Poly(*N*-bromoacrylamide): A New Polymeric Recyclable Oxidizing and Brominating Reagent

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ABSTRACT: Poly(*N*-bromoacrylamide) was conveniently prepared from commercially available polyacrylamide and was developed as a new insoluble polymeric oxidizing and brominating reagent for organic substrates. The polymer was characterized by elemental analysis and IR spectra. The reagent, which was prepared by the reaction of potassium hypobromite with polyacrylamide, has a capacity of 5.2–5.7 mmol of bromine per gram. Alcohols were oxidized to the corresponding carbonyl compounds in near quantitative yields at room temperature with this reagent. The reagent was also used to brominate unsaturated and aromatic substrates in high yields. Gel permeation chromatography analysis of the polymer before and after the reaction did not show any peak due to low molecular weight fractions, indicating the absence of any side reactions that degrade the polymer. The reagent can be stored for months without any loss of activity, can be handled easily, and can be recycled for further use. The capacity and reaction efficiency of the polymeric reagent was found to be practically unchanged even after seven cycles of operation. The reactions can also be carried out on a column, suggesting the possibility of automation.

Introduction

The preparation and investigation of chemically active species bound to polymeric supports continue to be an active interdisciplinary field of research with applications in organic chemistry, inorganic chemistry, chemical technology, biochemistry, and biology.[1-9] Polymeric reagents are reactive species bound to a polymeric backbone. They possess physical properties of the high polymer and the chemical properties of the attached reagent function. The most significant advantages of these reagents over their soluble counterparts are their ease of separation from the reaction mixture and their regenerability. In addition, the polymer matrix can provide a specific microenvironment that might induce selectivity in the chemical reaction due to steric effects arising from the macromolecular structure, cross-link density and pore size in the case of the cross-linked polymers, or a dilute distribution of reactive functions on the polymer chain.[10]

A number of polymer-supported reagents have been reported for the oxidation[11-13] and bromination[14,15] reactions of organic substrates. These reagents are mainly based on cross-linked polystyrene or poly(vinylpyridines). *N*-Halogenated amides and imides are well-known for their oxidizing and halogenating ability.[16] Here we report on our studies of the incorporation of the *N*-halogeno function in polar polyacrylamide chains and the preparative conversions of organic substrates using these reactive *N*-halogenopolyacrylamides. The incorporation of the *N*-chlorosuccinimide and *N*-bromosuccinimide functions into polymeric systems has been reported earlier. Okawara, as early as in 1957 and 1969, reported the synthesis of linear and cross-linked polyimides and their subsequent *N*-bromination.[17,18] These *N*-bromoimides were of low capacity, and they were much less reactive than *N*-bromosuccinimide and could not find much use in a preparative level. Yaroslavsky et al. have used this type of polymer for brominating styrene derivatives.[19] *N*-Chloronylons have been introduced as oxidizing agents for a number of different types of substrates by Schulz and co-workers.[20] The poly(*N*-bromoacrylamide) we report here differs from these systems basically in the sense that they are primary *N*-bromoamides attached as pendant groups on the polymer chain and also in the relatively much higher capacity and the comparatively shorter duration of reaction necessary for the substrate conversions.

Results and Discussion

Commercially available polyacrylamide was brominated in carbon tetrachloride with aqueous potassium hypobromite at 0 °C to give the insoluble poly(*N*-bromoacrylamide). The product polymer can be washed free of the unbound bromine and alkali, washed with methanol, and dried to obtain an orange powder. It undergoes extensive swelling in alcoholic and aqueous solvents due to the polar hydrophilic nature of the pendant *N*-bromoamide grouping. However, the solubility in organic solvents and the swellability of the product *N*-bromo resin were observed to be much less compared with the starting polyacrylamide.

