sodium thiobenzoate was added, and the mixture was stirred magnetically at room temperature for 3–180 min (Table II). Reaction monitoring was accomplished by TLC. After completion of the reaction, the suspension was filtered, and was washed with ethanol (2 × 5 mL). High to excellent yields (71–95% (Table II) of the *S*-alkyl thioester compounds is obtained by evaporation of the solvent. If further purification is needed, flash chromatography on silica gel [eluent: n-hexane-ethyl acetate (90/10)] provides highly pure products.

Preparation of S-benzyl thiobenzoate (Entry 3, in Table II) by using [P_4-VP] SCOPh: A typical procedure

To a mixture of benzyl iodide (218 mg, 1 mmol) and ethanol (5 mL) in a round-bottomed flask (50 mL), 1.49 g (3 mmol) of crosslinked poly(4-vinylpyridine) supported sodium thiobenzoate was added, and the mixture was stirred magnetically at room temperature for 10 minutes. The suspension was filtered and was washed with ethanol (2 × 5 mL). 89 % yield (203 mg) of the pure S-benzyl thiobenzoate was obtained by evaporation of the solvent. m.p = 33–35°C (lit: 34-36[62] and 39.5[63]); FTIR (neat) ν_{max} (cm^{-1}) = 3059 (C—H, aromatic), 2950 (C—H, aliphatic), 1653

TABLE I
Optimization of the Reaction Conditions

Entry	Solvent	Time (min)	[P_4-VP]SCOPh/ benzyl iodide (mmol)	Isolated yield (%)
1	Ethanol	60	1	25
2	Ethanol	60	1.25	27
3	Ethanol	60	1.5	35
4	Ethanol	60	1.75	41
5	Ethanol	60	2	50
6	Ethanol	60	2.25	57
7	Ethanol	30	2.5	62
8	Ethanol	30	2.75	79
9	Ethanol	10	3	89
10	Ethanol	10	3.5	89
11	Ethyl acetate	60	3	31
12	Acetone	60	3	75
14	Chloroform	60	3	45
15	Dichloromethane	60	3	51
16	Hexane	60	3	11
17	Acetonitrile	60	3	80

(C=O), 1405–1496 (C=C), 1174 and 1208 (C—S); ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm) = 4.37 (CH_2, s), 7.30 (1H, m), 7.37 (2H, t), 7.43 (2H, d), 7.48 (2H, t), 7.61 (2H, t), 8.014 (2H, d), ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm) = 33.8 (CH_2), 77.47 (solvent), 127.75, 127.77, 129.07, 129.09, 129.42, 133.88, 137.26, and 137.92 (Ar), 191.7 (C=O).

Regeneration of [P_4-VP] SCOPh

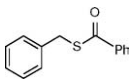
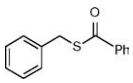
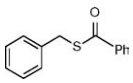
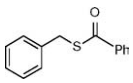
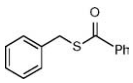
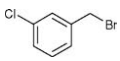
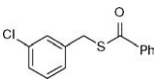
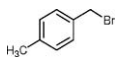
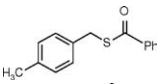
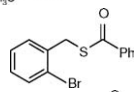
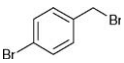
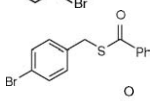
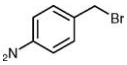
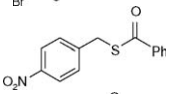
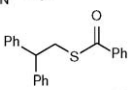
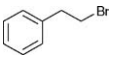
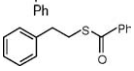
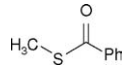
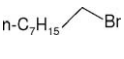
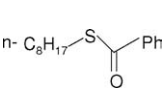
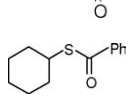
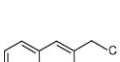
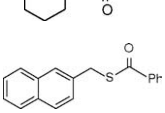
To a solution of sodium thiobenzoate (0.50 g) in distilled water (20 mL), cream-colored spent polymeric reagent (1.00 g) was added and the mixture was allowed to slowly stir at room temperature for 24 h. The mixture was filtered and was washed with distilled water several times. It was then washed with ether and dried overnight at 40°C under vacuum to give [P_4-VP] SCOPh (1.20 g). Determination of its capacity shows the same efficiency as that prepared starting form the original polymeric reagent (entries 3–5 in Table II).

