

Structural Features of the Polymer Matrix Affecting the Efficiency of Acyl Transfer Reactions

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SYNOPSIS

Polystyrene and polyacrolein were prepared using divinylbenzene (DVB) and tetraethylene glycol diacrylate (TEGDA) as crosslinking agents with varying extents of crosslinking. These polymeric supports were used to prepare acyl transfer reagents like oximino esters and oximino dithiocarbonic anhydrides. The reactivity of the acylating function was determined as a function of the varying macromolecular characters. Investigations revealed a significant influence of the nature of macromolecular support, nature and extent of crosslinking, and the chemical environment of the reagent functions in deciding the extent of the acyl transfer reaction. In the case of DVB crosslinked reagents, the reactivity decreased with increase in the extent of crosslinking, whereas in the case of TEGDA crosslinked reagents, the reactivity increased up to 4% crosslinking and then decreased as the degree of crosslinking was increased. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

There has been increased interest in the application of functionalized polymers as participants in chemical reactions, based on the reactivity of the functional groups and the properties of the polymer molecule.¹⁻⁴ Investigations with various polymeric reagents revealed that the nature of the polymeric backbone does influence the kinetics and extent of functional group conversions in polymer-aided reactions.^{1,5-7} The whole macromolecule cannot be considered as a single species,⁸ but it contains many functional entities depending on the number of attached reactive groups.⁹ Thus, the binding of a functional group to a polymer chain generally results in a new reagent with a different structure, reactivity, and selectivity. Apart from the effect of possible heterogenization, polymer attachment gives systems containing several active species per molecule which can behave differently from the low molecular weight analog, because of cooperative interactions.^{10,11} The chemical reactivity of an immobilized functional group is governed by its distribution and accessibility on the polymer backbone.¹²

The presence of other groups in the macromolecule can also be important for hydrophobic interactions with the substrates and for selectivity if groups with particular steric requirements are used.¹³⁻¹⁵

Use of polystyrene- and polyacrolein-supported oximino esters and oximino dithiocarbonic anhydrides as reagents for solid-phase acylation of organic substrates has been described elsewhere.¹⁶⁻¹⁸ These polystyrene and polyacrolein support systems appeared to be amenable to structural variations for studying the effect of the nature and extent of crosslinking, functional group capacity, and solvent effects on the reactivity of the attached functional groups. This article describes the effect of these parameters on the extent of the functionalization reaction and on the reactivity of oximino esters and oximino dithiocarbonic anhydrides as reagents in polymer-supported solid-phase acylation reactions. The two types of crosslinking agents used were divinylbenzene (DVB) and tetraethylene glycol diacrylate (TEGDA).

EXPERIMENTAL

Materials and Methods

The monomers, styrene, DVB, TEGDA, and acrolein (Aldrich) were purified by low-pressure distil-

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lation. Styrene–DVB and styrene–TEGDA copolymer supports were prepared by adopting procedures reported for parallel cases. Polystyrene-bound aldehyde was prepared from polystyrene by chloromethylation and subsequent oxidation. Acetyl, benzoyl, and *p*-nitrobenzoyl polystyrenes were prepared by the Friedel–Crafts acylation with the respective acyl halides and AlCl_3 . 3-Nitro-4-chloromethyl polystyrene resins (**3**) and 3-nitro-4-keto polystyrene resins (**7a**, **9a**, **11a**) were prepared by the nitration of chloromethyl resin (**2**) or keto polystyrene resin (**6a**, **8a**, **10a**) with fuming nitric acid at 0°C .

Preparation of Styrene–Acrolein–DVB Terpolymer: Suspension Polymerization

The monomers were washed with a sodium hydroxide solution (1%, three times) and with water (three times) to remove the inhibitor. Polyvinylpyrrolidone (150 mg) was dissolved in water (100 mL) and heated to $80\text{--}90^\circ\text{C}$. The mixture of monomers, say, styrene (16.78 mL), acrolein (1.11 mL), and DVB (0.95 mL), for the (2%) crosslinked resin and azobisisobutyronitrile (200 mg) as the initiator was added to the hot solution with vigorous stirring. The mixture was heated at 90°C with stirring for 12 h. The precipitated polymer was filtered, washed with water, carbon tetrachloride, benzene, ethanol, and methanol and dried at 60°C . Yield, 14.5 g. Polymers with crosslink densities of 1, 2, 4, 10, and 20% were prepared by changing the percentage of styrene and DVB. The mol % of acrolein was kept constant at 10%.