The bromine content of the product polymer was determined by iodometric titration and elemental analysis. The capacity was found to be in the range 5.2–5.7 mmol of bromine per gram of the polymer. The sample was found to have 10.25% of elemental nitrogen for the specimen with a capacity of 5.25 mequiv of Br/g. The estimated percentage of nitrogen in the starting polyacrylamide was 18.67%, in contrast to the theoretical value of 19.71%. The capacity of 5.25 mequiv/g corresponds to 78.7% conversion. The difference in the estimated and theoretical value is due to the 2.8% of residual matter present in the starting polyacrylamide. When the estimated value of 18.67% for the polyacrylamide and 78.7% conversion in the case of the brominated product were taken into account, the theoretically expected value for the product would be 10.5%; this value is in agreement with the experimental value of 10.25%, where the 2.3% residue in the product is also accounted for. The observed C and H values of 34.4% and 5.98% are also accountable for by considering the 2.3% noncombustible residue and the percentage conversion. The IR spectrum of the polymer showed absorptions at 3200–3500 (weak), 2940, 2870, 1690 (C=O), 1455, 1375, 1200, and 765 cm^{-1}. On comparison with the IR spectrum of the starting polyacrylamide, the intensity of the broad band in the region 3200–3500 cm^{-1} in the case of the product poly(*N*-bromoacrylamide) decreased considerably. The solubility of the sample in deuteriated solvents was too low for running the NMR spectra. The sample did not contain any amino group that could be formed by the possible Hoffmann-type degra-

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Table I
Oxidation of Alcohols Using Poly(*N*-bromoacrylamide) in Chloroform at Room Temperature

alcohol	mmol of alcohol	mmol of reagent	time, h	product[a]	yield,[b] %
benzoin	0.47	2.21	5	benzil	99
benzhydrol	0.54	1.69	4	benzophenone	98
benzyl alcohol	4.83	11.2	28	benzaldehyde	99
3-nitrobenzyl alcohol	0.84	4.2	7	3-nitrobenzaldehyde	90
1-phenylethanol	4.14	12.4	7.5	acetophenone	90
cyclohexanol	2.85	11.2	10	cyclohexanone	96
menthol	0.63	3.2	5	menthone	97
2-adamantanol	0.65	3.25	5.5	2-adamantanone	95
1-acenaphthenol	0.58	3.0	10.5	1-acenaphthenone	90
borneol	0.64	2.6	7	camphor	87

[a] Characterized by comparison (mp, bp, or IR) with authentic samples. [b] Isolated products.

Table II
Effect of Temperature, Solvent, and Molar Excess of the Reagent on the Extent of Conversion of Benzoin

entry no.	molar excess of reagent	temp, °C	solvt	catalyst	time for complete conversion,[a] h
1	molar equiv	27	chloroform	2 mL of 10% H_2SO_4	[b]
2	2	27	chloroform	2 mL of 10% H_2SO_4	16
3	3	27	chloroform	2 mL of 10% H_2SO_4	12
4	4	27	chloroform	2 mL of 10% H_2SO_4	9
5	5	27	chloroform	2 mL of 10% H_2SO_4	5
6	5	27	chloroform	2 mL of water	5.5
7	5	27	chloroform	none	no reaction
8	5	reflux	chloroform	2 mL of 10% H_2SO_4	0.5
9	5	reflux	chloroform	2 mL of water	0.75
10	5	27	benzene	2 mL of 10% H_2SO_4	6.5
11	5	27	[c]	2 mL of 10% H_2SO_4	4

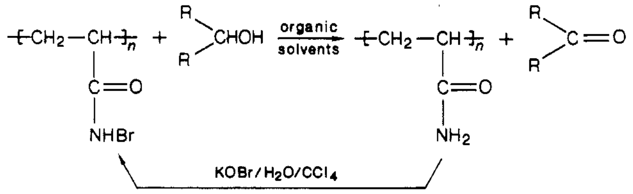
[a] As determined by TLC. [b] 50% conversion after 12 h. [c] The reagent was suspended in chloroform for 3 days prior to reaction.

dation of amides on treatment with sodium hypobromite. This was confirmed by carrying out the sensitive ninhydrin color reaction, which detects amino groups to a level of 0.1 μmol.

Poly(*N*-bromoacrylamide) was found to easily oxidize primary alcohols and secondary alcohols under very mild conditions at room temperature in 96–100% isolable yields (Table I). The oxidation reactions of different substrates were investigated under varying sets of reaction conditions such as temperature, solvent, molar excess of the polymeric oxidizing agent, and differing reaction periods. From these experiments it was evident that traces of water and an excess of the polymeric reagent have a pronounced effect in bringing down the period required for the completion of the oxidation reaction. The presence of small amounts of dilute acid was also found to have a catalytic effect on the course of the oxidation reactions.

