Polyethylene-Supported *N*-Bromosuccinimide Polymeric Reagent for Use in Some Oxidation Reactions

Poonam K. Dhiman, R. K. Mahajan, Inderjeet Kaur

Department of Chemistry, Himachal Pradesh University, Shimla 5, India

ABSTRACT: We report a three-step preparation of a polymer-supported oxidizing reagent, polyethylene-*g*-*N*-bromosuccinimide (PE-*g*-NBS), through the graft copolymerization of maleic anhydride (MAn) onto polyethylene (PE) by a photochemical method with 1% benzophenone as a photosensitizer. The postgrafting treatment of polyethylene-*g*-maleic anhydride (PE-*g*-MAn) with urea on fusion gives polyethylene-*g*-succinimide (PE-*g*-succinimide), which, on further treatment with an aqueous solution of sodium hydroxide and bromine, gives the required reagent, PE-*g*-NBS. The maximum percentage grafting (25%) was obtained with 3.57 mol of MAn and 0.5 mL of 1% benzophenone in 120 min. Fourier transform infrared spectroscopy and thermogravimetric analysis methods were used to characterize the graft copolymer PE-*g*-MAn, PE-*g*-succinimide, and the polymeric support, that is, PE-*g*-NBS. The grafted PE and the polymeric support were found to be thermally stable. The polymer-supported *N*-bromosuccinimide was used successfully for the efficient oxidation of a series of alcohols, including 2-propanol, *n*-butanol, ethylene glycol, cyclohexanol, poly(vinyl alcohol), benzoin, benzyl alcohol, and chloromycetin, to their corresponding aldehydes and ketones. The selectivity of PE-*g*-NBS toward the oxidation of secondary alcoholic groups without the disturbance of the primary alcoholic groups was reflected during the oxidation of chloromycetin. The oxidized products were characterized by Fourier transform infrared and ^{1}H-NMR spectral methods. The reagent was reused for the oxidation of fresh alcohols, and it was found to oxidize them successfully, although with a little lower product yield. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 2584–2590, 2011

Key words: FT-IR; functionalization of polymers; graft copolymers; NMR; radical polymerization

INTRODUCTION

Polymeric reagents[1] have recently been developed for use in simple processes, such as epoxidation,[2] oxidation,[3] acylation,[4] halogenation,[5] and Wittig reactions.[6] In all of these applications, advantage is taken of the selectivity, insolubility, and reusable capacity of the polymeric reagent. The oxidation of alcohols to carbonyl compounds is a fundamental functional transformation in organic chemistry.[7] Numerous oxidizing agents are available to effect this transformation. However, most of these oxidizing agents are either toxic or very expensive. Therefore, from an environmental and economical point of view, polymer-supported (PS) oxidations are being carried out.

The electrocatalytic oxidation of 2,5-dimercapto-1,3,4-thiadiazole by polyaniline, (*N*,*N*-diphenyl-*p*-phenylenediamine) was carried out by Mihashi et al.[8] The PS peroxodisulfate oxidizer was prepared from a strong basic ion-exchange resin with potassium peroxodisulfate in water at room temperature; this could be used as a stable, mild, and efficient oxidizing agent to produce corresponding carbonyl compounds from hydroxyl compounds or oximes and disulfides from thiols under aprotic and nonaqueous conditions in organic solvents.[9] The clean oxidation reaction of a variety of substrates with PS (diacetoxyiodo)benezene, which proceeded in high to excellent yields with maximum purity, has been described and included the isolation and regeneration of the polymer reagent.[10] Cells of the fungus *Geotrichum candidum* were immobilized on a water-absorbing polymer and used for stereoselective oxidation and reduction in an organic solvent with cyclohexanone, cyclopentanol, or 2-alkanols as additives.[11] Alcohols were oxidized rapidly to their corresponding carbonyl compounds by montmorillonite KSF or silica-supported barium manganate under solvent-free conditions and microwave irradiation.[12] Kanna and Taylor[13] studied the direct conversion of primary alcohols into oximes using manganese dioxide and alkoxy amines/hydroxylamines as their hydrochloride salts or supported on Amerlyst 15. Hara et al.[14] studied the photocatalytic oxidation of water by silica-supported tris(4,4′-dialkyl-2,2′-bipyridyl)ruthenium polymeric sensitizers and colloidal iridium oxide. Divinyl benzene crosslinked polystyrene supported β-diketone linked complexes of Mn(II) have been prepared and characterized, and