Preparation of Styrene–Acrolein–TEGDA Terpolymer: Suspension Polymerization

Polyvinylpyrrolidone (150 mg) was dissolved in water (100 mL) and heated to $80\text{--}90^\circ\text{C}$. The mixture of inhibitor-free monomers, say, styrene (16.78 mL), acrolein (1.11 mL), and TEGDA (0.91 mL), for 2% crosslinked resin and azobisisobutyronitrile (200 mg) as the initiator was added to the hot solution with vigorous stirring. The mixture was heated at 90°C with stirring for 12 h. The precipitated polymer was filtered, washed with water, carbon tetrachloride, ethanol, and methanol and dried at 60°C . Yield, 15.8 g. Polymers with crosslink densities of 1, 2, 4, 10, and 20% were prepared by changing the percentage of styrene and TEGDA. The percentage of acrolein was kept constant at 10%.

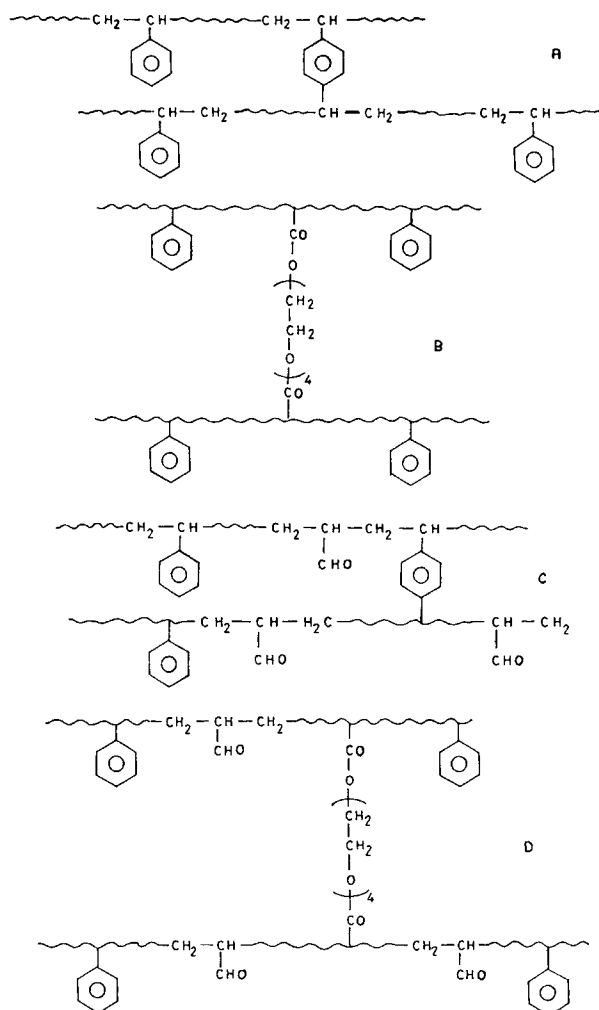


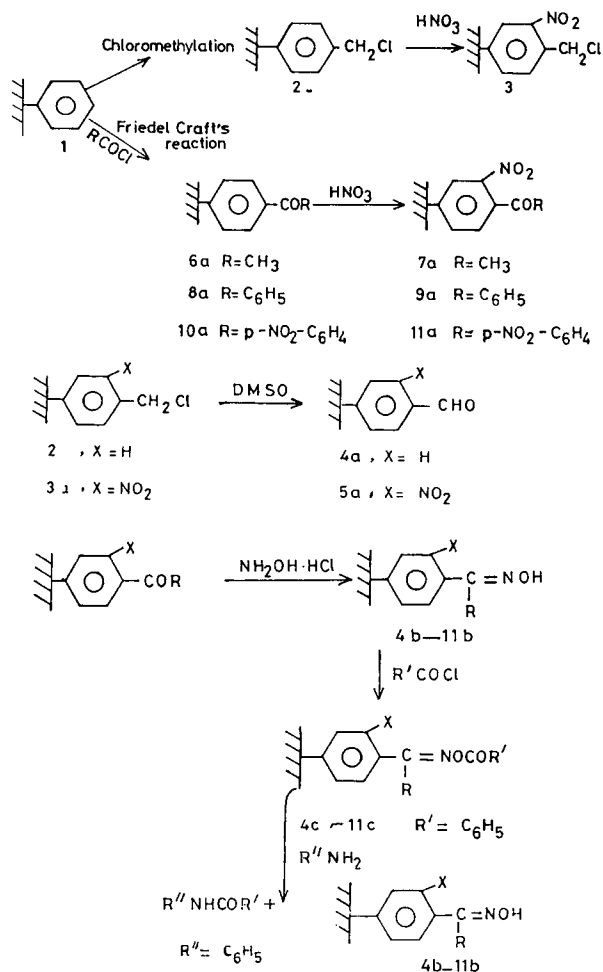
Figure 1 Schematic representation of the structure of the differently crosslinked polymeric supports: (A) Styrene–DVB; (B) styrene–TEGDA; (C) styrene–acrolein–DVB; (D) styrene–acrolein–TEGDA.