The oxidation reaction was also conducted with the low molecular weight *N*-bromoacetamide[21] under identical conditions of solvent and dilute acid. The reaction was completed after stirring the mixture for 12 h. But the separation of the excess reagent and the byproduct acetamide from the reaction mixture was difficult. The literature procedure for oxidation of secondary alcohols using *N*-bromoacetamide was by stirring molar equivalents of substrate, reagent, and pyridine in the presence of water.[22] The reported yield was 74%. The most rapid conversion occurred when a five-fold molar excess of the reagent was used in chloroform solvent at 40–50 °C in presence of 2 mL of 10% sulfuric acid. The reaction was complete in 30 min under these conditions in the case of benzoin (Table II). In general, a more polar solvent like $CHCl_3$ facilitated the oxidation reaction more than a nonpolar solvent like benzene. This is attributable to the polar nature of the poly(*N*-bromoacrylamide). The pronounced effect of the temperature is evident in the oxidation of benzoin in chloroform at room temperature and at refluxing temperature. In the former case it required 4 h, whereas in the latter the reaction was complete in 0.5 h. More penetration of the solvent and extensive swelling are possible under these conditions, and this would enhance the diffusion of the soluble substrate into the polymeric reagent matrices and thereby facilitate the reaction. The availability of the reagent function was tested by carrying out the oxidation of the alcohol with a limited amount of the reagent. The residual capacity of the recovered resin from the experiment with the reagent of capacity 5.5 mmol/g was only 0.07 mmol/g, corresponding to almost complete (≃99%) consumption of the reagent functions. This points to the ready availability of all the reagent functions in the polymeric reagent under the experimental conditions.

Scheme I
Oxidation of Alcohols Using Poly(*N*-bromoacrylamide) and the Recycling Process



After the oxidation is affected in the organic solvent (see Scheme I), the polymeric byproduct, which remains insoluble in the solvent, can be separated by filtration. The product remains in the solution and can be isolated by removal of the solvent. The spent resin after washing with organic solvents can be converted back to the starting poly(*N*-bromoacrylamide) by reaction with potassium hypobromite. This can be used for further oxidation reactions.

Poly(*N*-bromoacrylamide) reacted with olefinic compounds to give the corresponding dibromo derivatives in

Table III
Bromination Reactions Using Poly(*N*-bromoacrylamide) in Chloroform at Room Temperature

substrate	mmol of substrate	mmol of reagent	product[a]	time, h	yield,[b] %
trans-stilbene	0.55	4.1	*trans*-α,α'-dibromostilbene	10	77
cinnamic acid	0.67	3.5	3-phenyl-2,3-dibromopropanoic acid	7	73
styrene	1.74	5.2	styrene dibromide	7.5	75
phenol	1.06	5.6	2,4,6-tribromophenol	12	60
resorcinol	0.22	2.6	2,4,6-tribromoresorcinol	5	90
toluene	4.7	11.2	benzyl bromide	24	75

[a] Characterized by comparison (mp, bp, or IR) with authentic specimens. [b] Isolated products.

Table IV
Effect of Recycling on Reactivity of Poly(*N*-bromoacrylamide)[a]

no. of regeneration cycles	% conversion of benzoin[b] after		
	15 min	30 min	60 min
1	49.5	93	100
2	35	70	100
3	33.5	64	100
4	32	61	95

[a] All reactions were carried out by using 5 times the molar excess of the reagent and 0.47 mmol of benzoin in chloroform (10 mL) at 60 °C in the presence of 2 mL of 10% H_2SO_4. [b] Spectrophotometric determination of benzil at 390 nm.

72–76% yield (Table III). Phenol on reaction with this polymeric brominating reagent afforded 2,4,6-tribromophenol in 60% yield. Toluene afforded benzyl bromide under these conditions. GPC analysis of the poly(*N*-bromoacrylamide) before and after the oxidation or bromination reactions did not show any peak due to low molecular weight fractions, indicating the absence of any side reactions that degrade the polymer. The molecular weight and polydispersity data could not be obtained from the GPC measurements under the experimental conditions in hand because the molecular weight of the polymer exceeded the limit of the column (μBondagel E linear).