RESULTS AND DISCUSSION

During our investigation of multiple phase techniques in organic synthesis, we observed that crosslinked poly(4-vinylpyridine) supported sodium thiobenzoate, [P_4-VP]SCOPh, can be easily prepared and used as a mild and efficient polymeric reagents for conversion of alkyl halides to the corresponding *S*-alkyl thioesters (Scheme 1). Poly(4-vinylpyridine) crosslinked with 2 % DVB, [P_4-VP] 2 % DVB, was purchased from Fluka company and in reaction with methyl iodide was converted to crosslinked Poly (N-methyl-4-vinylpyridinium) iodide, [P_4-VP]I (equation 1 in Scheme 1), then [P_4-VP]SCOPh was prepared by an exchange reaction between [P_4-VP]I and a slight excess of aqueous sodium thiobenzoate (equation 2 in Scheme 1). Using this heterogeneous reagent, alkyl halides were converted to *S*-alkyl thioesters in ethanol (equation 3 in Scheme 1). For optimization of the reaction conditions, benzyl iodide was chosen as a model substrate and was treated with different molar ratio of [P4-VP]SCOPh/substrate, and in different solvents, and the results are summarized in Table I.

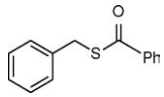
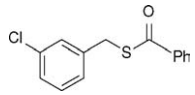
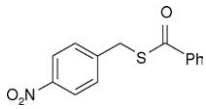
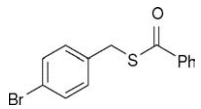
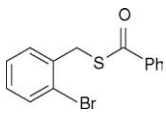
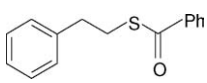
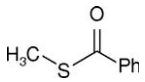
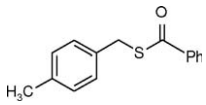
Inspection of Table I reveals that, in this procedure ethanol, is the best solvent. Probably, because there is a stronger hydrogen bonding between the oxygen atom of the thiobenzoate ion (oxygen atom is harder than sulfur atom), with hydrogen atom of the ethanol, and the sulfur atom is better nucleophile than oxygen atom hence, no O-alkylation by-product is observed, and only *S*-alkyl thiobenzoates were obtained. Also as seen in Table I, 3 is the best molar ratio of reagent/substrate. This method represents an extremely convenient procedure for obtaining a wide variety of alkyl thioesters in high to excellent yields (71–95%) and sufficiently pure. The reactions were performed under mild and completely heterogeneous

TABLE II
Conversion of Alkyl Halides to Corresponding *S*-Alky Thiobenzoates Using [P_4- VP]SCOPh in Ethanol at Room Temperature

Entry	Substrate	Product[a]	Time (min)	Yield[b] (%)
1			25	87
2			15	87
3			10	89
4[c]			11	88
5[c]			12	89
6			30	88
7			3	90
8			9	86
9			8	92
10			5	75
11	Ph_2CH-Cl		35	73
12			53	95
13	CH_3-I		60	93
14			120	71
15			180	80
16			150	85

[a] Products were characterized by comparison of their IR and NMR spectra and physical data with those of known samples.
[b] Yields of isolated compounds.
[c] The entries 4 and 5 refer to the use of [P_4-VP]SCOPh that is recycled second and third time, respectively, under identical conditions.