Preparation of Polymeric Oximes: General Procedure

The aldehyde or keto resin (10 g) was mixed with hydroxylamine hydrochloride (25 g) and pyridine (30 mL) in chloroform (50 mL). The mixture was refluxed at 90°C for 20 h. The resin was filtered and then washed successively with chloroform, water, ethanol, and methanol (20 mL \times 3 times each). The resin was then dried in vacuum to constant weight.

Preparation of Dithiocarbonate Resins: General Procedure

The oxime resin (10 g, 40 mmol) was added to a fivefold molar excess of an equimolar mixture of CS_2 (16 mL, 200 mmol) and NaOH (10 g,



Scheme 1 Preparation of polystyrene-based oximino benzoates and their acyl transfer reaction.

200 mmol). The mixture was shaken for 10 h at room temperature. The resin was collected by filtration and washed with water, ethanol, and methanol (25 mL \times 3 min \times 5 times each) and dried in vacuum to afford the dithiocarbonate resin.

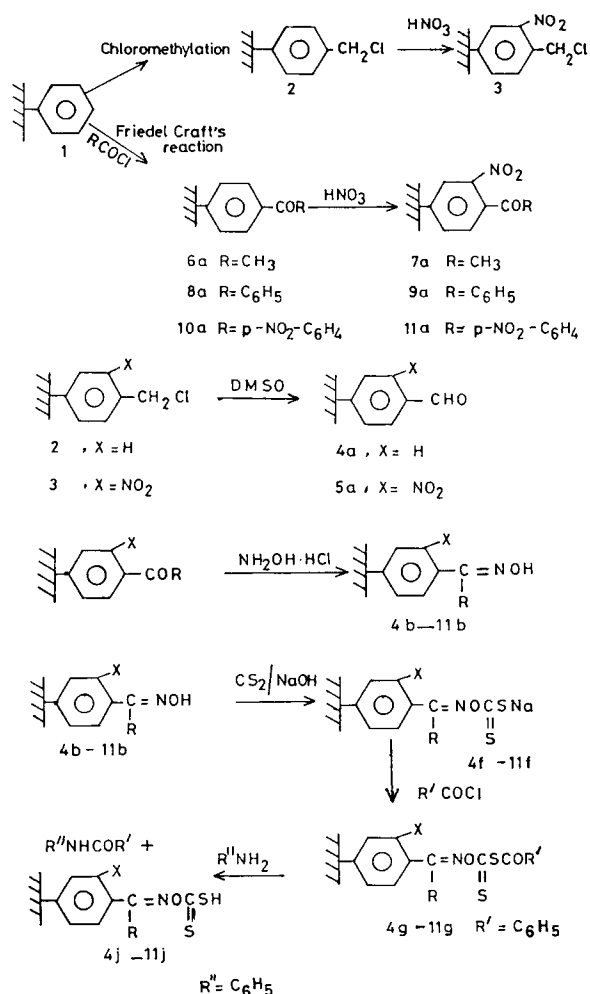
Acylation of Polymeric Oximes and Polymeric Dithiocarbonates: General Procedure

The oxime resin or the dithiocarbonate resin (10 g) was suspended in an acetonitrile : chloroform mixture (1 : 1 v/v, 50 mL) and a threefold molar excess of benzoyl chloride was added to the suspension. Pyridine (5 mL) was added and the mixture was stirred for 8 h. The reaction mixture was filtered at the pump to collect the resin particles, washed with acetonitrile, hot water, ethanol, and

methanol (20 mL \times 2 min \times 3 times each), and dried in vacuum.

Acyl Transfer Reactions Using Polymeric Oximino benzoate and Polymeric Oximino Dithiobenzoic Anhydride Resins: General Procedure

The polymeric oximino benzoate or oximino dithiobenzoic anhydride resin (1 mmol) was suspended in chloroform (20 mL) and the amine (0.5 mmol) was added to it. The mixture was stirred at room temperature for a definite period when maximum conversion was obtained as indicated by TLC. The mixture was then filtered and washed with chloroform. To the filtrate, dilute HCl (25 mL) was added and shaken well to remove the excess amine. The organic layer was collected and chloroform was evaporated off to obtain the amide.



Scheme 2 Preparation of polystyrene-based oximino dithiobenzoic anhydrides and their acyl transfer reaction.