The details of the regenerability of this polymeric reagent after the oxidation/bromination reactions are presented in Table IV. It can be seen that even after cycles of reaction/regeneration operation the capacity and reaction efficiency of the reagent remain practically unchanged. Thus, there is no significant difference between the yield of oxidation reactions of benzoin with a fresh sample of the polymeric reagent and the yield when the poly(*N*-bromoacrylamide) after recycling/regeneration was used (Table IV).

The polymeric brominating reagent poly(*N*-bromoacrylamide), which can be obtained as an orange powder or in the granular form depending upon the experimental conditions, is stable under ordinary laboratory conditions. It can be stored indefinitely without appreciable loss of capacity. The hygroscopic nature of the parent acrylamide polymer is not there in the case of this poly(*N*-bromoacrylamide), presumably due to the reduced hydrogen bonding. The reagent is noncorrosive and easy to handle.

The oxidation and bromination reactions using this polymeric *N*-bromoacrylamide could also be effected in a column. The solution of the organic substrate was allowed to percolate through the column filled with the polymeric reagent. The eluate on removal of the solvent afforded the pure oxidized or brominated product.

Preliminary studies indicated that the reagent could effect the oxidation of thiols to sulfides and α-bromination of ketones. Studies are under way to establish different parameters such as the effect of cross-linking, capacity, the nature of the solvent, etc., which could influence the course of this polymeric heterogeneous oxidation reaction.

Experimental Section

Preparation of Poly(*N*-bromoacrylamide). Polyacrylamide (BDH, $\bar{M}_v$ = 5 000 000, 5 g) was suspended in 75 mL of carbon tetrachloride containing 4.5 mL of bromine in a 250-mL round-bottom flask. Potassium hydroxide solution (25%, 25 mL) was slowly added to the suspension with stirring and cooling in ice. Stirring was continued for a period of 10 h. The insoluble product polymer was filtered, washed with water (4 × 10 mL) and methanol (2 × 10 mL), and dried in an air oven at 60 °C to afford 5.5 g of poly(*N*-bromoacrylamide) as orange granules.[23] GPC analysis of the polymer did not show any peak due to low molecular weight fractions.[24] Microanalysis: C, 34.36%; H, 5.98%; N, 10.25%; residue, 2.3%.[25]

Determination of the Capacity of the Poly(*N*-bromoacrylamide) by Iodometric Titration. Approximately 100 mg of powdered poly(*N*-bromoacrylamide) was accurately weighed and suspended in 20 mL of water for 4 h. Potassium iodide solution (10%, 10 mL) and 10% sulfuric acid (10 mL) were added to the suspension, and the liberated iodine was titrated against standard thiosulfate solution with starch as the indicator. From the titer value the amount of available bromine per gram of the polymer sample was calculated. The capacity of the samples from different lots varied in the range 5.2–5.7 mmol of bromine per gram of the reagent.

Oxidation and Bromination Reactions Using Poly(*N*-bromoacrylamide). General Procedure. The organic substrate (100 mg) was dissolved in 10 mL of chloroform containing 2 mL of 10% sulfuric acid. A molar excess of the poly(*N*-bromoacrylamide) was added, and the reaction mixture was shaken for the indicated period (Tables I–III). The reactions were followed by thin-layer chromatography. After complete conversion, the insoluble spent resin was filtered, washed with a little water to remove the traces of acid, and then washed with the solvent. The filtrate was extracted with a little more of the solvent, and the solvent was removed from the extract to afford the oxidized or brominated organic compound. The details of the different oxidation reactions are presented in Tables I–III.

Recycling of the Spent Polymeric Reagent. The spent polymer obtained from the different oxidation and bromination reactions was combined and washed thoroughly with chloroform to remove any residual soluble organic substrate or product. The washed polymer was dried and suspended in carbon tetrachloride. The suspension was treated with bromine and potassium hydroxide solution as described in the original preparation of poly(*N*-bromoacrylamide).