Correspondence to: I. Kaur (ij_kaur@hotmail.com).

their role as catalysts in the oxidation of alcohols by Cr(VI) have been studied.[15] Poly(ethylene glycol)-supported 2,2,6,6-tetramethyl-1-piperidinyloxy has been prepared, and its catalytic activity in the chemoselective oxidation of alcohols with stoichiometric amounts of organic or inorganic oxidants has been investigated.[16] The preparation of a resin-bound cobalt phosphine complex and assessment of its use in catalytic oxidation and acid anhydride synthesis has been investgated.[17] Poly(ethylene glycol)-based aqueous biphasic systems have been investigated as tunable reaction media to control the oxidation of cyclohexene to adipic acid with hydrogen peroxide.[18]

In this article, we report the synthesis of polyethylene (PE)-supported *N*-bromosuccinimide (NBS) through the graft copolymerization of maleic anhydride (MAn) onto PE, which was successfully used for oxidation reactions. The support was found to be selective and could also be reused.

EXPERIMENTAL

Materials and methods

Commercial PE beads were dissolved in xylene and precipitated by the addition of methanol. The precipitates were filtered and dried in an oven at 50°C. A benzophenone solution (1%) in acetone was used as the photosensitizer for the grafting reaction. MAn (Burgoyne Urbidges and Co., Mumbai, India) was used as received. A UV lamp (125 W) was used as the source for the UV rays. Urea (Ranbaxy Laboratories, Ltd., Mumbai, India) and a Br_2 solution were used as received. CCl_4 (reagent grade) was used. Benzene and methanol in different proportions were used as the solvent for thin-layer chromatography (TLC).

Preparation of polyethylene-*g*-maleic anhydride (PE-*g*-MAn)

Dried PE (100 mg) was suspended in 10 mL of xylene in a beaker. A known amount of MAn in 5 mL of acetone and a definite amount of the sensitizer were added to the reaction mixture. The mixture was irradiated with the UV lamp for different time periods. To prevent a rise in temperature during the reaction, a constant flow of water was maintained outside the reaction vessel. After the stipulated time

period, the reaction was stopped, and excess methanol was added to the reaction mixture. The product was filtered through dried and weighed Whatmann filter paper and washed thoroughly with water to remove any unreacted MAn. The grafted PE was dried to a constant weight. The percentage grafting was calculated from the increase in the initial weight of the PE in the following manner:

$$\text{Percentage grafting} = \frac{W_1 - W_0}{W_0} \times 100$$

where W_0 and W_1 are the weights of the original PE and grafted PE, respectively, after the complete removal of the unreacted MAn. The percentage grafting was also measured from the IR spectra and was found to be with in the limits of that obtained by the thermogravimetric method.

The percentage grafting was determined as a function of monomer concentration, amount of photosensitizer, and reaction time; we thus evaluated the optimum conditions for obtaining the maximum grafting percentage.

Synthesis of the PE-based NBS reagent

A mixture of 0.500 g of PE-*g*-MAn (resin I) and 0.100 g (0.0016 mol) of urea was placed in a dry, round-bottom flask and was fused between 130 and 135°C for 0.5 h to give polyethylene-*g*-succinimide (PE-*g*-succinimide; resin II). The product was washed with water, dried, suspended in 30 mL of CCl_4, and heated at 40–50°C under continuous stirring for 2 h. Meanwhile, an aqueous solution of NaOH (2 g in 15 mL) was prepared, cooled in an ice bath, and added to the solution of resin II in CCl_4. To this was added a CCl_4–bromine solution (3 mL of Br_2 in 10 mL of CCl_4) in small portions from a dropping funnel under continuous stirring. The reaction mixture was stirred for the next 6 h. After the stipulated time of reaction, the product, polyethylene-*g*-*N*-bromosuccinimide (PE-*g*-NBS; resin III), was filtered and dried (Scheme 1).