Table I Effect of Crosslink Density on the Degree of Functionalization in Chloromethylation and Friedel–Crafts Acylation Reactions

Crosslink Density (Mol %)	Chlorine Capacity ^a (meq/g)		Acetyl Capacity ^b (meq/g)	Benzoyl Capacity ^c (meq/g)	<i>p</i> -Nitro-benzoyl Capacity ^c (meq/g)
	(2)	(4a)	(6a)	(8a)	(10a)
1	5.45	0.07	3.10	3.50	3.80
2	4.01	0.16	2.75	2.96	3.20
4	3.53	0.25	2.05	2.45	2.98
10	3.00	0.35	1.62	2.01	2.40
20	1.98	0.46	1.12	1.93	2.10

The numbers 2, 4a, 6a, 8a, and 10a have the same significance as given in Scheme 1.

^a Chlorine capacity determined by Volhard's method.

^b Acetyl group capacity determined by the iodoform method.

^c Benzoyl and *p*-nitrobenzoyl group capacity determined by weight change analysis.

Estimation of Acyl Group Capacity: General Procedure

The acylated resin (either polymeric oximinobenzoate or polymeric oximino dithiobenzoic anhydride resins) (1 mmol) was suspended in chloroform (20 mL). Aniline (0.05 mL, 0.5 mmol) was accurately measured and added to the suspension. The mixture was stirred for 3 h, filtered, and washed several times with chloroform. The excess aniline present in the filtrate was extracted with 1 : 1 HCl, made up to 250 mL, and estimated by the iodometric method. The amount of excess or unreacted aniline in each case was estimated, from which the amount of aniline reacted was calculated. The acyl group capacity of resins is thus obtained.

RESULTS AND DISCUSSION

Polystyrene- and polyacrolein-supported acylating reagents were prepared using DVB and TEGDA as

the crosslinking agents. The structure of these different polymers are schematically represented in Figure 1. The extent of crosslinking was varied from 1 to 20% (1, 2, 4, 10, and 20%).

Polystyrene–DVB System

The differently crosslinked polystyrene resins were functionalized to generate the oximino ester as well as the oximino dithiocarbonic anhydride functions by the methods already reported^{16,17} (Schemes 1 and 2). The extent of functionalization of polystyrene resins was found to be highly dependent on the degree of crosslinking. This has been the case both in chloromethylation and in the introduction of keto groups by the Friedel–Crafts acylation reaction. In these cases, the functional group capacity was found to be maximum with the 1% crosslinked resin. It then gradually decreased as the degree of crosslinking was increased to 2, 4, 10, and 20%. The results are presented in Table I.

Table II Effect of Crosslink Density on the OH Capacity of Polystyrene Oximes

Resin ^a	OH Capacity (meq/g) ^b				
	1%	2%	4%	10%	20%
4b	2.69	2.42	1.82	1.42	0.83
5b	2.75	2.52	2.01	1.81	1.21
6b	2.88	2.66	1.88	1.49	0.94
7b	2.92	2.81	2.19	1.86	1.32
8b	2.57	2.01	1.75	1.35	0.77
9b	2.71	2.12	1.96	1.67	1.18
10b	2.42	1.98	1.62	1.28	0.75
11b	2.48	2.01	1.75	1.32	1.05

^a The numbers 4b–11b have the same significance as given in Scheme 1.

^b OH capacity determined by the acetylation method.

Table III Effect of Crosslink Density on the Benzoyl Group Capacity of Polystyrene-bound Oximinobenzoates (4c–11c)

Resin ^a	Benzoyl Group Capacity (meq/g) ^b				
	1%	2%	4%	10%	20%
4c	1.75	1.60	1.52	1.18	0.80
5c	2.15	2.05	1.62	1.28	1.04
6c	1.80	1.75	1.62	1.25	0.80
7c	2.20	2.10	1.75	1.28	0.86
8c	1.60	1.52	1.32	1.18	0.76
9c	1.75	1.60	1.52	1.32	0.80
10c	1.55	1.40	1.24	1.13	0.72
11c	1.60	1.52	1.28	1.24	0.80

^a The numbers **4c–11c** have the same significance as given in Scheme 1.

^b Benzoyl group capacity determined by the titrimetric method.

The OH capacity of polystyrene-bound oximes (**4b–11b**) and the benzoyl group capacity of polystyrene-bound oximino esters (**4c–11c**) and oximino dithiocarbonic anhydride resins (**4g–11g**) with varying crosslink densities are given in Tables II–IV. The OH capacity was determined by acetylation method using an acetylating mixture¹⁹ and benzoyl group capacity was determined by acylation of a standard solution of aniline. These capacity values decreased with increase in the degree of crosslinking.