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Registry No. Benzoin, 119-53-9; benzhydrol, 91-01-0; benzyl alcohol, 100-51-6; 3-nitrobenzyl alcohol, 619-25-0; 1-phenylethanol, 98-85-1; cyclohexanol, 108-93-0; menthol, 1490-04-6; 2-adamantanol, 700-57-2; 1-acenaphthenol, 6306-07-6; borneol, 507-70-0; benzil, 134-81-6; benzophenone, 119-61-9; benzaldehyde, 100-52-7; 3-nitrobenzaldehyde, 99-61-6; acetophenone, 98-86-2; cyclohexanone, 108-94-1; menthone, 89-80-5; 2-adamantanone, 700-58-3; 1-acenaphthenone, 2235-15-6; camphor, 76-22-2; *trans*-stilbene, 103-30-0; cinnamic acid, 621-82-9; styrene, 100-42-5; phenol, 108-95-2; resorcinol, 108-46-3; toluene, 108-88-3; *trans*-α,α'-dibromostilbene, 20432-10-4; 3-phenyl-2,3-dibromopropanoic acid, 6286-30-2; styrene dibromide, 6607-46-1; 2,4,6-tribromophenol, 118-79-6; 2,4,6-tribromoresorcinol, 2437-49-2; benzyl bromide, 100-39-0.

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(23) This yield is much less than the theoretically expected value. This is due to the dissolution of the polymer in water. Moreover, it was also observed that the polyacrylamide sample used contained about 18% water (by thermogravimetric analysis). The hygroscopic nature of the polyacrylamide does not permit complete removal of the water under the present conditions.
(24) GPC analyses were performed with DMSO as the mobile phase on a Waters GPC instrument with a μBondagel E linear column, R401 RI detector, and U6K injector.
(25) Microanalyses were done at Regional Sophisticated Instrumentation Centre, Lucknow.

Notes

Comparison of Diffusion Coefficients in Ternary Polymer Solutions Measured by Dynamic Light Scattering and Forced Rayleigh Scattering

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Several dynamic light scattering (DLS) studies of ternary solutions (polymer A/polymer B/solvent) have recently been reported.[1-14] By selecting a solvent isorefractive with polymer B and employing sufficiently small concentrations of (chemically distinct) polymer A, the resulting autocorrelation functions are reasonably interpreted as reflecting the dynamics of the A chains. Furthermore, the measurements have generally been restricted to the range $qR < 1$, and thus the measured diffusion coefficients have (with one exception[2]) been identified with the translational diffusion of A. This technique has been demonstrated as an effective means to investigate two areas of great current interest: diffusion mechanisms in semidilute and concentrated solutions and thermodynamics of multicomponent systems. Nevertheless, there are several reasons for caution in this identification of the measured diffusion coefficient as the tracer or pure center-of-mass translational diffusion of component A. These include (i) the concentration of A is necessarily nonvanishing in order to effect the measurements, (ii) the refractive index increment for component B in the solvent may not be exactly zero, (iii) the inevitable molecular weight polydispersity of the A chains has a substantial influence on the correlation function as the matrix concentration increases, even for nearly monodisperse samples,[7] and (iv) the DLS properties for semidilute binary solutions are as yet incompletely understood, as illustrated both by the variety in number of modes reported and in their differing assignment to dynamical processes.[15-20]

We have previously reported extensive DLS measurements on the system polystyrene (PS)/poly(vinyl methyl ether) (PVME)/*o*-fluorotoluene (oFT) and have interpreted the results consistently as reflecting the translational diffusion coefficients of the PS chains, for linear,[3,6,7,9] 3-arm star,[8] and 12-arm star[10] diffusants. Furthermore, in all cases the observed decay rate distribution was unimodal, although the breadth of the distribution was a strong function of matrix concentration. Hanley et al. have shown that in principle the distribution should be bimodal when either the matrix isorefractivity condition or the vanishing probe concentration condition is not met.[21] The failure to observe bimodality is strong but not conclusive evidence that both of these conditions are satisfied for this chemical system; for example, the two modes might overlap to an extent that prohibits their resolution, while contaminating the extracted mean decay rates. In this work we report further measurements of PS diffusion in PVME solutions, by both DLS and forced Rayleigh scattering (FRS), as a function of matrix concentration. In addition, at fixed PVME concentrations the DLS measurements have been repeated as a function of PS concentration. Two important questions are thus addressed directly: (i) Is the diffusion coefficient measured by DLS identical with that obtained by FRS and thus correctly identified as the translational diffusion coefficient? (ii) Is it necessary to correct for the error arising from the finite PS concentrations employed in the DLS measurements?

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