TABLE III
Characteristic Spectral Data of Selected *S*-Alkyl Thioester Products

Entry	Product	ν_{max} (cm^{-1})	^1H NMR δ (ppm)	^{13}C NMR δ (ppm)
1		3059 and 2950 (C—H), 1653 (C=O), 1405-1496 (C=C), 1174,1208 (C—S)	4.37 (CH_2, s), 7.30 (1H, m), 7.37 (2H, t), 7.43 (2H, d), 7.48 (2H, t), 7.61 (2H, t), 8.014 (2H, d)	33.8 (CH_2), 77.47 ($CDCl_3$), 127.75, 127.77, 129.07, 129.09, 129.42, 133.88, 137.26, and 137.92 (Ar), 191.7 (C=O)
2		3045 and 2960 (C—H), 1660.8 (C=O), 1447 and 1596 (C=C), 1175,1205 (C—S)	4.31 (CH_2, s), 7,25–7.31(3H, m), 7.41 (1H, s), 7.48 (2H, t), 7.62 (1H, m), 8.01 (2H, d)	33.1 (CH_2), 77.47 ($CDCl_3$), 127.58, 127.78, 127.96, 129.12, 129.49, 130.29, 134.04, 134.81, 137.02 and 140.12 (Ar), 191.3(C=O)
3		2980 and 3050 (C—H), 1657 (C=O), 1519, 1596 (C=C), 1174,1208 (C—S)	4.4 (CH_2, s), 7.49 (2H, t), 7.59 (1H,d), 7.614 (1H, t), 7.986 (2H, d), 8.2 (2H, d)	—
4		2970 and 3085 (C—H), 1658 (C=O), 1445–1578 (C=C), 1172,1205 (C—S)	4.31 (CH_2, s), 7,25–7.31(3H, m), 7.41 (1H, s), 7.48 (2H, t), 7.62 (1H, m), 8.01 (2H, d)	33.05 (CH_2), 77.52 ($CDCl_3$), 121.69, 127.76, 129.16, 131.13, 132.17, 134.04, 137.06 and 137.20 (Ar), 191.4 (C=O)
5		2970–3030 (C—H), 1662 (C=O), 1448–1582 (C=C), 1175, 1205(C—S)	4.48 (CH_2, s), 7.16(1H, t), 7.29 (1H, t), 7.476 (2H, t), 7.59 (3H, m), 8.01 (2H, d)	34.28 (CH_2), 77.43 ($CDCl_3$), 125.08, 127.75, 128.12, 129.06, 129.49, 131.80, 133.32, 133.92, 137.16 and 137.55 (Ar), 193.50 (C=O)
6		2920–3035 (C—H), 1669 (C=O), 1447, 1580 (C=C), 1174, 1205(C—S)	3.06 (2H, t), 3.40 (2H, t), 7.29 (1H, m), 7.359 (2H, d), 7.402 (2H, t). 7.51 (2H, t), 7.62 (1H, t), 8.05 (2H, d)	30.92 (CH_2-Ph), 36.43 (CH_2-S), 77.58 ($CDCl_3$), 127.03, 127.40, 127.070, 129.03, 129.08, 129.13, 133.81, 137.63 and 140.56 (Ar), 192.2(C=O)
7		—	2.51 (3H, s), 7.47 (2H, t), 7.59 (1H, m), 7.99 (2H, d)	12.13 (CH_3), 77.47($CDCl_3$), 127.55, 129.02, 133.68, and 137.51 (Ar), 192.2 (C=O)
8		2920–3055 (C—H), 1653(C=O), 1444–1578(C=C), 1170 and 1206 (C—S)	2.39 (3H, s), 4.33 (2H, s) 7.16 (2H, d), 7.30 (2H, t), 7.47 (2H, t), 7.60 (1H, t), 7.99 (2H, d)	21.5 (CH_3), 33.5 (CH_2), 77.45 ($CDCl_3$), 127.72, 129.036, 129.039, 129.78, 133.81, 134.79, 137.31 and 137.48 (Ar), 191.86 (C=O)