Oxidation of alcohols

The following general procedure was followed for the oxidation reactions. The polymer support,
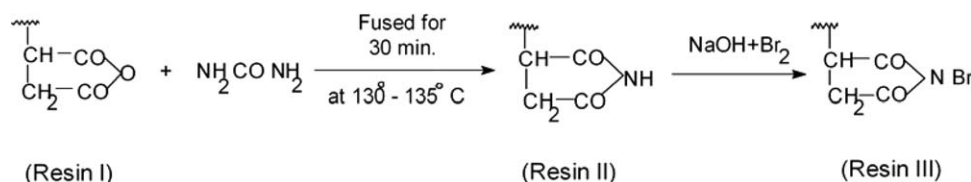
Scheme 1 Synthesis of PE-supported NBS.

TABLE I
Oxidation of Alcohols with PE-*g*-NBS as the PS Oxidizing Reagent

Reactant	Product	Time (h)	R_f Reactant	Product	Yield (%)
Isopropyl alcohol	Acetone	3.5	—	—	66.25
Cyclohexanol	Cyclohexanone	12	0.83	0.88	50
PVA	Hydroxyl ketone	3.5	—	—	—
Benzyl alcohol	Benzaldehyde	13	0.66	0.75	70
Benzoin	Benzil	12	0.68	0.86	35
Ethylene glycol	Glyoxal	6	—	—	73
Butanol	Butanal	8	0.21	0.42	67
Chloromycetin	Ketone	8	—	—	50

PE-*g*-NBS (0.150 g), was suspended in 20 mL of CCl_4 containing 1 mL of pyridine [except for poly(vinyl alcohol) (PVA) and *n*-butanol, for which warm water and benzene, respectively, were used]. To this was added a known amount of the alcohol, and the reaction mixture was heated under refluxing. The progress of the reaction was monitored with TLC. After the completion of the reaction, the resin was filtered off, and the product was extracted by fractional distillation. The solid products were separated on a silica column.

The time taken for oxidation, R_f values of the reactants (where R_f is the ratio of distance traveled by solute over distance traveled by solvent on TLC plates.) and the products, and the percentage yields of the products are presented in Table I.

Characterization

The characterization of PE, PE-*g*-MAn, PE-*g*-succinimide, and the polymeric support, that is, PE-*g*-NBS, was carried out by Fourier transform infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA). FTIR spectra were obtained on a Beckman spectrophotometer (USA), and TGA was done on a Shimadzu simultaneous thermal analyzer (Japan) in air at a heating rate of 10°C/min.

FTIR spectroscopy

On comparison of the IR spectra of PE and PE-*g*-MAn (Fig. 1), we observed that two peaks at 1795 and 1835 cm^{-1} due to the carbonyl stretching of the anhydride group and two peaks at 1080.35 and 1021.98 cm^{-1} of the anhydride group due to C—O stretching in the IR spectrum of the grafted PE were absent in PE. This confirmed the formation of the graft copolymer of PE and MAn.

The FTIR spectrum of PE-*g*-succinimide, in addition to the regular bands of PE, showed additional amide I and amide II bands at 1718 and 1661.4 cm^{-1}, respectively, due to $v_{C=O \; str}$ and a strong coupled interaction between N—H deformation and C—N stretching. A peak at 3430.7 cm^{-1} due to N—H stretching of the secondary amide was also observed. The presence of these peaks confirmed the presence of a succinimide group attached to the PE backbone as a graft.

The FTIR spectrum of PE-*g*-NBS (Fig. 2) revealed a peak at 1634.4 cm^{-1} due to two C=O groups and a peak at 3438.5 cm^{-1} due to N—Br stretching. This confirmed that PE had a bromosuccinimide group attached to its chain. Additional peaks at 1463.7 and 1462.9 cm^{-1} due to C—N—C stretching. in the IR spectra of PE-*g*-succinimide and PE-*g*-NBS, respectively, were also observed.

