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Poly(4-vinylpyridine) Complexes with Bromine and Bromine Chloride as Reactive Polymers in Addition Reactions

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ABSTRACT: The following general features of poly(4-vinylpyridine)–halogen complexes (PVP–XY; X = Br, Y = Br, Cl) were observed, when reacting with olefinic and acetylenic compounds, as compared with the free halogens under similar conditions of solvent and temperature: reactions took place at much slower rates, allowing in most cases mixing of the total amounts of reacting materials in the reactor; when inert solvents were used, the isolated crude adducts were nearly pure compounds; with PVP–BrCl only small amounts of dibromo or dichloro adducts were formed; side reactions frequently accompanying additions of free halogens to double and triple bonds, such as HBr evolution, were absent. When addition to double bonds was carried out in a reactive solvent such as acetic acid, one-fourth to one-third of the product was a bromo–acetate adduct, while addition to acetylenic compounds gave no such byproducts. After the halogen of the polymeric reagent was consumed, the polymer could be filtered and regenerated for reuse. PVP–XY undergoes quaternization reactions concurrently with halogen addition to double or triple bonds. Such reactions may also lead to further cross-linking of the PVP network. Analogous quaternizations using monomeric pyridine–halogen reagents and acetylenic substrates point to various possible quaternization paths of the polymeric reagent: N-vinylation of one pyridyl group, attachment of two *N*-pyridyl groups at the 1,2-positions of a vinylidene group, or further transformations of the quaternary compounds, depending on the nature of the acetylenic substrate.

Introduction

The development of polymeric reagents has become an important branch of modern chemistry. Some reviews relevant to our subject have appeared.[1-3] Reactive polymers have been investigated in various halogenation processes in the past. The polymeric analogues of *N*-chloro- and *N*-bromoamides behaved similarly to or differently from the monomeric reagent, depending on the

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reaction conditions used.[4-6] Instead of *N*-bromosuccinimide, the bromine complex of vinylpyridine copolymer was used for side-chain bromination of aromatic compounds.[7] Polymeric analogues of *tert*-butyl hypohalites have been recently reported.[8] The possibility of using polymeric reagents for addition to double bonds or for ring substitution in aromatic substrates has been studied by various investigators.[1b,3b] Cross-linked poly(vinylpyridine) formed stable complexes with halogens, which were proposed as halogen transfer reagents, including reactions with unsaturated compounds.[9] Perbromide salts of poly(vinylpyridine) copolymers were used in α-keto bromination and double-bond addition reactions.[10] The complexes of bromine with poly(vinylpyridine–styrene),[11] poly(vinylpyridine oxide–styrene),[11,12] and poly(vinylpyridinium bromide–styrene)[11,12] were reacted with double-bond-containing compounds. These reagents showed stereospecificity in the addition (anti adduct), and the latter complex was the most reactive.[12] The effects of chirality of quaternized poly(vinylpyridine) perbromide on olefin addition were also studied.[13]

In the present paper the behavior of poly(vinylpyridine) complexes with bromine or bromine chloride is investigated both from the point of view of the reaction with unsaturated substrates and from that of the processes taking place in the polymeric matrix. The latter are mainly quaternization reactions, which can be expected to concur with the completion of the halogen addition mechanism.

Experimental Section

Reagents. Bromine (Dead Sea Bromine), chlorine (Electrochemical Industries), and ethene (Union Carbide) were of purity higher than 99%. Cyclohexene, styrene, and indene (all Aldrich) were freshly distilled midcuts taken within a 0.5–2 °C range; all other organic reagents were of the best quality available from various suppliers (Aldrich, Eastman, Fluka).

Product Characterization. Products were characterized by their physical properties and elemental analyses (C, H, N, O, Br, and Cl) and with the aid of the following instrumental methods: GLC (Packard 419), ^{1}H NMR (Varian EM-360), IR (Perkin-Elmer 357), and MS (analytical services of The Weizmann Institute of Science). Other analytical methods are described below.

Poly(vinylpyridine) (PVP). Bead-polymerized 4-vinylpyridine cross-linked with 3–5% of 1,3,5-triacrylylhexahydro-1,3,5-triazine was prepared in the laboratory, essentially as described in the literature.[14] Cross-linking with divinylbenzene is also possible, but we found it to be harder to wet and swell this copolymer, especially with hydroxylic solvents such as methanol, acetic acid, and water. Beads in the size range 30–50 or 50–80 mesh were used in this work.

Poly(vinylpyridine)–Bromine Complex (PVP–Br_2). This may be prepared in several ways, achieving partial or total complexation of the pyridyl groups of the polymer. (a) Pour the required amount of liquid bromine (273 g) intermittently on dry PVP (200 g, N 11.95%), shake vigorously in order to attain uniformity, and remove any excess bromine by aeration. (b) PVP (200 g) may be swollen by covering with CCl_4 solvent for 24 h or a hydroxylic solvent (H_2O, MeOH, AcOH) for a shorter period. The excess solvent is then decanted or filtered, and the polymer is placed for several hours in a concentrated bromine solution (1 L containing 273 g of bromine) prepared with the same solvent. When water is used as solvent, it is easier to add the liquid bromine to a stirred suspension of the swollen PVP in 1 L of water. After filtering, washing, and titrating any unabsorbed bromine, the complex is ready for use as reagent by adding it to a solution of substrate (as in the present work, using 5–10 g of PVP) or otherwise by drying it under vacuum at 40 °C before storage. The dried complex is almost odorless, may be handled outside a fumehood, and can be stored for many months in well-covered containers. The color varies from yellow to deep red, depending on the bromine concentration.

Poly(vinylpyridine)–Bromine Chloride Complex (PVP–BrCl). This complex cannot be effectively prepared with the neat halogen due to the instability[15] of neat BrCl or in hydroxylic solvents due to its reactivity.[16] Into a halogenated solvent (1 L), such as methylene dichloride, chloroform, or carbon tetrachloride, cooled to −10 °C, chlorine is bubbled until the desired increase in weight (61 g) is attained, an equimolar amount of bromine (137 g) is added, and the solution is stirred under illumination for 2 h in order to increase the rate of halogen interchange.[15] The required amount (200 g) of previously swollen PVP is added to the solution, and the suspension is stirred until absorption is complete. The final steps are the same as those with the bromine complex. Reactions were carried out by using dried PVP–BrCl from stock. The dried complex has a mildly pungent odor and deteriorates slowly on storing. The color varies from that of the polymer to light brown.