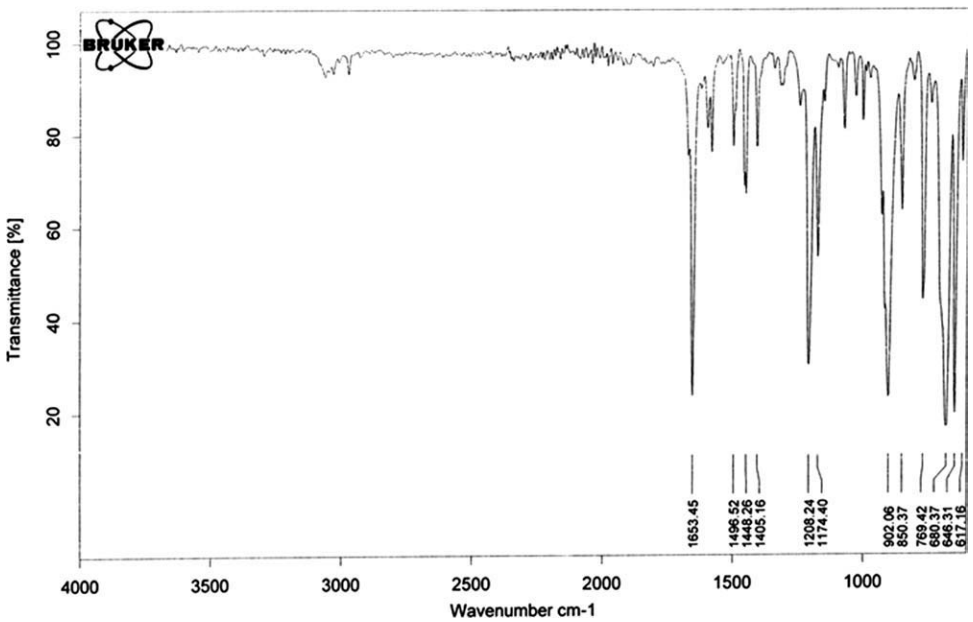


Figure 1 FTIR spectrum of benzyl thiobenzoate.

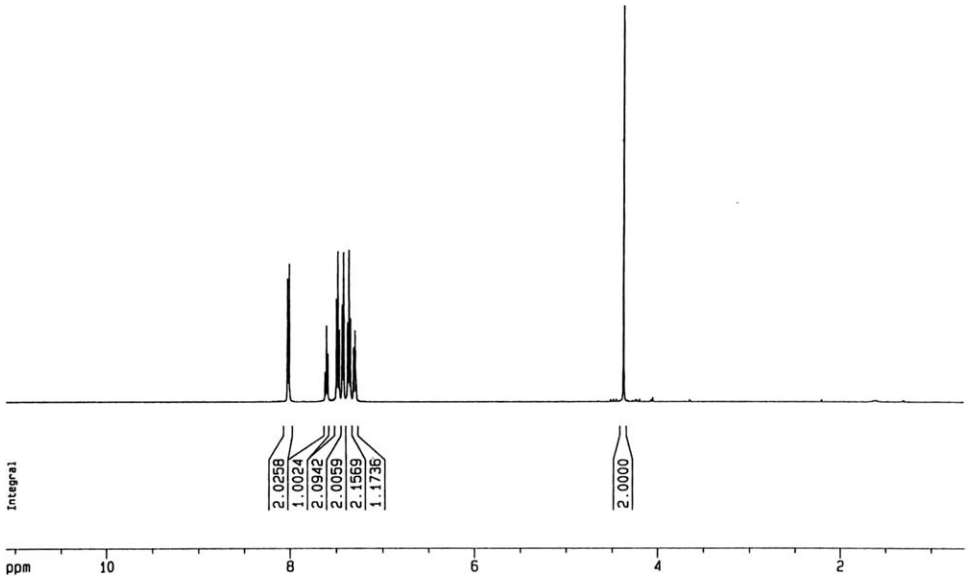


Figure 2 ^{1}H-NMR (500 MHz) spectrum of benzyl thiobenzoate.