TGA

The primary thermograms of PE, PE-*g*-MAn, PE-*g*-succinimide, and PE-*g*-NBS are presented in Figures 3–6, respectively. The initial decomposition temperature (IDT), final decomposition temperature
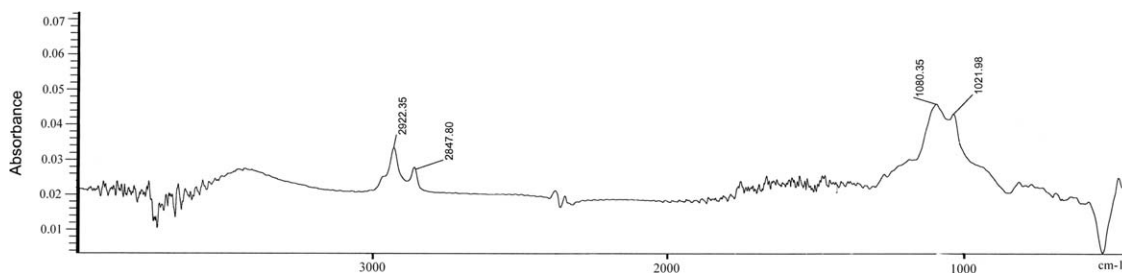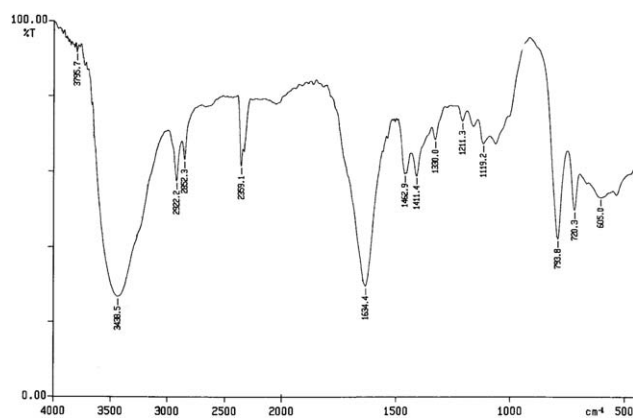

Figure 1 FTIR spectrum of PE-*g*-MAn.

Figure 2 FTIR spectrum of PE-*g*-NBS.

Figure 4 Primary thermogram of PE-*g*-MAn.

(FDT), and decomposition temperature (DT) at every 10% weight loss are presented in Table II.

The thermograms of both PE and PE-*g*-MAn showed a single stage of decomposition. The IDT (439.36°C) and FDT (504.35°C) of PE-*g*-MAn were higher than those for PE (423.91 and 497.83°C, respectively). The decompositions at every 10% weight loss of the grafted PE also occurred at higher temperatures compared to those of the unmodified PE. Both of the samples, that is, the ungrafted and grafted PE, decomposed completely with no leftover residue. Higher IDT, FDT, and DT values at every 10% weight loss of the grafted samples indicated that the thermal stability of PE increased upon grafting.