The percentage yield of amides formed from the benzoylation studies using polystyrene-bound oximino esters (**4c–11c**) and oximino dithiocarbonic

Table IV Effect of Crosslink Density on the Benzoyl Group Capacity of Polystyrene-bound Oximino Dithiobenzoic Anhydride Resins (4g–11g)

Resin ^a	Benzoyl Group Capacity (meq/g) ^b				
	1%	2%	4%	10%	20%
4g	1.60	1.55	1.45	1.13	0.76
5g	1.75	1.60	1.55	1.24	0.80
6g	1.75	1.65	1.52	1.18	0.76
7g	2.05	1.75	1.60	1.24	0.92
8g	1.52	1.40	1.28	1.08	0.68
9g	1.55	1.52	1.40	1.11	0.72
10g	1.28	1.32	1.18	1.04	0.62
11g	1.45	1.40	1.28	1.08	0.68

^a The numbers **4g–11g** have the same significance as given in Scheme 2.

^b Benzoyl group capacity determined by the titrimetric method.

Table V Effect of Crosslink Density on the Extent of Acylation of Aniline Using Polystyrene-bound Oximinobenzoates (4c–11c)

Resin ^a	Extent of Acylation (%) ^b				
	1%	2%	4%	10%	20%
4c	65	62	58	48	32
5c	71	68	62	52	38
6c	66	65	62	51	32
7c	72	70	65	52	34
8c	62	58	54	48	30
9c	65	62	58	54	32
10c	60	55	50	46	28
11c	62	58	52	50	32

^a The numbers **4c–11c** have the same significance as given in Scheme 1(b). Molar ratio, 1 : 2; temp, 30°C; solvent, chloroform.

anhydride resins (**4g–11g**) are given in the Tables V and VI. Acylation of aniline using these reagents was carried out as the model reaction. A molar ratio of 1 : 2 was selected in chloroform at room temperature. The amount of benzanilide formed was determined after a period of 3 h.

From this observation of the diminution of the functional group capacity and reaction rate with the increase in the degree of crosslinking, it can be assumed that the reactivity of the functional group attached to the polymeric network is highly dependent on the variables of gel preparation as in many other reported cases.^{20,21} It might be expected that groups placed close to crosslinks might be less accessible to reagents in the continuous phase. This

Table VI Effect of Crosslink Density on the Extent of Acylation of Aniline Using Polystyrene-bound Oximino Dithiobenzoic Anhydride Resins (4g–11g)

Resin ^a	Extent of Acylation (%) ^b				
	1%	2%	4%	10%	20%
4g	62	60	56	46	30
5g	65	62	60	50	32
6g	65	63	58	48	30
7g	68	65	62	50	35
8g	58	55	52	42	26
9g	60	58	55	45	28
10g	52	50	48	38	24
11g	56	55	52	42	26

^a The numbers **4g–11g** have the same significance as given in Scheme 2(b). Molar ratio, 1 : 2; solvent, chloroform; temperature, 30°C.

Table VII Effect of Crosslink Density on the Extent of Functionalization in Chloromethylation and Friedel–Crafts Acylation Reactions

Crosslink Density (Mol %)	Chlorine Capacity ^a (meq/g)		Acetyl Capacity ^b (meq/g) (6a)	Benzoyl Capacity ^c (meq/g) (8a)	<i>p</i> -Nitro-benzoyl Capacity ^c (meq/g) (10a)
	(2)	(4a)			
1	2.51	0.07	2.42	1.86	1.78
2	3.15	0.60	2.83	2.01	1.95
4	3.27	0.04	4.38	3.32	2.27
10	2.90	0.21	2.62	2.15	1.72
20	1.99	0.26	1.82	1.44	1.18

The numbers **2**, **4a**, **6a**, **8a**, and **10a** have the same significance as given in Scheme 1 (TEGDA crosslinked system).

^a Chlorine capacity determined by Volhard's method.

^b Acetyl capacity determined by the iodoform method.

^c Benzoyl and *p*-nitrobenzoyl group capacities determined by weight change analysis.

leads to nonequivalence of the reactive groups attached to the polymer network.²² Each polymer bead will consist of two regions, one having a higher crosslink ratio and the other lightly crosslinked. Thus, a considerable extent of heterogeneity occurs.²³ Lightly crosslinked styrene–DVB resins could achieve a high functional group capacity and reactivity. Thus, in the case of chloromethylation of 1% crosslinked polystyrene, the capacity was found to be 5.45 meq/g. For 2% crosslinked resin, this was reduced to 4.01 meq/g; for 4% crosslinked resin, 3.53 meq/g; for 10% crosslinked resin, 3.0 meq/g; and for 20% resin, only 1.98 meq/g.