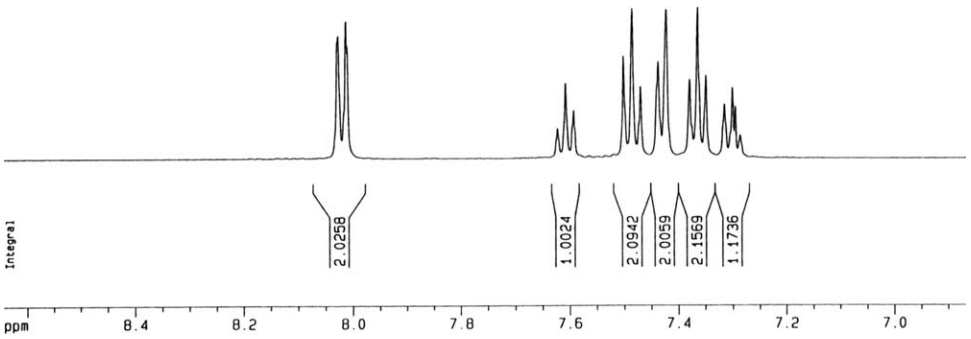


Figure 3 Expanded ^{1}H-NMR spectrum of benzyl thiobenzoate.

conditions in a green solvent (ethanol) at room temperature and *S*-alkyl thioesters were obtained by filtration and evaporation of the solvent. The results and reaction conditions are summarized in Table II.

Inspection of Table II reveals that, in this procedure steric hindrance, is important and the order of reactivity of alkyl halides, are benzyl $>$ 1° $>$ 2° $>$ 3°, which is in agreement with a S_N2 nucleophilic substitution process (the larger R group in alkyl halide, decreases its activity) (entries 13 and 14 in Table II).

Also based on the leaving group effect, the order of reactivity of alkyl halides are RI $>$ RBr $>$ RCl (entries 1–3 in Table II).

The reaction is believed to follow the typical pathway shown in Scheme 1 (eqs. (1)–(3) in Scheme 1). The spent polymeric reagent was easily regenerated

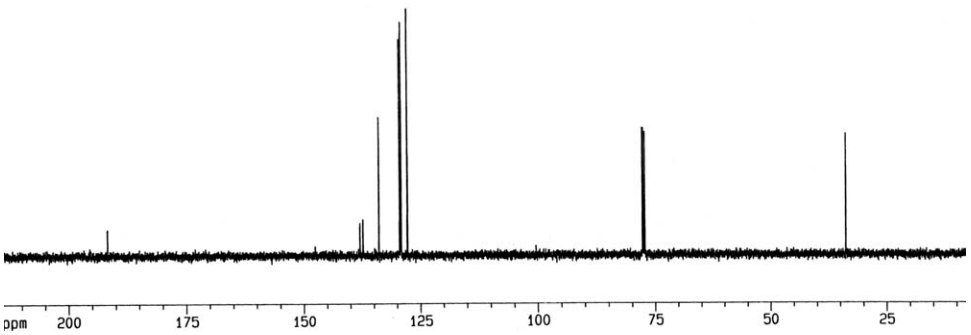
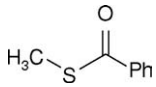
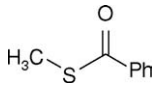
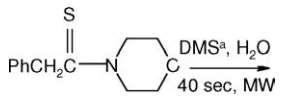
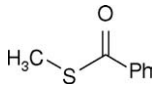
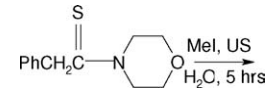
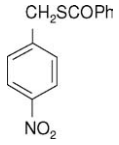
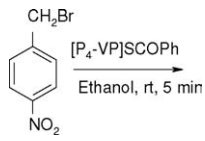
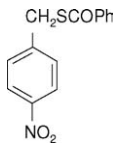
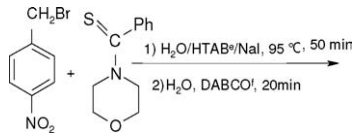


Figure 4 ^{13}C-NMR spectrum of benzyl thiobenzoate.