The initial decomposition of the PE-*g*-succinimide and PE-*g*-NBS, on the other hand, began at much lower temperatures, 365 and 398.67°C, respectively, compared to that of PE (423.91–C). The lower IDT of the grafted sample was due to the early decomposition of the pendant succinimide and NBS groups. Beyond the initial decomposition, the degradation of all of the samples continued with increasing temperature until the final decomposition curve set in. FDT of PE-*g*-succinimide (465°C) was lower than that of the unmodified PE (497.83°C) with 93.33% weight
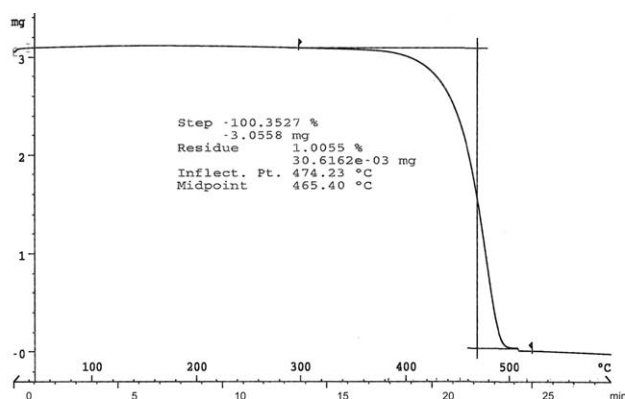
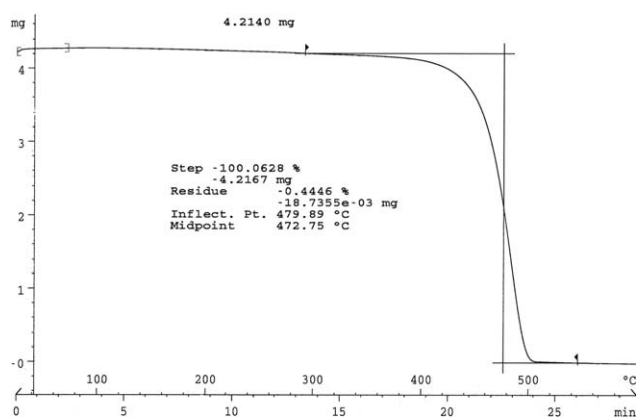loss, whereas PE was almost completely decomposed with 99.29% weight loss. In the case of PE-*g*-NBS, FDT was higher (510.67°C) with 84.35% weight loss. On careful perusal of the DT values at every 10% weight loss, we observed that the DT values of PE-*g*-succinimide were lower than the DT values of PE. The DT values of PE-*g*-NBS were also lower than the DT values of PE up to 40% weight loss, beyond which the values were higher for the grafted sample. However, the temperature differences between the DT values of each 10% weight loss were much higher for PE-*g*-NBS and PE-*g*-succinimide than observed in the case of the ungrafted PE.

A lower percentage weight loss at the beginning of the final decomposition, a higher temperature difference between the DT values of the grafted samples, and a higher percentage residue (15.65%) in the case of PE-*g*-NBS indicated that the thermal behavior improved upon grafting.

RESULTS AND DISCUSSION

Irradiation of the polymeric backbone in the presence of UV light causes the formation of free-radical sites where the grafting of vinyl monomers can take place. The process is accelerated by the use of a
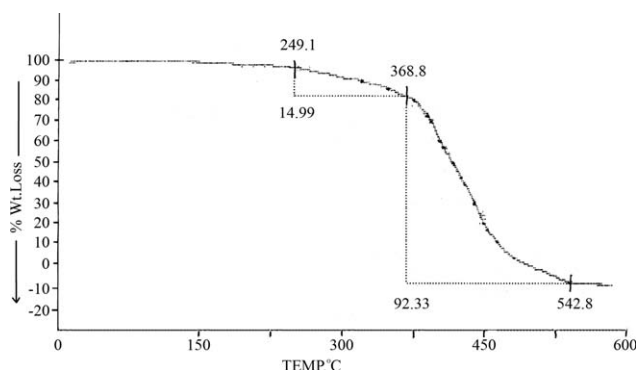

Figure 3 Primary thermogram of PE.

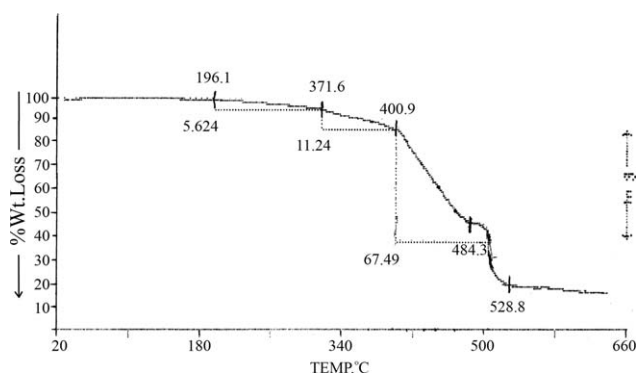**Figure 5** Primary thermogram of PE-*g*-succinimide.

Figure 6 Primary thermogram of PE-*g*-NBS.

photosensitizer. In this study, the graft copolymerization of MAn onto PE by a photochemical method with benzophenone as a photosensitizer was carried out, and the optimum conditions pertaining to the maximum percentage grafting were evaluated. The maximum percentage grafting of MAn (25%) onto PE was obtained at optimum conditions of 3.57 mol of MAn with 0.5 mL of 1% benzophenone and 10 mL of xylene in 120 min.