The benzoyl group capacity and extent of acyl transfer using polystyrene-bound oximino dithiocarbonic anhydride resins (**4g–11g**) were found to be lower when compared to the corresponding oximino esters (**4c–11c**) (compare Tables III–VI). In

the conversion of polymeric oximino ester resins to dithiocarbonate resins, a corresponding decrease in the extent of functionalization was observed. Thus, the benzoyl group capacity and extent of acylation for oximino dithiocarbonic anhydride resins showed lower values compared to the corresponding oximino esters. All the available oximino groups could not be converted to the dithiocarbonate functions due to the inhomogeneity between the hydrophobic polystyrene matrix and the polar reagent used for the conversion.

Polystyrene–TEGDA System

Copolymers of styrene with TEGDA of varying crosslink densities were prepared.²⁴ These copolymers were functionalized to incorporate the oximino

Table VIII Effect of Crosslink Density on the OH Capacity of Polystyrene-bound Oximes (4b–11b)

Resin ^a	OH Capacity (meq/g) ^b				
	1%	2%	4%	10%	20%
4b	1.34	1.90	2.42	2.10	1.18
5b	1.42	2.10	2.58	2.25	1.23
6b	1.72	2.15	2.89	2.25	1.32
7b	1.88	2.25	3.28	2.40	1.41
8b	1.23	1.65	2.75	1.62	1.08
9b	1.30	1.80	2.90	1.75	1.12
10b	1.18	1.50	1.90	1.32	0.98
11b	1.23	1.65	2.10	1.45	1.06

^a The numbers **4b–11b** have the same significance as given in Scheme 1 (TEGDA crosslinked system).

^b OH capacity determined by the acetylation method.

Table IX Effect of Crosslink Density on the Benzoyl Group Capacity of Polystyrene-bound Oximinobenzoate Resins (4c–11c)

Resin ^a	Benzoyl Group Capacity (meq/g) ^b				
	1%	2%	4%	10%	20%
4c	1.28	1.55	2.05	1.60	1.08
5c	1.32	1.60	2.30	1.75	1.18
6c	1.40	1.65	2.10	1.55	1.11
7c	1.52	1.75	2.20	1.75	1.18
8c	1.24	1.40	1.75	1.52	1.04
9c	1.28	1.55	2.05	1.55	1.06
10c	1.18	1.28	1.60	1.24	0.76
11c	1.24	1.40	1.65	1.28	1.04

^a The numbers **4c–11c** have the same significance as given in Scheme 1 (TEGDA crosslinked system).

^b Benzoyl group capacity determined by the titrimetric method.

Table X Effect of Crosslink Density on the Benzoyl Group Capacity of Polystyrene-bound Oximino Dithiobenzoic Anhydride Resins (4g–11g)

Resin ^a	Benzoyl Group Capacity (meq/g) ^b				
	1%	2%	4%	10%	20%
4g	1.24	1.52	1.75	1.55	1.06
5g	1.32	1.60	2.25	1.70	1.18
6g	1.32	1.60	2.05	1.55	1.10
7g	1.52	1.70	2.10	1.60	1.15
8g	1.24	1.28	1.60	1.40	1.04
9g	1.28	1.52	1.80	1.55	1.08
10g	1.15	1.24	1.55	1.18	0.72
11g	1.24	1.40	1.60	1.24	1.04

^a The numbers **4g–11g** have the same significance as given in Scheme 2 (TEGDA crosslinked system).

^b Benzoyl group capacity determined by the titrimetric method.

esters and oximino dithiocarbonic anhydride functionalities by the methods reported earlier.^{16,17} The effect of crosslink density on the degree of functionalization is shown in Tables VII–X. In the chloromethylation reaction and in the Friedel–Crafts acylation reaction, the functional group capacity of each resin was found to be maximum with the 4% crosslinked variety. The capacity first increased from 1% and attained a maximum value at 4% crosslinking and then decreased. The capacity was found to be minimum for 20% crosslinked resin (Tables VII–X).

Further functional group transformations were also dependent on the extent of crosslinking. The OH capacity of polystyrene-bound oximes (**4b–**

Table XI Effect of Crosslink Density on the Extent of Acylation Using Polystyrene-bound Oximinobenzoates (4c–11c)

Resin ^a	Extent of Acyl Transfer (%) ^b				
	1%	2%	4%	10%	20%
4c	52	60	68	62	42
5c	54	62	75	65	48
6c	55	63	70	60	45
7c	58	65	72	65	48
8c	50	55	65	58	38
9c	52	60	68	60	40
10c	48	52	62	50	30
11c	50	55	63	52	38

^a The numbers **4c–11c** have the same significance as given in Scheme 1 (TEGDA crosslinked system).

^b Substrate, aniline; molar ratio, 1 : 2; solvent, chloroform; temperature, 30°C; time, 3 h.