TABLE IV
Comparison of Different Reported Methods for Synthesis of *S*-Alkyl Thioesters

Entry	Product	Reaction conditions	m.p (°C)	Yield (%)	Reference
1		CH_3-I, [P_4-VP]SCOPh, Ethanol, rt, 60 min	Colorless oil	93	Entry 13 in Table 1
2		 DMS[a], H_2O, 40 sec, MW	Colorless oil	73	63
3		 MeI, US, H_2C, 5 hrs	Colorless oil	79	63
4	$PhCH_2SCOPh$	TBTU[b], DIPEA[c], EtOAc, 150 min; $PhCH_2SH$, 25 °C	Colorless oil	78	64
5	$PhCH_2SCOPh$	$PhCOCl + PhCH_2SH$, 2 sec, MW-900W, Cs-Cellite	Colorless oil	89	65
6	$PhCH_2SCOPh$	$PhCH_2Cl$, [P_4-VP]SCOPh, Ethanol, rt, 25 min	Colorless oil which crystallized with time (m.p: 33–35)[d]	89	Entry 1 in Table
7	$PhCH_2SCOPh$	$PhCH_2Br$, [P_4-VP]SCOPh, Ethanol, rt, 15 min	Colorless oil which crystallized with time (m.p: 33–35)[d]	87	Entry 2 in Table 1
8	$PhCH_2SCOPh$	$PhCH_2I$, [P_4-VP]SCOPh, Ethanol, rt, 10 min	Colorless oil which crystallized with time (m.p: 33–35)[d]	88	Entry 3 in Table 1
9	$PhCH_2SCOPh$	$(PhCH_2S)_2$, Zn, $AlCl_3$, 40 min,40 °C; PhCOCl, 40 min,40 °C	–	79	66
10		 [P_4-VP]SCOPh, Ethanol, rt, 5 min	93–95	75	Entry 10 in Table 1
11		 1) H_2O/HTAB[e]/NaI, 95 °C, 50 min; 2) H_2O, DABCO[f], 20min	–	93	67

[a]Dimethyl sulfide.
[b]Hexadecyltrimethylammonium bromide.
[c]N, N-diisopropyl amine.
[d] Literature melting point = 34–36[61] and 39.5.[62] [e]2-(1-H-binzotriazol-1-yl)-1, 1, 3, 3-tetraethyl uranium tetrafluoroborate.
[f]1, 4-Diazabicyclo[2, 2, 2]octane.

by treatment with an aqueous solution of sodium thiobenzoate (eq. (4) in Scheme 1). The pure *S*-alkyl thioesters were identified by FTIR, ^{1}H and ^{13}C NMR spectra and physical data with those of known samples. In this respect, the appearance of a strong peak at 1651–1689 cm^{-1} for —S—CO— and a strong peak at 1132–1208 cm^{-1} for C—S stretching in their FTIR spectra, and the appearance of a signal at 191.2–192.8 ppm for carbonyl group in their ^{13}C NMR spectra indicate the formation of *S*-alkyl thioesters. Selected spectral data of S- alkyl thioester products are listed in Table III and the FTIR, ^{1}H and ^{13}C NMR spectra of S-benzyl thiobenzoate are shown in Figures 1–4.

In Table IV, other reported methods, for preparation of *S*-alkyl thioesters are compared with this method. As it is demonstrated, the reaction time will be developed which is shorter than previously reported methods. This can probably be attributed to the local concentration of thioester ion species inside the pores.

In summary, it was demonstrated that crosslinked poly(4-vinylpyridine) supported sodium thiobenzoate is an efficient polymeric reagent for the suspended solution phase synthesis of *S*-alkyl thioesters from alkyl halides. *S*-alkyl thioesters were obtained in good to excellent yields (71–95%) and high purity by simple filtration and evaporation of the solvent. Exploitation of this reagent to improve the performance of other nucleophilic displacement is under investigation.

CONCLUSIONS

Crosslinked poly(4-vinylpyridine) supported sodium thiobenzoate has been introduced as an efficient *S*-acylating reagent of alkyl halides to give *S*-alkyl thioesters in high to excellent yields. The present method has the advantages of operational simplicity, mild reaction conditions, ready availability, fast reaction rates, and simple reaction workup. Also, this method is regioselective and no O-alkylation byproduct is observed, and only *S*-alkyl thiobenzoates were obtained. As it is demonstrated, the reaction time will be developed, which is shorter than previously reported methods.

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