

Polystyrene supported *t*-butyl chromates: Effect of the degree of crosslinking on reactivity

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Abstract. Polystyrene supported *t*-butyl chromate reagents were prepared using divinylbenzene as the crosslinking agent. The extent of crosslinking was varied from 2 to 20% (2, 5, 10, 15 and 20%). These polystyrene systems appeared to be amenable to structural variations for studying the effect of the nature and extent of crosslinking on the reactivity of the attached functional groups. Polystyrene supported *t*-butyl chromates, having varying crosslink densities, were used to oxidise alcohols to the carbonyl compounds. Reagents prepared from 2% crosslinked resins gave better results. A regular decrease in the extent of functionalization was noticed as the degree of crosslinking was increased and the capacity of the functional group was found to be minimum for 20% crosslinked resin.

Keywords. Polystyrene supported *t*-butylchromate; polymer analogous reaction.

1. Introduction

The chemical reactivity of a functional group immobilized on a polymer support is governed by the physical nature of the support, which in turn, depends on the extent of crosslinking. The mechanical stability of the matrix is found to be dependent on the density of crosslinking. Lightly crosslinked resins are swollen by good solvents to pseudo-gel and thus appear to be fragile towards mechanical agitation. Better physical stability can be achieved with increased crosslinking as the network then becomes more stiff. But the accessibility of reactive groups on highly crosslinked network is considerably diminished as they are flanked by a large frequency of crosslinks leading to a decreased reactivity¹⁻³. Linear polymers which can attain homogeneous macromolecular solutions can provide their functional groups free in the solution. But in the case of crosslinked polymers, due to their insolubility, the accessibility of the functional groups are diffusion-controlled and penetrant transport causes some sort of molecular relaxation making the functional groups buried deep into the polymer matrix⁴⁻⁶. Since the characteristic diffusion time depends on the size of the polymer sample, a relaxation-diffusion coupling is observed at penetrant transport⁷⁻⁹.

The topographical nature of the polymer matrix exerts a significant influence on the reactivity of the attached functional groups. Lloyd and Alfrey investigated the role of the topology of the gel network on chemical reactivity¹⁰⁻¹³.

The topography of the polymer matrix is determined by the nature of the monomers; the molar percentage of the crosslinks and the monomer dilution ratio. A knowledge of

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the dependence of the topographical nature of the polymer backbone on the reactivity of the attached functional group is required for the development of efficient polymer supported reagents^{14,15}. This paper describes the development of differently crosslinked polystyrenes as supports for the preparation of *t*-butyl chromate reagents. The term 'crosslink density' is used in the paper to mean molar percentage of the cross-linking agent used during polymerization.

2. Experimental

2.1 General

The monomers, styrene and divinyl benzene were purified by low-pressure distillation. Styrene-divinyl benzene copolymer supports were prepared by suspension polymerization. Solvents were of reagent grade and were distilled and purified by standard procedures. Microanalyses were performed at the Regional Sophistication Instrumentation Centre, Indian Institute of Technology, Madras. IR Spectra were recorded on a Perkin-Elmer 397 spectrometer using KBr pellets. Melting points were determined on a hot stage melting point apparatus and are uncorrected. Thin layer chromatography was performed on precoated silica gel plates. The quantitative analysis of the resin capacities was performed according to literature procedures¹⁶.

2.2 Preparation of *t*-butyl chromate reagents without a methylene spacer and with different crosslink densities

Polystyrene resin (2–20% crosslinked) (10 g) was treated with acetyl chloride (20 g) and anhydrous aluminium chloride in carbon tetrachloride (30 ml) and the mixture was refluxed for 5 h and kept overnight at room temperature. The reaction mixture was poured in aqueous ethanol to break the Lewis acid complex. The resin particles were collected and washed with water, ethanol, carbon tetrachloride and methanol and dried in vacuum.

The keto resin (9 g) was then treated with methyl magnesium iodide freshly prepared from methyl iodide (6 ml) and magnesium turnings (2.5 g) and a crystal of iodine in dry ether (75 ml). The reaction mixture was heated in a waterbath for 3 h. The resin was filtered, washed with alcohol, dil H₂SO₄, THF-water, THF and methanol and dried in vacuum.

The *t* alcohol resin (10 g) was treated with 2 M solution of chromium trioxide in acetonitrile-water medium to get the polystyrene supported *t*-butyl chromate resin, which was washed well with benzene, carbon tetrachloride, methanol, acetone and dried in vacuum.

2.3 Preparation of *t*-butyl chromate reagents with one methylene spacer and different crosslink densities

The procedure described earlier was followed with styrene-DVB copolymers of crosslink density 2%, 5%, 10%, 15% and 20% with bromoacetone in the Friedel-Crafts reaction step instead of acetyl chloride. All other steps were similar.