The oxidation of different alcohols, including 2-propanol, cyclohexanol, PVA, benzyl alcohol, benzoin, ethylene glycol, *n*-butanol, and chloromycetin, was carried out with PE-*g*-NBS as the PS oxidizing reagent. The product obtained in each case was characterized by FTIR and NMR spectral data.

FTIR spectroscopy studies of the oxidation products

The IR spectra of all of the alcohols used for oxidation showed the characteristic peak for aldehydes/ketones between 1632.5 and 1738.5 cm^{-1} due to carbonyl stretching. C—H stretching, usually a doublet due to the vibrational coupling between C=O and the overtone of C—H stretching in the range 2820–2730 cm^{-1}, and several bands in the range 1400–1000 cm^{-1} due to the C—CHO skeletal structure in the case of aldehydic products, such as benzaldehyde, glyoxal, and butanal, were also observed.

The primary and secondary alcoholic groups of chloromycetin (I; Fig. 7), respectively, appeared at peaks between 1350 and 1260 and 1050 cm^{-1}:

(I)
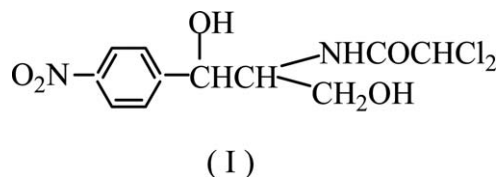
In the oxidized product, an additional peak at 1686.9 cm^{-1} due to the C=O group was observed along with a broad band between 3350 and 3263 cm^{-1} due to associated O—H group stretching. This inferred the presence of a primary —CH$_2$OH group, which could associate with other molecules through hydrogen bonding. The secondary —CHOH— group, being in steric crowding, was less likely to form a hydrogen-bonded association. Further C—H stretching of the aldehydic group, which appears as a doublet, was also missing in the spectrum. This indicates that the secondary alcoholic group was selectively oxidized by the PS-NBS reagent.

^{1}H-NMR spectroscopy studies of the oxidation products

In all of the NMR spectra, a peak between 3 and 5 δ due to the alcoholic protons was missing, which indicated that the alcohols were successfully oxidized by the PS oxidizing reagent, PE-*g*-NBS.

The NMR spectra were taken on a JEOL FT-NMR AL 300-MHz spectrophotometer (Japan).

The NMR spectrum of acetone obtained upon the oxidation of 2-propanol showed a singlet at 1.20 δ, equivalent to 6H due to the methyl protons (a) attached to the carbonyl group:
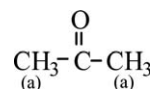

The NMR spectrum of cyclohexanone obtained from the oxidation of cyclohexanol illustrated three peaks at (1) 1.17 δ (pentet) due to the coupling of protons (a) with two identical neighboring methylene

**TABLE II**
TGA Studies of the Unmodified and Modified PE

| Sample | IDT (°C)[a] | FDT (°C)[a] | DT at every 10% weight loss (°C) | | | | | | | | | Residue (%) |
			10%	20%	30%	40%	50%	60%	70%	80%	90%	
Unmodified PE	423.91 (4.29%)	497.83 (99.29%)	429.35	446.74	459.78	463.04	466.74	472.83	477.17	483.69	486.96	0.005
PE-*g*-MAn	439.36 (3.93%)	504.35 (100.37%)	439.13	454.35	463.04	468.48	476.09	481.52	483.69	489.13	493.48	−0.445
PE-*g*-succinimide	365 (5%)	465 (93.33%)	320	380	395	410	420	435	440	450	460	0
PE-*g*-NBS	398.67 (6%)	510.67 (84.33%)	372	414.67	436	446.67	468	505.33	—	—	—	15.65