Halogen Analysis of Poly(vinylpyridine)–Halogen Complexes. Elemental halogen analysis (total halogen) can be performed by the Schoeniger method with receipt of a solution adequate for the halogens to be determined.[17a] Complexed halogen may be determined as follows:[18] 20–50 mg of the complex is added to 20 mL of ice-cooled dimethylformamide and 0.5–1 g of potassium iodide is added to the suspension; the well-closed container is shaken occasionally and kept in a dark place; after a few hours the iodine appearing in solution is titrated with $^1/_{20}$ N solution of sodium thiosulfate until disappearance of the brown color of iodine (no indicator should be added) in solution; this is repeated two to three times until all the complexed halogen has reacted.

Addition to Double and Triple Bonds. Stoichiometric amounts of the PVP complex and substrate (10–20 g of reagent per 100 mL of solvent is usually adequate) are stirred together until the halogen color disappears or does not show further change. The polymer is filtered and washed, and the crude products are obtained by evaporation of the filtrate. The following example illustrates the method: PVP (5.25 g) swollen under carbon tetrachloride was complexed with bromine (5.4 g) dissolved in the same solvent (50 mL). After 19 h the bromine was totally absorbed. The supernatant was decanted and replaced by fresh solvent (50 mL) to which propynol (1.95 g; **13**) was added. After the suspension was stirred for 3 h, protected from light at room temperature, the bromine discoloration disappeared, the suspension was filtered and washed with carbon tetrachloride, the solvent was evaporated, and the residue (2.14 g) was distilled, yielding the product (1.562 g, bp 64–66 °C (1.0 Torr), n^{20}_D 1.5763, yield 22%). The conditions used and results obtained on reacting Br_2, BrCl, and their PVP complexes with various organic substrates and the properties by which the products were characterized are summarized in Table I. Some analyses of the spent polymeric reagent are shown in Table II. In cases where quaternization of the polymer was not extensive, e.g., ethene, the spent reagent could be reloaded by following the procedure described above for fresh PVP and used again.

Analogues of Pyridine–Bromine Complex. The complexes of various compounds containing the pyridyl moiety were prepared in carbon tetrachloride solvent according to reaction 1, as described in the literature for the pyridine bromine complex (see reaction 1, R = H).[19] The bromine complexes were characterized by their bromine content (iodometry) and their mp (°C) as follows: pyridine,[19] 58–60; 3-methylpyridine, 48–50; 4-methylpyridine, 70; isoquinoline, 90–2; 4,4′-bipyridyl, 220–30 (dec).

Quaternization Reactions of Analogues of Pyridine–Bromine Complex. The pyridine–bromine complex analogues were reacted with various types of acetylenic compounds, yielding the products summarized in Table III. The following procedures exemplify the various preparation methods. ^{1}H NMR spectra were determined in D_2O solution (for D*H*O, $\delta \sim 4.80$). Due to the relative instability of the perbromide counterions (Br_3^-) present in the original product, these were exchanged with others (see below) such as perchlorate (ClO_4^-) and picrate ($C_6H_2N_3O_7^-$) as shown in Table III.

Reaction of Pyridine–Bromine Complex with Propynol. A suspension of the complex prepared in situ in carbon tetrachloride containing 1.5 g of pyridine and 3 g of bromine was cooled to 0 °C, and 1.2 mL of propynol was added. Stirring was continued for 2 h, and then the temperature was allowed to rise

Table I
Bromination and Chlorobromination of Some Olefinic and Acetylenic Compounds with Free and Complexed Halogens[a,b]