2.4 Preparation of *t*-butyl chromate reagents with two, three, four and five methylene spacer groups and different crosslink densities

The copolymer beads (2 to 20% crosslinked) were thoroughly washed with chloroform (20 ml × 3 times) and methylene chloride (20 ml × 3 times) and dried in vacuum. To a suspension of the resin (10 g), pre-swollen (12 h) in carbon disulphide, a previously prepared solution of the aliphatic acid anhydride/acid chloride (14 g) and aluminium

chloride (20 g) was added with stirring during a period of 30 min. The reaction mixture was refluxed for 6 h. After cooling, water (100 ml) was added and the resin particles were collected on a sintered glass filter, washed successively with water, methanol, chloroform and acetone (10 ml \times 3 times each) and dried in vacuum.

The polymeric ketonic acid resin obtained was suspended in toluene (20 ml) for 12 h and added to amalgamated zinc, followed by toluene (50 ml), water (50 ml) and conc. HCl (75 ml). The mixture was heated under reflux for 30 h. The resin was cooled, filtered at the pump, washed with water, methanol, chloroform and acetone (20 ml \times 3 times each) and dried in vacuum.

Polymeric carboxylic acid resin thus obtained was suspended in toluene (20 ml) for 12 h. Dimethyl formamide (1 ml) and thionyl chloride (40 ml) were added and refluxed on a waterbath for 6h until the evolution of HCl ceased. The reaction mixture was cooled and filtered at the pump, washed with toluene, chloroform, benzene and acetone (20 ml \times 3 times) and dried in vacuum.

Polymeric carboxylic acid chloride resin (7 g) pre-swollen (12 h) in THF (20 ml) was added slowly with stirring to ethoxymagnesium diethylmalonate (freshly prepared). The mixture was heated under reflux for 5 h. The mixture was cooled, and shaken with dilute sulphuric acid (25 g conc. H_2SO_4 in 200 ml water). The acyl malonate resin was collected on a sintered glass filter, washed with water, methanol, chloroform and acetone, dried and weighed.

The polymeric acyl malonate resin was then suspended in THF (20 ml) for 12 h. It was treated with a solution of glacial acetic acid (60 ml), conc. H_2SO_4 (7.6 ml), water (40 ml) and THF (50 ml). The reaction mixture was refluxed for 4 h until the evolution of carbon dioxide ceased. After cooling, the resin was filtered at the pump, washed with water, sodium bicarbonate solution, water, ethanol and acetone (20 ml \times 3 times each), dried in vacuum and weighed. The keto resin so obtained was subjected to Grignard reaction to get the *t*-butyl alcohol resin, which was then converted to *t*-butyl chromate resin as described earlier.

2.5 Effect of degree of crosslinking on the oxidation of benzoin

Benzoin (100 mg, 0.47 mmol) was dissolved in 10 ml CHCl_3 . The polymeric *t*-butyl chromate reagent (0.95 m mol) was added to benzoin solution and stirred. After definite time intervals, 0.5 ml of the reaction mixture was withdrawn using a micropipette, transferred to a small flask and the solvent evaporated. The residue was dissolved in 5 ml of CHCl_3 and the optical density was measured on a spectrophotometer at 390 nm. From the optical density, the percentage of benzil formed was calculated using a calibration curve. The experiment was repeated using each type of resin.

3. Results and discussion

Polystyrene supported *t*-butylchromate reagent was prepared from divinyl benzene crosslinked polystyrene resin by a series of polymer analogous reactions.

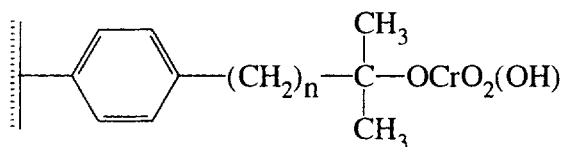
3.1 Preparation of differently crosslinked polystyrene resins

The copolymers were prepared by suspension polymerization of the monomer mixture in water at 80°C with benzoyl peroxide as the initiator. Commercial sample of divinyl benzene containing 55% of *p*-DVB was used for the polymerization. The crosslink density (2, 5, 10, 15 and 20%) was adjusted by changing the mole percentage of the divinyl monomer.

Lightly crosslinked polymers were obtained in a well defined bead form. They are swellable in benzene, carbon tetrachloride, toluene, chloroform, dichloromethane etc. Polymer samples with higher extent of the crosslinking agent were found to be more rigid and were obtained in the powder form.