Table XII Effect of Crosslink Density on the Extent of Acylation Using Polystyrene-bound Oximino Dithiobenzoic Anhydride Resins (4g–11g)

Resin ^a	Extent of Acyl Transfer (%) ^b				
	1%	2%	4%	10%	20%
4g	50	58	65	60	40
5g	54	62	74	64	48
6g	54	62	68	60	44
7g	58	64	70	62	46
8g	50	52	62	55	38
9g	52	58	66	60	42
10g	46	50	60	48	28
11g	50	55	62	50	35

^a The numbers **4g–11g** have the same significance as given in Scheme 2 (TEGDA crosslinked system).

^b Substrate, aniline; molar ratio, 1 : 2; solvent, chloroform; temperature, 30°C; time, 3 h.

11b) and the benzoyl group capacity of polystyrene-bound oximino esters (**4c–11c**) and oximino dithiocarbonic anhydride resins (**4g–11g**) with varying crosslink densities showed that the capacity first increased with increase in crosslink density, attained a maximum value at 4% crosslinking, and then decreased gradually (Tables VIII–X). The OH capacity was determined by the acetylation method¹⁹ using a reaction with the acetylating mixture and the benzoyl group capacity was determined by acylation of a standard solution of aniline (Tables VIII–X).

The acylation reaction of polymer-bound oximino esters (**4c–11c**) and oximino dithiocarbonic an-

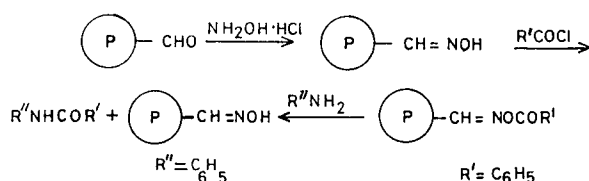
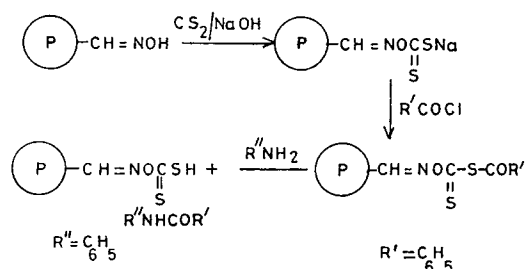
**Scheme 3** Preparation of polyacrolein-based oximino-benzoate and its acyl transfer reaction.**Scheme 4** Preparation of polyacrolein-based oximino dithiobenzoic anhydride and its acyl transfer reaction.

Table XIII Effect of Crosslink Density on Functionalization Reactions and on the Extent of Acyl Group Transfer in the Polyacrolein–DVB System

Functional Groups	Extent of Functionalization				
	1%	2%	4%	10%	20%
Percentage of nitrogen in polyacrolein oxime	5.80	5.60	5.45	4.60	3.80
OH capacity (meq/g) of polyacrolein oxime	2.82	2.76	2.50	2.05	1.82
Benzoyl group capacity (meq/g)	2.72 ^a	2.55 ^a	2.32 ^a	1.60 ^a	1.45 ^a
	2.55 ^b	2.43 ^b	2.15 ^b	1.52 ^b	1.18 ^b
Percentage yield in acyl transfer reaction ^c	84 ^a	80 ^a	76 ^a	62 ^a	56 ^a
	80 ^b	78 ^b	71 ^b	58 ^b	48 ^b

^a Using polyacrolein oximinobenzoate resin.^b Using polyacrolein oximino dithiobenzoic anhydride resin.^c Substrate-to-reagent ratio, 1 : 2; solvent, chloroform; time, 3 h; temperature, 30°C; substrate, aniline.

hydride resins with aniline also showed that the extent of the acyl group transfer increased with increase in crosslink density, reached a maximum value at 4% crosslinking, and then decreased gradually. A substrate-to-resin ratio of 1 : 2 was chosen in chloroform at room temperature. The amount of benzanilide formed after a period of 3 h was determined. Results are given in Tables XI and XII.

From the foregoing observations, it is clear that, compared to styrene–DVB, styrene–TEGDA copolymers showed a significant increase in the reactivity of the bound functionality. The enhanced reactivity of the styrene–TEGDA resin can be attributed to the increased polarity and flexibility of the TEGDA crosslinks and also to the increased compatibility with the substrate and solvents.^{25–27} For 20% crosslinked resins also, there exists a reasonable functional group reactivity for TEGDA crosslinked polymers.

Styrene–Acrolein–DVB Terpolymer System

Terpolymers of styrene–acrolein–DVB with varying crosslink densities (1, 2, 4, 10, and 20%) were prepared by the suspension polymerization of the monomer mixture in water with azobisisobutyronitrile as the initiator. The percentage of acrolein was kept constant at 10%. The crosslink density was adjusted by changing the mol % of styrene and DVB.