reagents[c]	time (temp)	yields,[d] %	comments and products
		I. Ethene (**3**)[e]	
1. PVP–BrCl/CCl_4 or CH_2Cl_2 (8.8 mequiv/g)	11.5 h (3–5 °C)	100 r	excess ethylene bubbled through suspension in absorption towers: **4c**, <1%; **4b**, 96%; **4a**, 1–4%; other products, 1–2%
2. BrCl/CCl_4 or CH_2Cl_2	0.3 h (0 °C)	100 rs	**4c**, ca. 10%; **4b**, 70–80%; **4a**, 20–10%
		II. Cyclohexene (**5**)[f–h]	
3. PVP–Br_2/CCl_4 (4.25 mequiv/g)	0.25 h (0 °C)	41 p, 47 r	light yellow crude; stable on storage; **6a**[i] with traces of unknown components (for spent reagent, see Table II)
4. Br_2/CCl_4 (0 °C)	0.25 h	100 s	crude product evolved HBr; GLC showed many major components; distilled **6a** evolved HBr after 2 days; darkened and became heterogeneous later[j]
5. PVP–Br_2/AcOH (6.8 mequiv/g)	0.1 h (room temp)	100 r	**6a** and **6e** in 3:2 ratio with traces of unknown components
6. PVP–BrCl/CCl_4 (7.9 mequiv/g)	21.5 h (room temp)	94 r	reactants in concentd equimolar mixture: **6b**, 97.2%; **6a**, 2.8%
7. PVP–BrCl (7.9 mequiv/g)	21.5 h (room temp)	94 r	neat cyclohexene in 20-fold excess: **6b**, 98.3%; **6a**, 1.7%
8. PVP–BrCl/AcOH (7.9 mequiv/g)	6 h (room temp)	100 rs	conditions as in example 6: **6b**, 74.9%; **6a**, 1.1%; **6e**, 24%
9. BrCl/CCl_4	1 h (25 °C)	100 rs	slow addition of dilute substrate, acid fumes evolved: **6b**, ca. 65%; **6a**, ca. 15%; other impurities, ca. 20%, including compounds of formula $C_6H_8Br_3Cl$, $C_6H_9Br_3$, $C_6H_8Br_2Cl_2$, and $C_6H_9Br_2Cl$ as shown by MS
		III. Styrene (**7**)[h]	
10. PVP–BrCl/CCl_4 or petroleum ether (5 mequiv/g)	68 h (room temp)	80 r	20% excess styrene: **8b**,[k] 95.7%; **11**,[l] 0.3%; **12**,[m] 1.6%; **8c**,[n] trace, other products, 2.3%
11. BrCl/CCl_4	1 h	100 rs	slow addition of dilute styrene, acid fumes evolved: **8b**, 80.6%; **11**, 1.2%; **12**, 5.1%; **8c**, 6.3%; other products, 6.8%
		IV. Acenaphthylene (**9**)[o]	
12. PVP–Br_2/CCl_4 (6.2 mequiv/g)	83 h (room temp)	80 p	crude: **9**, ca. 20%; **10a**,[p] ca. 80% (for spent reagent, see Table II)
13. PVP–Br_2/AcOH (6.2 mequiv/g)	83 h (room temp)	80 p	only **10a** obtained on workup
14. Br_2/CCl_4	3 h (room temp)	100 rs	crude contained only **10a**; acid fumes evolved from reaction and crude
15. Br_2/AcOH	0.25 h (room temp)	100 rs	acid fumes evolved during reaction; on workup dark brown crystals obtained, presumably containing cis–trans mixture of **10a**, but no acetates (NMR) and light brown crystals similar to those in examples 12 and 13
		V. Propynol (**13**)[q]	
16. PVP–Br_2/CCl_4 (6.3 mequiv/g)	3 h (room temp)	22 p, 100 r	light yellow crude from which very pure **14a** was distilled (for spent reagent, see Table II)
17. PVP–Br_2/AcOH (6.3 mequiv/g)	20 h (room temp)	40 p, 100 r	see example 16; no acetates formed
18. PVP–Br_2/MeOH (7.1 mequiv/g)	15 h (room temp)	55 p, 100 r	clear crude from which very pure **14a** was distilled; no methoxy compounds formed
19. Br_2/AcOH	15 h (room temp)	100 r	presumably **14a–14c**: ca. 30 mol % acetates, ca. 35 mol % tribromo compounds, and substantial amounts of (*Z*) isomers, possibly **15a–15c**[q]
20. PVP–BrCl/CCl_4 (9 mequiv/g)	24 h (room temp)	68 p, 100 r	crude mixture contains ca. 95% of **15d** and **15e** in 1:2 ratio and ca. 5% of **15f**[r]
		VI. 3-Butyn-2-ol (**16**)	
21. PVP–Br_2/CCl_4 (6.8 mequiv/g)	1 h (room temp)	42 p, 100 r	substrate (Fluka) was 55% solution in water; pure **17**[s] distilled
		VII. 2-Butyne-1,4-diol (**18**)	
22. PVP–Br_2/AcOH (6.8 mequiv/g)	0.5 h (room temp)	100 r	technical-grade substrate; crude consisting mainly of crystalline **19**[t]
23. PVP–Br_2/H_2O (6.2 mequiv/g)	16 h (room temp)	80 p, 100 r	see example 22