[a] The weight loss is shown in parentheses.
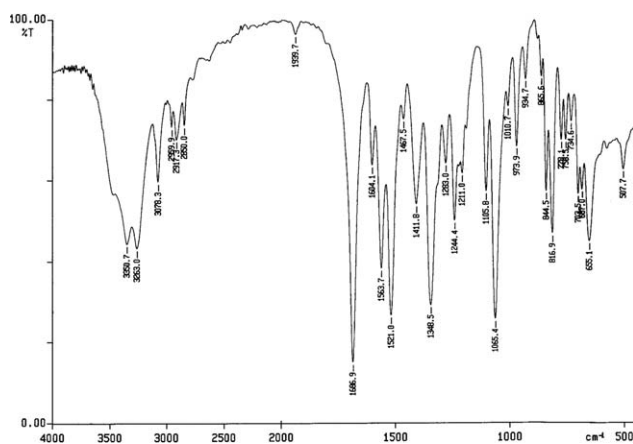
Figure 7 FTIR spectrum of the oxidized product of chloromycetin.

protons (b), (2) 1.21 δ (pentet) of methylene protons (b) coupling with neighboring methylene protons (a and c), and (3) 1.27 δ triplet methylene protons (c) due to the coupling of methylene protons (b):
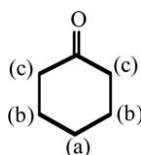
Benzaldehyde obtained by the oxidation of benzyl alcohol showed a characteristic peak at 10.00 δ (singlet) for the aldehydic proton and a multiplet at 7.52 δ for the aromatic protons, whereas benzyl, the oxidized product of the benzoin, showed only a multiplet at 7.68 δ due to 10 equivalent aromatic protons in the NMR spectrum. The peak due to the alcoholic proton of the reactant, that is, benzoin, was absent; this confirmed the oxidation.

The ^{1}H-NMR spectra of glyoxal and butanal, the oxidized products of the ethylene glycol and butanol, respectively, showed the characteristic aldehydic proton peak between 10 and 11 δ. Several peaks in the region 0.96–1.59 δ due to the alkyl group of the butanal were also observed.

The ^{1}H-NMR spectra of the oxidized product of chloromycetin showed a characteristic peak between 12 and 14 δ due to the C=C—OH proton, the enolic form of —CH—C=O. The presence of this peak also confirmed that the 2° alcoholic group of chloromycetin was selectively oxidized to a ketonic group and not the 1° alcoholic group.

A review of the oxidation and dehydrogenation reactions with NBS and related N-haloimides by Filler[19] reported the oxidation of 2-propanol,[20] cyclohexanol,[20] PVA,[21] bezoin,[22] ethylene glycol,[23] and butanol[23] with NBS and that of benzyl alcohol[24] with N-bromoacetamide (NBA) as oxidizing agents. From the comparison of the respective yields of the oxidation products obtained by NBS/NBA and that by NBS supported on a polymeric support, it was observed that 2-propanol (60 and 66.25%) and benzyl alcohol (75 and 70%) were comparable, whereas in the cases of cyclohexanol (61 and 50%) and benzoin (95 and 35%), the yields were lower. When the oxidation of ethylene glycol and butanol was carried out with PS-NBS, the percentages yield of the product were very high (73 and 67%) compared to those obtained by simple oxidation by NBS (9 and 0.8%), respectively. Thus, the oxidizing reagent, that is, NBS supported on the polymeric backbone, PE, offers a promising reagent with good oxidizing ability along with the additional advantages of PS reagents.

Reusability and regeneration of the PS oxidizing reagent

To check that whether the polymeric support was reusable after the reaction, the PS oxidizing reagent was reused after drying for the same oxidation reactions. The oxidation reactions were carried out effectively, although with a lower percentage yield, with the used reagent, PE-*g*-NBS.

The PS oxidizing reagent, PE-*g*-NBS, could also be easily regenerated by washing with a very dilute HCl solution followed by a very dilute NaOH solution and rinsing with water. The washed polymers were treated with subsequent simple organic reagents to introduce a functional moiety, that is, NBS, and were then used for further oxidation reactions. Table III shows the percentage yield of the products obtained upon by the oxidation of benzyl alcohol with used PE-*g*-NBS and regenerated PE-*g*-NBS. The data shows that the percentage yield was lower with used PE-*g*-NBS, which was almost regained after the regeneration of the polymeric support.