3.2 Preparation of *t*-butyl chromate resins with varying degrees of crosslinking

Divinyl benzene crosslinked polystyrene resins with the degree of crosslinking varying from 2–20 mole % was suitably functionalised to generate the *t*-butyl chromate reagent function having five, four, three, two, one and zero methylene spacer units (structures A to F). The functionalization reaction was performed according to previously reported procedures^{16,17}. The functional group capacities of the various resins were determined by usual chemical methods which were suitably modified to adapt to heterogeneous conditions¹⁶. The extent of functionalization was found to be highly dependent on the degree of crosslinking. This has been the case in the initial introduction of keto groups by Friedel-Crafts reaction and all other subsequent functional group conversions. In these cases the functional group capacity was found to be maximum with the 2% crosslinked resin. It gradually decreased as the degree of crosslinking was increased to 5, 10, 15 and 20%. As the number of spacer methylene groups increased from zero to five, the effect of increasing crosslink density in reducing the extent of functional group conversion, diminished gradually. Even with the *t*-butyl chromate reagent containing a five methylene spacer arm, the capacity of the reagent function was negligible for the 20% crosslinked resin. The variation in functional group capacity as a function of the increasing degree of crosslinking and number of spacer methylene groups is represented in tables 1–6.



$$n = 0, 1, 2, 3, 4 \text{ \& } 5$$

Structure (A–F)

Table 1. Preparation of *t*-butyl chromate reagent without a methylene spacer: Effect of degree of crosslinking

Crosslink density (mole %)	Functional group capacity (meq/g)		
	Acetyl resin ^a	<i>t</i> -butyl alcohol resin ^b	<i>t</i> -butyl chromate resin ^c
2	3.20	2.90	2.00
5	2.98	2.21	1.78
10	2.12	1.98	1.26
15	1.48	1.21	1.08
20	1.24	0.97	0.84

^aCapacity determined by iodoform reaction

^bCapacity determined by gravimetric method

^cCapacity determined by iodometric method

Table 2. Preparation of *t*-butyl chromate with one methylene spacer: Effect of degree of crosslinking

Crosslink density (mole %)	Functional group capacity (meq/g)		
	2-oxopropyl resin ^a	<i>t</i> -butyl alcohol resin ^b	<i>t</i> -butyl chromate resin ^c
2	4.50	3.71	2.50
5	3.70	3.01	2.33
10	2.92	1.98	1.45
15	2.70	1.53	1.21
20	1.11	1.12	0.91

^aCapacity determined by iodoform reaction^bCapacity determined by gravimetric method^cCapacity determined by iodometric method**Table 3.** Preparation of *t*-butyl chromate reagent with two methylene spacer groups: Effect of degree of crosslinking

Crosslink density (mole %)	Functional group capacity (meq/g)						
	β -keto ethanoic acid resin ^a	Propionic acid resin ^a	Propionyl chloride resin ^b	Propionyl malonate resin ^c	2-oxo butyryl resin ^c	<i>t</i> -alcohol resin ^c	<i>t</i> -butyl chromate resin ^d
2	4.90	4.40	4.00	4.10	3.90	3.30	3.00
5	4.08	3.98	3.72	3.28	3.01	2.90	2.60
10	3.78	3.24	2.56	2.21	2.70	2.40	2.20
15	2.79	2.28	1.98	1.78	1.36	1.28	1.60
20	2.01	1.92	1.72	1.01	1.21	1.31	1.10

^aCapacity determined by volumetric method^bCapacity determined by Volhards method^cCapacity determined by gravimetric method^dCapacity determined by iodometric method**Table 4.** Preparation of *t*-butyl chromate reagent with three methylene spacer groups: Effect of degree of crosslinking

Crosslink density (mole %)	Functional group capacity (meq/g)						
	γ -keto propionic acid resin ^a	Butyric acid resin ^a	Butyryl chloride resin ^b	Butyryl malonate resin ^c	2-oxo pentyl resin ^c	<i>t</i> -alcohol resin ^c	<i>t</i> -butyl chromate resin ^d
2	5.2	5.1	4.9	4.8	4.0	4.1	3.2
5	5.0	4.1	3.9	3.7	3.4	3.3	2.8
10	4.5	3.9	3.5	3.7	3.6	3.2	2.5
15	3.8	3.7	3.4	3.2	2.9	2.5	1.9
20	2.4	2.3	1.9	2.0	1.9	1.9	1.2

^aCapacity determined by volumetric method^bCapacity determined by Volhards method^cCapacity determined by gravimetric method^dCapacity determined by iodometric method

Table 5. Preparation of *t*-butyl chromate reagent with four methylene spacer groups: Effect of degree of crosslinking