[a] In mass spectra d and t stand for doublets and triplets, starting at the given *m/e* value with increments of 2.[17] The doubly charged multiplets have increments of 1 *m/e* unit. [b] In ^1H NMR spectra, calculated chemical shifts δ_{calc}, and those of an example δ_{ex}, were based on data taken from ref 21 for allylic protons and from ref 22 for ethylenic protons. [c] Concentration of free halogen in dry complex is mentioned. [d] Yields estimated from recovery of desired product (p), unreacted complexed halogen in spent reagent (r), or unreacted substrate (s). [e] GLC: 10% SE-30/Chromosorb W 80-100, 1/8 × 100 in., 70 °C, He. [f] GLC: as in note d but at 125 °C. [g] GLC: Carbowax 20N/Chromosorb W 80 100, 1/8 × 100 in., 125 °C, He. [h] GLC: 10% DC-710/Celite 100-120, 1/8 × 100 in., 120 °C, He. [i] ^1H NMR: identical with literature.[16] [j] See for example ref 9. [k] MS: *m/e* 218 (t, M^+), 125 (d, $C_7H_6Cl^+$). [l] α-Chlorostyrene (**11**) results from spontaneous dehydrobromination of **8b**. [m] (Bromoacetyl)benzene (**12**) is an autooxidation product concurrent with halogen addition. [n] MS: *m/e* 174 (t, M^+), 125 (d, $C_7H_6Cl^+$). [o] Mp 87–89 °C. ^1H NMR (CCl_4): δ 6.95 (s, 1 H, ace), 7.48 (m, 3 H, arom). [p] Mp 122–123 °C. ^1H NMR (CCl_4): 5.93 (s, 1 H, C*H*Br), 7.57 (m, 3 H, arom), possibly cis isomer has C*H*Br at δ 5.87. MS: *m/e* 310 (t, M^+), 231 (d, $C_{12}H_8Br^+$), 230 (d, $C_{12}H_7Br^+$), 231 (d, $C_{12}H_8Br^+$), 115.5 (d,[a] $C_{12}H_8Br^{2+}$). [q] The ^1H NMR assignments proposed for these products were made on the basis of spectra of mixtures presumably containing compounds **14a** and **14b**, according to ref 23. (*E*)-2,3-Dibromo-2-propen-1-ol (**14a**). Bp: 118–122 °C (35 Torr); n^{25}_D 1.5763. GLC: see **6e**. ^1H NMR (CCl_4): δ 4.37 (s, 1 H, variable, O*H*), 4.45 (d, 2 H, *J* = 0.6 Hz, CH_2, δ_{ex} 4.13), 6.57 (t, 1 H, *J* = 0.6 Hz, C=C*H*, δ_{calc} 6.65). ^1H NMR (neat): δ 4.82 (s, 2 H, CH_2), 5.37 (s, 1 H, O*H*), 7.00 (s, 1 H, C=C*H*). MS: *m/e* 214 (t, M^+), 197 (t, $C_3H_3Br_2^+$), 184 (t, $C_2H_2Br_2^+$), 183 (t, $C_2HBr_2^+$), 171 (t, $CHBr_2^+$?), 135 (d, $C_3H_3Br^+$). (*E*)-1,2,3-Tribromopropene (**14b**). ^1H NMR (CCl_4): δ 4.27 (m, CH_2Br, δ_{calc} 4.00), 6.90 (m, C=C*H*, δ_{calc} 6.79). (*E*)-2,3-Dibromo-2-propen-1-yl acetate (**14c**). ^1H NMR (CCl_4): δ 2.13 (s, CH_3CO_2), 4.93 (s, CH_2O, δ_{ex} 4.6), 6.60 (m, C=C*H*, δ_{calc} 6.65). (*Z*)-2,3-Dibromo-2-propen-1-ol (**15a**). ^1H NMR (CCl_4): δ 6.60 (s, C=C*H*, δ_{calc} 6.65); see also **14a**. (*Z*)-1,2,3-Tribromopropene (**15b**). ^1H NMR (CCl_4): δ 7.10 (m, C=C*H*, δ_{calc} 6.99); see also **14b**. (*Z*)-2,3-Dibromo-2-propen-1-yl acetate (**15c**). ^1H NMR (CCl_4): δ 2.13, 4.93 (see **14c**), 6.73 (see also **15a**). [r] The ^1H NMR assignments proposed for these products were made on the basis of spectra of mixtures presumably containing compounds **15d** and **15e**, according to ref 23. GLC: see note *g*. (*E*)-3-Bromo-2-chloro-2-propen-1-ol (**15d**). ^1H NMR (CCl_4): δ 4.32 (s, 1 H, variable, O*H*), 4.45 (m, 2 H, CH_2), 6.45 (t, C=C*H*, δ_{calc} 6.44). (*Z*)-3-Bromo-2-chloro-2-propen-1-ol (**15e**). ^1H NMR (CCl_4): δ 4.32 (s, 1 H, variable, O*H*), 4.45 (m, 2 H, CH_2), 6.38 (t, C=C*H*, δ_{calc} 6.33). (*E*)-2-Chloro-1,3-dibromopropene (**15f**). ^1H NMR (CCl_4): δ 6.58 (t?, C=C*H*, δ_{calc} 6.58). [s] (*E*)-3,4-Dibromo-3-buten-2-ol (**17**). Bp: 109–114 °C (31 Torr). GLC: see **6e**. ^1H NMR (CCl_4): δ 1.30 (d, 3 H, *J* = 6 Hz, CH_3), 4.40 (s, 1 H, O*H*), 4.92 (quartet, 1 H, *J* = 6 Hz, CH_3CHO), 6.47 (s, 1 H, C=C*H*, δ_{calc} 6.65). MS: *m/e* 228 (t, M^+), 213 (t, $C_3H_3Br_2O^+$), 183–189 (mult, ?), 149 (d, $C_4H_6BrO^+$), 106.5 (t,[a] $C_3H_3Br_2O^{2+}$), 105 (d, $C_2H_2Br^+$). [t] (*E*)-2,3-Dibromo-2-butene-1,4-diol (**19**). Mp: 112–113 °C. ^1H NMR (acetone-d_6, δ 2.10): δ 4.55 (see also ref 19). MS: *m/e* 244 (t, M^+), 226 (t, $C_4H_4Br_2O^+$), 213 (t, $C_3H_3Br_2O^+$), 195–204 (mult, ?), 183 (t, $C_2HBr_2^+$), 182 (t, $C_2Br_2^+$), 165 (t, $C_4H_6,Br_2O_2^+$), 147 (d, $C_4H_4BrO^+$).

Table II
Some Examples of Recovered Spent PVP-Br_2 Reagent

substrate[a]	gain in wt,[b] %	analysis, % N	Br(total)	Br_2	Br^-
cyclohexene (3)	21	9.14	22.11	20.25	*c*
acenaphthylene (12)	34	7.71	29.75	0	17.10
propynol (16)	79	6.23	28.55	0	13.94
propynol (20)	17	8.04	*d*	*d*	*d*
acetylenedicarboxylic acid[e]	139	4.92	32.14	0	6.15
4-cyclohexene-*cis*-1,2-dicarboxylic acid[f]	61	6.62	27.32	0	24.70
indene[f]	16	8.38	13.69	0	13.11

[a] Number in parentheses indicates the entry number in Table I. [b] Gain relative to the weight of PVP used in the reaction. [c] It is difficult to determine bromide ions attached to the polymer in the presence of complexed Br_2. [d] Total halogen 5.04 mequiv/g, of which 3.70 mequiv/g is Br and 1.34 mequiv/g is Cl, namely 34.36% total halogen content. [e] Reaction in acetic acid solvent under conditions similar to those of entry 17 of Table I. One-third of the substrate was recovered unchanged, and the rest became attached to the polymer. [f] Reaction in acetic acid solvent under conditions similar to those of entry 17 of Table I.

to 20 °C. After the suspension settled, the supernatant solution was discarded and the semisolid residue was washed several times with the same solvent. On recrystallization from ethanol–ethyl acetate solvent, the perbromide (**20**, X = Br_3^-) was reduced to bromide (X = Br^-). Other anions were introduced in the quaternized products as described below. Compounds obtained in this manner had the following ^1H NMR bands in D_2O solvent: $\delta \sim 4.95$, $=CCH_2O$ protons; δ 7.50, $=CH-$ proton; a broad split multiplet centered at $\delta \sim 8.50$, the pyridinium protons.

Reaction of Pyridine–Bromine Complex with Dialkyl Acetylenedicarboxylate. The complex (0.02 mol) and ester (0.01 mol) were stirred together for 5 h in 25 mL of methanol cooled to −3 °C. The temperature was then allowed to rise slowly to 20 °C. The yellow perbromide (**21**, $X^- = Br_3^-$) was filtered, washed with methanol, and dried. Elemental analysis of the perbromide showed a slight loss of bromine. Other anions were introduced as described below. Similarly the reaction of pyridine–bromine complex analogues was carried out. The ^1H NMR proton bands in D_2O shown by compounds to which structure **21** was assigned were those expected from R′ in the ester group and the aromatic rings.