Styrene–acrolein–DVB terpolymers of varying crosslink densities were first converted to the oximes and further to the oximinobenzoate and oximino dithiobenzoic anhydride resins by the methods already discussed^{16,18} (Schemes 3 and 4). Similar to the previous cases, here, also, the extent of functional group conversion was found to be dependent markedly on the degree of crosslinking. Functional group conversions were found to be maximum with 1% cross-

Table XIV Effect of Crosslink Density on Functionalization Reactions and on the Extent of Acyl Transfer Using the Polyacrolein–TEGDA System

Functional Groups	Extent of Functionalization				
	1%	2%	4%	10%	20%
Percentage of nitrogen in polyacrolein oxime	5.60	5.85	5.95	5.80	4.50
OH capacity (meq/g) of polyacrolein oxime	2.69	2.90	3.10	2.82	2.02
Benzoyl group capacity (meq/g)	2.32 ^a	2.55 ^a	2.85 ^a	2.30 ^a	1.60 ^a
	2.30 ^b	2.43 ^b	2.80 ^b	2.30 ^b	1.55 ^b
Percentage yield in acyl transfer reaction ^c	76 ^a	80 ^a	86 ^a	75 ^a	62 ^a
	75 ^b	78 ^b	85 ^b	75 ^b	60 ^b

^a Using polyacrolein oximinobenzoate resin.^b Using polyacrolein oximino dithiobenzoic anhydride resin.^c Substrate-to-resin ratio, 1 : 2; solvent, chloroform; time, 3 h; temperature, 30°C; substrate, aniline.

linked resins. Then, they gradually decreased as the crosslink density was increased. These changes are manifest in the percentage of nitrogen and OH capacities of polyacrolein–DVB supported oximes and the values are given in Table XIII.

The benzoyl group capacity and extent of acyl group transfer using polyacrolein oximinobenzoate and oximino dithiobenzoic anhydride resins with varying crosslink densities are given in Table XIII. For the estimation of the benzoyl group capacity, acylation of a standard solution of aniline was conducted using these resins and the unreacted aniline was estimated titrimetrically. Acylation of aniline was done using these resins with a 1 : 2 molar ratio in chloroform at room temperature. The amount of benzanilide formed was measured after a period of 3 h. Both the benzoyl group capacity and the percentage of acylation decreased with increase in crosslink density.

From the above observations, it could be seen that the degree of crosslinking of the polymer support is detrimental in deciding the net polarity of the polymeric reagent system. As the crosslink density increases, hydrophobicity attains prominence. The accessibility of reactive groups on highly crosslinked networks are considerably diminished due to the presence of an intermittent array of crosslinks which enclose the reactive groups.^{25,28,29}

Styrene–Acrolein–TEGDA Terpolymer System

Styrene–acrolein–TEGDA terpolymers were prepared by suspension polymerization of the monomer mixture in water with azobisisobutyronitrile as the initiator. The percentage of acrolein was kept constant at 10%. The crosslink density was adjusted by changing the mol % of styrene and TEGDA. Polymers with 1, 2, 4, 10 and 20 mol % of the crosslinking agent were prepared.

The differently crosslinked styrene–acrolein–TEGDA terpolymers were functionalized to incorporate the oximinobenzoate and oximino dithiobenzoic anhydride functionalities.^{16,18} In this case, also, as the crosslink density was increased, the functional group capacity gradually increased up to a crosslink density of 4% and then it decreased gradually. This variation is represented by the change in the percentage of nitrogen and OH capacity of polyacrolein–TEGDA oximes and the values are given in Table XIV. It may be seen that the change in the functional group capacity values was not so drastic as in the previous cases.

Both the benzoyl group capacity and the percentage yield in the acyl transfer reaction increased

with increase in crosslink density up to 4% crosslinking and then decreased gradually and reached a minimum value at 20% crosslinking (Table XIV). But compared to the DVB crosslinked system, the decrease in the reactivity of the functional groups was not as devastating. The presence of the flexible and hydrophilic crosslinker, TEGDA, in larger amounts makes the polymer capable of imbibing large amounts of the solvents, thereby keeping the gel network still expanded so that the functional groups are exposed to the continuous phase. The access of reactive groups on 20% crosslinked resins are considerably diminished as they are flanked by a large frequency of crosslinks, leading to a decreased reactivity.

From the foregoing observations, it was clear that the acyl transfer reagent obtained from TEGDA crosslinked polystyrene was found to be more efficient. Thus, the reactivity varied with varying polarity of the polymer support. The hydrophobic/hydrophilic nature of the polymer support can be varied at will by the incorporation of the crosslinking agents like DVB, TEGDA, etc. At a very high degree of crosslinking, the steric factors imposed by the polymer network adversely affected the reactivity considerably. This has been the case with both the DVB and TEGDA crosslinked systems.

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