Crosslink density (mole %)	Functional group capacity (meq/g)						
	δ -keto butyric acid resin ^a	Pentanoic acid resin ^a	Pentanoyl chloride resin ^b	Pentanoyl malonate resin ^b	2-oxo hexyl resin ^c	<i>t</i> -alcohol resin ^c	<i>t</i> -butyl chromate resin ^d
2	5.3	5.2	5.2	5.1	4.2	4.1	3.4
5	4.8	4.8	4.3	4.1	3.7	3.6	3.2
10	4.5	4.1	3.8	3.4	3.5	3.1	2.9
15	3.1	3.0	3.2	3.0	2.9	2.8	2.6
20	2.5	2.4	2.1	2.0	2.6	1.6	1.3

^aCapacity determined by volumetric method^bCapacity determined by Volhards method^cCapacity determined by gravimetric method^dCapacity determined by iodometric method**Table 6.** Preparation of *t*-butyl chromate reagent with five methylene spacer groups: Effect of degree of crosslinking

Crosslink density (mole %)	Functional group capacity (meq/g)						
	ω -keto pentanoic acid resin ^a	Hexanoic acid resin ^a	Hexanoyl chloride resin ^b	Hexanoyl malonate resin ^c	2-oxo heptyl resin ^c	<i>t</i> -alcohol resin ^c	<i>t</i> -butyl chromate resin ^d
2	5.8	5.6	5.5	5.0	4.5	4.9	3.6
5	4.9	4.8	4.6	4.0	3.9	3.7	3.3
10	4.6	4.4	4.0	3.9	2.5	3.2	3.0
15	3.7	3.2	3.0	2.9	2.9	2.8	2.7
20	2.7	2.5	2.3	2.3	1.8	1.6	1.3

^aCapacity determined by volumetric method^bCapacity determined by Volhards method^cCapacity determined by gravimetric method^dCapacity determined by iodometric method

3.3 Effect of crosslink density on the efficiency of oxidation reactions using *t*-butyl chromate reagents

Polystyrene supported *t*-butyl chromates having varying crosslink densities were used for the oxidation of alcohols to carbonyl compounds. It was observed that the reagents prepared from 2% crosslinked polystyrenes were most efficient in terms of reaction period and product yield. Oxidation of benzoin to benzil was taken as the model reaction for studying these effects. The amount of benzil formed after a fixed time interval was measured spectrophotometrically at 390 nm. The results are presented in table 7.

The measurements were done after 30 h. Within this reaction period, the reagents prepared from 20% crosslinked polystyrene gave only less than 30% conversion. In the case of *t*-butyl chromates prepared from 2% crosslinked polystyrene, within the time interval of 30 h, almost 80 and 90% conversion occurred with reagents having four and

Table 7. Effect of degree of crosslinking on the extent of oxidation of benzoin

Crosslink density (mole %)	Percentage of benzil formed ^a					
	<i>n</i> = 0	<i>n</i> = 1	<i>n</i> = 2	<i>n</i> = 3	<i>n</i> = 4	<i>n</i> = 5
2	44	58	70	74	80	90
5	40	55	64	72	78	80
10	34	52	58	62	69	72
15	26	48	53	59	65	68
20	20	22	24	26	28	30

n = Number of methylene spacer groups

^aMeasurements were made after 30 h; alcohol to resin ratio 1:2 (based on chromate capacity) Solvent used, chloroform; temperature, 30°C

five methylene spacer groups. In the case of reagents with one methylene spacer, 58% conversion was observed during this reaction period. With 5%-crosslinked resin, relatively higher extents of conversion were obtained for reagents having four and five methylene spacer groups. Reagents prepared from 2% crosslinked resins gave extremely good results.

It can be assumed that the reactivity of the *t*-butyl chromate function attached to the polymer network is highly dependent on the variables of gel preparation. It might be expected that groups adjacent to crosslinks might be less accessible to reagents in the continuous phase. This leads to non-equivalence of the reactive groups attached to the polymer network.

In crosslinked polystyrenes, prepared by suspension polymerization of styrene and divinyl benzene, in the initial stages of the polymerization reaction, the crosslinks begin to be formed by an intramolecular process, followed by an eventual intermolecular process, leading to microgelation of the whole droplet and the monomer molecules are incorporated in the initially formed macrogel network^{16,18-20}. This leads to higher crosslink density in regions centered on the original points of initiation, i.e. in the microgels. Thus, each polymer bead will consist of two regions, one having higher crosslink ratio and the other which is lightly crosslinked. Thus, a considerable extent of heterogeneity occurs. At higher concentrations of the divinyl monomer, this heterogeneity occurring from the intramolecular crosslinking, increases. When gel-type resins are prepared with high percentage of divinyl benzene, some extent of permanent chain entanglement occurs in addition to crosslinking and the extent of swelling in good solvents is thereby, considerably reduced. This decreases the availability of the free phenyl units for functionalization.

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