Reaction of 4,4′-Bipyridyl–Bromine Complex with Dimethyl Acetylenedicarboxylate. A solution of 4,4′-bipyridyl (0.8 g) in acetic acid (30 mL) was mixed slowly with a solution of bromine (0.5 mL) in the same solvent (10 mL). A fine precipitate indicated the formation of the complex. Dimethyl acetylenedicarboxylate (0.8 mL) was added to the suspension, and the mixture was heated in a water bath for 10 min. The solid was filtered. The mother liquor was concentrated under vacuum at 40 °C, leaving an orange residue, which was washed repeatedly with ether, dissolved in about 2 L of hot ethanol, precipitated with ether, filtered, washed with ether, and dried. The yellow-brown solid **24** was hygroscopic, and its ^1H NMR spectrum in D_2O solvent showed both OCH_3 at δ 3.35 and aromatic protons as an AB quartet centered at δ 8.80. The analyses of the picrate and perchlorate derivatives are shown in Table III.

Reaction of Pyridine–Bromine Complex with Acetylenedicarboxylic Acid. A pyridine–bromine complex (19.18 g) suspended in methanol (100 mL) was mixed with acetylenedicarboxylic acid (9.6 g) dissolved in the same solvent (15 mL). The reaction mixture was refluxed for 2 h, and a white solid started to precipitate. The mixture was left overnight, and the precipitate (2.57 g) was filtered, washed with methanol, and recrystallized from hot ethanol. Analogue products were obtained from methylpyridine–bromine complexes. Compounds of type **23** all had ^1H NMR spectra with a band at δ 7.4 and the aromatic protons, similar to compounds of type **20** above.

Picrates. Perbromide salts of structure **20**, **21**, or **24** with $X^- = Br_3^-$ were suspended in an excess of concentrated ethanolic picric acid solution. The suspension was stirred in a boiling water bath. After the evolution of bromine vapors ceased, the mixture was cooled and filtered. The sparingly soluble picrate was recrystallized from a large volume of hot ethanol.

Perchlorates. A perchloric acid solution in ethanol was prepared in a 2:10 volumetric ratio, using 70% concentrated perchloric acid. The procedure for preparing perchlorate salts was analogous to the one described for picrates.

Results and Discussion

Four typical compounds containing labile carbon–carbon double bonds were chosen, for which the reactions with Br_2 and BrCl are well-known and may serve as a standard for comparison for the behavior of the corresponding polymeric reagents. Scheme I summarizes the main reaction path of these compounds, and Table I presents details of the experimental conditions under which such reactions were carried out.

The reaction of ethene with bromine is an important industrial process, which is carried out by simultaneously feeding bromine and gaseous ethene into a reactor containing 1,2-dibromoethane (**4a**), which is also the reaction product. The PVP-Br_2 complex (**2a**) gave the same product, but no practical advantage is to be gained from such a process and various disadvantages are apparent: the product **4a** cannot be used as a solvent for the process, since slow deterioration of the polymer takes place by quaternization of the pyridyl groups, which are liberated as the reaction progresses; the simplicity and quantitative yield of the industrial process is unattainable with the polymeric reagent.

In contrast with this, PVP–BrCl (**2b**) showed a clear advantage over the neat halogen or its solutions. Bromine chloride is a rather unstable mixed halogen, which quickly undergoes an equilibrium reaction (2).[15] The effect of such disproportionation is shown by the composition of the products derived from the reaction of ethene with BrCl, which contains substantial amounts of dibromo (**4a**) and dichloro (**4c**) adducts in addition to the desired product (**4b**). Selectivity of **4b** production is much higher with PVP–BrCl, yielding a crude product of 96% purity with only minor amounts of **4a** and **4c**.

Similar behavior was shown by the polymeric reagents with cyclohexene in nonpolar solvents. PVP-Br_2 yielded essentially pure dibromo adduct (**6a**), which could be further purified by distillation. On comparison of examples 3 and 4 of Table I, it should be emphasized that on the addition of free bromine to cyclohexene very stringent working conditions should be observed in order that the desired adduct **6a** be pure and stable even after distillation.[20] The procedure with **2a** was problem free and led, nevertheless, to a stable product. The adduct derived from PVP–BrCl in CCl_4 or cyclohexene solvent was **6b** of 97–98% purity with **6a** as the main contaminant, while BrCl in CCl_4 yielded **6b** of 65% purity with substantial amounts of **6a** and many other byproducts, as shown in entry 9 of Table I.

Reaction of PVP–BrCl with styrene yielded the Markovnikov product **8b** of 95.7% purity, with only a trace of **8c** and minor byproducts such as α-chlorostyrene (**11**) and phenacyl bromide (**12**). The reaction with free BrCl led to a very complex mixture containing substantial amounts of **8c** and **12**, and acid fumes were evolved during the reaction.

Acenaphthylene yielded pure **10a** on treatment with PVP-Br_2 in CCl_4, while treatment with free bromine in the same solvent led to the evolution of acid fumes and unidentified byproducts.

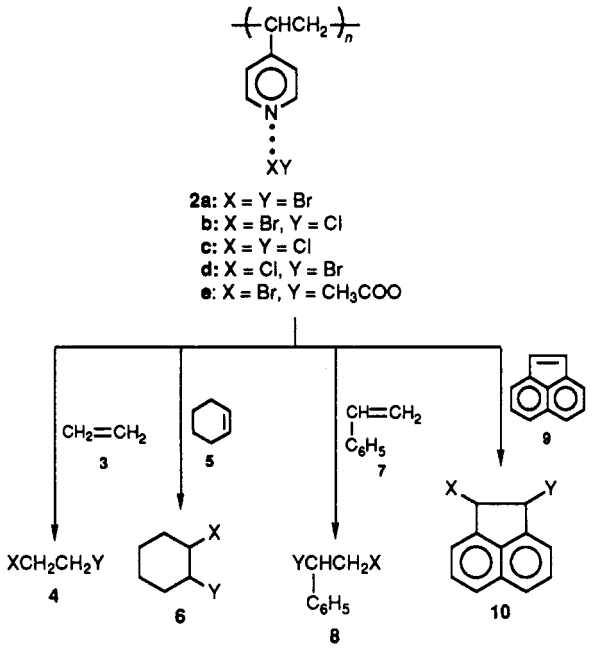
Three acetylenic alcohols with OH groups in propargylic positions (**13**, **16**, and **18**) were reacted with PVP-Br_2 in various solvents. They underwent bromine addition