CONCLUSIONS

Successful grafting of MAn onto PE and its conversion to a PS oxidizing reagent, PE-*g*-NBS, was achieved. The oxidations of various alcohols were

TABLE III
Oxidation of Benzyl Alcohol with the Used and Regenerated PS Oxidizing Agents

PS oxidizing reagent	Reactant	Product	Time (h)	Yield
PE-*g*-NBS (used)	Benzyl alcohol	Benzaldehyde	13	60%
PE-*g*-NBS (regenerated)	Benzyl alcohol	Benzaldehyde	13	68%

effectively carried out with this reagent. The support was still operative after its use and could also be easily regenerated for further oxidations.

References

1. Neckers, D. C. J Chem Educ 1975, 52, 695.
2. Frechet, J. M. J.; Haque, K. E. Macromolecules 1975, 8, 130.
3. Crosby, G. A.; Weinshenker, N. M.; Uh, H. S. J Am Chem Soc 1975, 97, 2232.
4. (a) Shambu, M. B.; Digenis, G. A. Tetrahedron Lett 1973, 18, 1627; (b) Shambu, M. B.; Digenis, G. A. J Chem Soc Chem Commun 1974, 619.
5. (a) Frechet, J. M. J.; Nuyens, L. T.; Farrall, M. J. J Macromol Sci Chem 1977, 11, 507; (b) Sherrington, D. C.; Graig, D. J.; Dagleish, J.; Domin, G.; Taylor, J. Eur Polym J 1977, 13, 73.
6. (a) McKinley, S. V.; Rakshys, J. W. J Chem Soc Chem Commun 1972, 134; (b) Camps, F.; Castells, J.; Font, J.; Vela, F. Tetrahedron Lett 1971, 20, 1715.
7. Trost, B. M.; Fleming, I.; Ley, S. V., Eds.; Comprehensive Org Synth 1991, p. 7251.
8. Mihashi, S.; Machida, H.; Hatozaki, O.; Oyama, N. Electrochemistry 2001, 69, 991.
9. Minghu, W.; Guichun, Y.; Zuxing, C. React Funct Polym 2000, 44, 97.
10. Ley, S. V.; Thomas, A. W.; Finch, H. J Chem Soc Perkin Trans 1999, 1, 669.
11. Nakamura, K.; Inoue, Y.; Matsuda, T.; Misawa I. J Chem Soc Perkin Trans 1999, 1, 2397.
12. Mojtahedi, M. M.; Sharifi, A.; Kaamyabi, S.; Saidi, M. R. J Chem Res 2002, 6, 286.
13. Kanna, H.; Taylor, R. J. K. Syn Lett 2002, 8, 1287.
14. Hara, M.; Lean, J. T.; Mallouk, T. E. Chem Mater 2001, 13, 4668.
15. Nair, V. A.; Mustafa, S. M.; Krishanpillai, S. J Polym Res 2003, 10, 267.
16. Pozzi, G.; Cavazzini, M.; Quici, S.; Benaglia, M.; Anna, G. D. Org Lett 2004, 6, 441.
17. Leadbeater, N. E.; Scott, K. A. J Org Chem 2000, 65, 4770.
18. Chen, J.; Spear, S. K.; Huddleston, J. G.; Holbrey, J. D.; Swatloski, R. P.; Rogers, R. D. Ind Eng Chem Res 2004, 43, 5358.
19. Filler, R. Chem Rev 1963, 63, 21.
20. Stuckwisch, C. G.; Hammer, G.; Blau, N. F. J Org Chem 1957, 22, 1678.
21. Saigusa, T.; Oda, R. J Chem Soc Jpn Ind Chem Sect 1954, 57, 950.
22. Barakat, M. Z.; Wahab, M. F.; El-Sadr, M. M. J Am Chem Soc 1955, 77, 1670.
23. Saigusa, T.; Moriga, H.; Oda, R. Bull Inst Chem Res Kyoto Univ 1955, 33, 49; Chem Abstr 1956, 50, 14620.
24. Lecomte, J.; Gault, H. Compt Rend 1954, 238, 2538.