Table III
Structure and Elemental Analysis of Quaternization Compounds Obtained from Pyridine–Bromine Complexes and Acetylenic Compounds[a]

type	R	R′	X⁻	mp, °C	molecular formula	mol wt
20	H		Br^-	174–5 dec	$C_8H_9Br_2NO$	295.0
20	H		ClO_4^-	109–10	$C_8H_9BrClNO_5$	314.5[a]
20	H		$C_6H_2N_3O_7^-$	138–40	$C_{14}H_{11}BrN_4O_8$	443.2
21	H	Me	Br_3^-	>260 dec	$C_{16}H_{16}Br_6N_2O_4$	779.7[b]
21	H	Me	ClO_4^-	230–2	$C_{16}H_{16}Cl_2N_2O_{12}$	449.2
21	H	Me	$C_6H_2N_3O_7^-$	212–4 dec	$C_{28}H_{20}N_8O_{18}$	756.5
21	H	Et	ClO_4^-	227–8 dec	$C_{18}H_{20}Cl_2N_2O_{12}$	527.3
21	H	Et	$C_6H_2N_3O_7^-$	196–8 expl	$C_{30}H_{24}N_8O_{18}$	784.6
21	3-Me	Me	ClO_4^-	232–3 dec	$C_{18}H_{20}Cl_2N_2O_{12}$	527.3
21	3-Me	Me	$C_6H_2N_3O_7^-$	189–90 expl	$C_{30}H_{24}N_8O_{18}$	812.6
21	3-Me	Et	ClO_4^-	206–8 dec	$C_{20}H_{24}Cl_2N_8O_{12}$	555.3
21	3-Me	Et	$C_6H_2N_3O_7^-$	196–8 dec	$C_{32}H_{28}N_8O_{18}$	812.6
21	4-Me	Me	ClO_4^-	217–9 dec	$C_{18}H_{20}Cl_2N_2O_{12}$	527.3
21	4-Me	Me	$C_6H_2N_3O_7^-$	192 expl	$C_{30}H_{24}N_8O_{18}$	784.6
21	4-Me	Et	ClO_4^-	233–4	$C_{20}H_{24}Cl_2N_8O_{18}$	555.3
21	4-Me	Et	$C_6H_2N_3O_7^-$	180–1 expl	$C_{32}H_{28}N_8O_{18}$	812.6
21	IQ[c]	Me	ClO_4^-	143–4 dec	$C_{24}H_{20}Cl_2N_2O_{12}$	599.3[d]
21	IQ[c]	Me	$C_6H_2N_3O_7^-$	178–80 dec	$C_{36}H_{24}N_8O_{18}$	856.65[e]
24	BP[f]	Me	ClO_4^-	112–5 dec		*g*
24	BP[f]	Me	$C_6H_2N_3O_7^-$	81–3 dec		*h*
23	H			dwm[i,j]	$C_9H_7NO_4$	193.2
23	2-Me			215 dec[j,k]	$C_{10}H_9NO_4$	207.2
23	3-Me			216–7 dec[k]	$C_{10}H_9NO_4$	207.2
23	4-Me			dwm[i,k]	$C_{10}H_9NO_4$	207.2

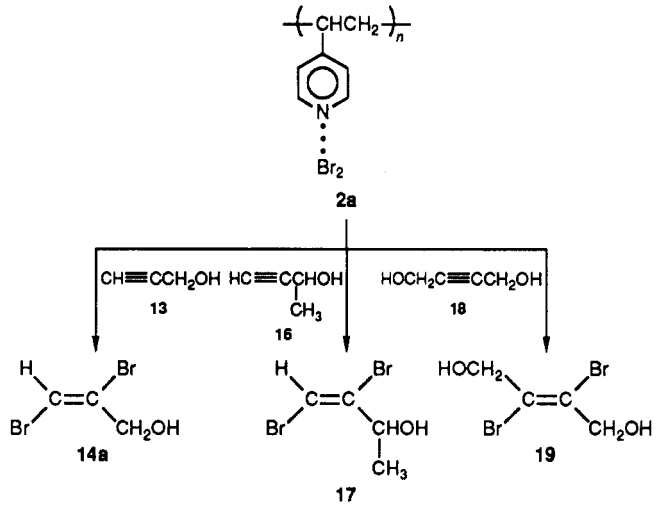
[a] Elemental analyses performed on C, H, N, O, and halogen were satisfactory, for all compounds, unless otherwise indicated. [b] Perbromides are unstable and decompose partially to bromide; hence, they showed a somewhat lower Br content and a slightly higher content of the other elements. [c] IQ is *N*-isoquinolinium replacing RC_5H_4N- in Scheme II. [d] Possibly containing ethanol of crystallization. Anal. Calcd (found): C, 48.09 (50.6); H, 4.46 (3.75); N, 4.67 (4.15); Cl, 11.83 (10.35). [e] Possibly incomplete picrate formation, as it showed a slightly low N analysis. Calcd (found): 13.08 (11.8). [f] BP is 4,4′-bipyridyl replacing RC_5H_4N- in Scheme II. The starting complex contains two Br_2 molecules. [g] Analysis of products: C, 38.8; H, 3.45; N, 5.15; O, 35.85; Cl, 12.8; Br, 4.05 (by difference). [h] Analysis of products: C, 42.65; H, 2.75; N, 13.55; O, 37.75; Br, 3.3 (by difference). [i] Decomposes without melting. [j] ^1H NMR in D_2O: δ 7.40 (s, C=C*H*), 8.40 (m, aromatic *H*). [k] ^1H NMR in D_2O: δ 2.75 (s, arom ring CH_3), 7.40 (s, C=C*H*), 8.40 (m, aromatic *H*).

Scheme I
Reaction of Poly(vinylpyridine)–Bromine and Bromine Chloride Complexes with Reactive Carbon–Carbon Double Bonds



to yield compounds of entgegen configuration (*trans*-dibromo), as shown in Scheme II. With Br_2 alone mixtures of isomers and other byproducts were obtained, especially in hydroxylic solvents. The choice of substrates was made because of the reactivity of OH groups in propargylic positions. These groups did not react when the polymeric reagent was used, but they were subject to attack when Br_2 alone was used, as shown in Table I.

Scheme II
Reaction of Poly(vinylpyridine)–Bromine Complex with Acetylenic Compounds Containing the Propargyl Alcohol Structure



Example 20 of Table I shows the reaction of propynol with PVP–BrCl. Although the main product was 3-bromo-2-chloro-2-propen-1-ol, the reaction was not regiospecific, and a 2:1 mixture of entgegen (**15d**) and zusammen (**15e**) isomers was obtained. The small amount of compound **15f** also present in the crude mixture may be derived from some residual acidity formed in the polymeric reagent, during the preparation of the BrCl complex.

The reaction of PVP–Br_2 with acetylenedicarboxylic acid was remarkable in that very little adduct or unreacted substrate was recovered from solution, although the complexed bromine was depleted from the polymer. This behavior pointed to the possibility of attachment of the

substrate to the polymeric matrix. A possible structure resulting from such attachment is discussed below, when referring to Scheme III.

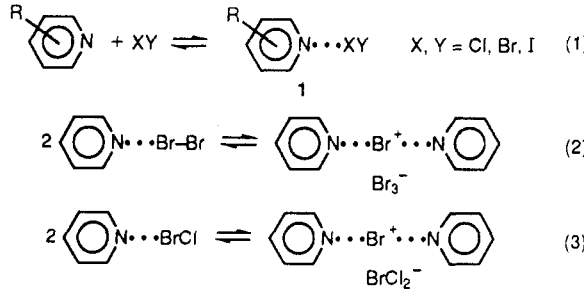
Poly(vinylpyridine)–bromine complex (PVP–Br_2) showed some special features in its behavior in addition reactions when compared with free bromine in a similar environment. First, the differences in reaction rate between the polymeric reagent, requiring from several minutes to several hours to complete the reaction, and the practically instantaneous reaction of the free halogen should be due both to mass-transfer effects and to diminished reactivity. The former effects are caused by the need of the substrate molecules to diffuse into the polymeric matrix and the products to diffuse out of it. The most significant cause for diminished reaction rate should be the diminished reactivity caused by the formation of a stable charge-transfer complex between the pyridyl moieties of PVP, acting as electron donors, and the halogen acting as electron acceptor. This should allow higher selectivity of the polymeric reagent. In the reaction with various types of double bonds shown in Scheme I, PVP–Br_2 reacted relatively quickly with cyclohexene (**5**) and more sluggishly with double bonds attached to aromatic systems, such as styrene (**7**) and acenaphthylene (**9**). The reaction of uncomplexed bromine with all these substrates is practically instantaneous. The mass-transfer effects are particularly evident in the reaction with ethene, where the gas has first to dissolve in the dispersing medium and then to diffuse into the polymer particle, while reaction with bromine in solution takes place at the gas/liquid interface when ethylene is bubbled into the reactor.

An aspect of practical interest is the fact that bromine addition to double and triple bonds took place with more specificity than is usual with free bromine under the same operating conditions, and the halogen adducts were always more easily purified and stable. With ordinary halogenation, careful distillation of the substrate, low temperatures, protection from light, and other measures are necessary in order to obtain a clean and stable dibromo adduct and to avoid many side reactions. With PVP–Br_2 and PVP–BrCl complexes good results may be attained with less painstaking procedures. Examples of this are items 3 and 4 in Table I, referring to the behavior of cyclohexene, and items 12–15, referring to acenaphthylene. The behavior of the polymeric reagent is probably due to quenching by the polymer matrix of the free-radical chain reactions that usually accompany halogen additions, when these are carried out in a carefree manner, e.g., without protection from light, at insufficiently low temperatures, or in the presence of peroxides produced during storage of the organic substrate. Hydrogen halide evolution is symptomatic to the occurrence of such reactions, and its possible participation in the promotion of side reactions is abated by the basic pyridyl moieties of the polymeric reagent.

The rate of reaction and stereoselectivity of the polymeric bromine complexes have been discussed to some extent by other research workers.[9-13] Of the bromine complexes tested[12] the polymer containing the pyridium perbromide moiety was the fastest, that containing the pyridine–bromine complex moiety shown in reaction 1 was the slowest, and that containing the pyridine oxide–bromine complex moiety was of intermediate rate. The reactivity of the two slowest complexes can be attributed to the relative stability of the charge-transfer complex between bromine and the aromatic moiety. The higher reactivity of the perbromide polymer may be due to the fact that the reacting moiety is the Br_3^- ion, which is free to diffuse in the polymer particle and to exchange Br^- ions of sites that have already reacted.

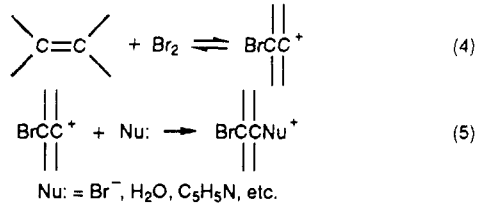
A better demonstration of the specificity of the polymer–halogen complex is shown in Table I, with the BrCl complexes. The mixed halogen undergoes extensive disproportionation in solution,[15] but it forms stable complexes with pyridine[19] and poly(vinylpyridine). This stabilized form has a great effect on the specificity of the reagent in additional reactions, as shown in Table I for ethene, cyclohexene, styrene, and propynol. The products obtained from the PVP–BrCl complex contained only reduced amounts of dibromo and dichloro adducts, as compared with the results obtained with BrCl in similar solutions.

The problem of discerning the exact reasons for the increased specificity of complexes PVP–XY in halogen adduct formation and its stereospecificity is complicated when taking into account the chemical analogy of the polymeric complexes with those obtained in reaction 1.[19] Spectroscopic evidence[24] shows that complexes 1 exist in an extensively dissociated form involving bromonium structures, as shown in reactions 2 and 3.



Participation of the analogous ions in the polymeric reagent could explain the reactivity of the electrophilicity of the complexed bromine—reacting as bromonium ion—and the completion of the reaction in an anti configuration by the Br_3^- or $BrCl_2^-$ ion, depending on whether PVP–Br_2 or PVP–BrCl was used. Spectroscopic evidence for the structure depicted in reaction 3 is inconclusive and other possibilities have been suggested.[25]

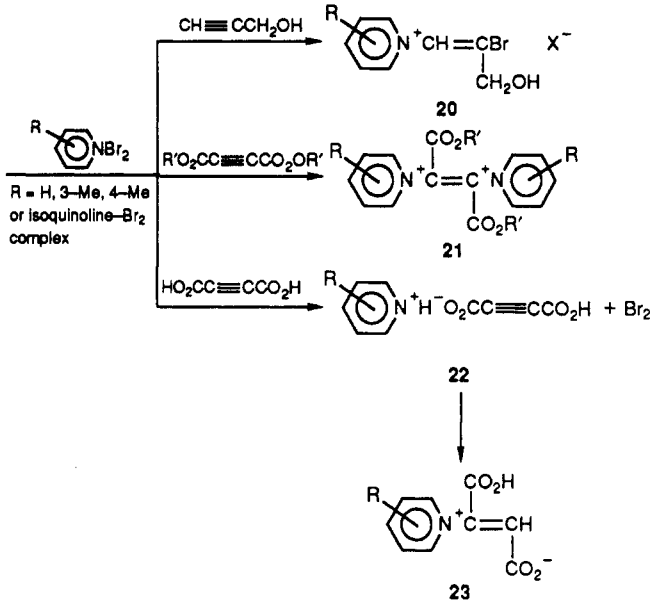
Analogous addition reactions have been studied for monomeric pyridine complexes with various olefinic systems.[26-30] Increased stereospecificity has been found to the pyridine–halogen complexes as compared with the free halogens. In contrast with the established mechanism for halogen addition, where the electrophilic attack depicted in reaction 4 is rate determining, a mechanism



has been proposed for the pyridine–bromine complex where the nucleophilic step shown in reaction 5 is rate determining.[27] In the case of pyridine–bromine chloride the same mechanisms may apply, but this requires further study. Kinetic measurements with the polymeric reagents will probably be obscured by transport phenomena within the polymeric particles.

The quaternization that the polymer undergoes during bromination of olefinic and acetylenic compounds poses interesting mechanistic problems. Detailed studies of the reaction between the pyridine–bromine complex and cy-

Scheme III
Three Quaternization Paths of Pyridine–Bromine Complex Concurrent with Bromine Addition to Acetylenic Compounds



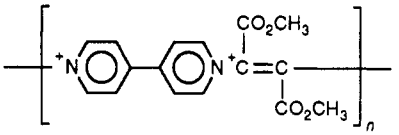
clohexene have been reported,[26] where the main product was quaternized pyridine. We found that with PVP–Br_2 the extent of quaternization with cyclohexene was much lower (about 5%), but other substrates had higher yields of quaternized spent polymer, for example, that recovered after bromination of propynol or the attempted bromination of acetylenedicarboxylic acid, as shown in Table II. This reaction also has practical aspects, as the original structure of the polymer becomes altered, and it is desirable to avoid this as much as possible in synthetic applications, where the polymeric reagent is regenerated. These problems are too complex to examine at the moment, since the altering factor remains attached to the polymer, which is difficult to analyze structurally. We proceeded, therefore, as a first stage, to investigate what quaternization processes can be expected in analogous nonpolymeric systems. Scheme III summarizes the systems that were studied, namely, bromine complexes with compounds containing the pyridyl moiety (or isoquinoline), reacting with various acetylenic compounds. The latter were chosen in preference to olefinic compounds, because of the easier workup and isolation of the quaternized byproducts, which are usually obtained only in low yields.

Three main types of quaternized compounds were obtained:

Single quaternization, yielding compounds of type **20**, where the nonbonded electron pair of the pyridyl group can compete with the halide ion (or a solvent moiety) as shown in reaction 5, after the electrophilic attack by bromine took place as shown in reaction 4. This should be the main path for quaternization of the polymer, taking place with the simplest olefinic and acetylenic substances. Evidence for quaternization of this type is shown by propynol in Table II, where about half of the bromine contained in the spent polymer is of the bromide type.

Double quaternization, yielding compounds of type **21**. A possible mechanism for this process could be the nucleophilic substitution of the bromine atom that became attached in a single quaternization process by a pyridyl moiety that became liberated in the main halogenation process. Double quaternization would lead to additional cross-linking when using a polymeric reagent. Evidence for quaternization of this type is shown by 4-cyclohexene-*cis*-1,2-dicarboxylic acid and indene in Table II, for which practically all the bromine contained in the spent polymer is of the bromide type.

The second quaternization step takes place in compounds such as diethyl acetylenedicarboxylate, where the three electronegative groups attached to the double bond after the first quaternization could lead either to nucleophilic substitution (second quaternization) or to C=C bond splitting. The mechanism of such reactions has been reviewed.[31] We do not know to what extent the bond splitting path takes place.



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The possibility of double quaternization induced us to test whether it can be used for polymerization reactions. Indeed, when the 4,4′-bipyridyl complex with bromine was used with esters of acetylenedicarboxylic acid, products were obtained that probably had the structure depicted by formula **24**, with an unknown degree of polymerization. These structures are totally conjugated and could have semiconductor properties.

Peculiar behavior was observed for acetylenedicarboxylic acid reacting with PVP–Br_2: the recovery of either a dibromo adduct or the original substrate was difficult. The results shown by this substrate in Table II, point to the possibility of part of the product and the substrate remaining attached to the spent polymer. Reaction of pyridine–bromine model complexes with acetylenedicarboxylic acid yielded compounds of type **23**, which were probably attained via the intermediate pyridinium salt **22** shown in Scheme III. This reaction course is similar to the N-acylvinylation of tertiary ammonium salts with acylacetylenes.[32] The structure of type **23** suggests that poly(vinylpyridine) may undergo interesting modifications by treatment with acetylenedicarboxylic acid: for example, changing the nature of the polymer from a weak anion exchanger to a weak cation exchanger or affording reactive intermediates after ring opening with nucleophilic reagents.[33] The behavior of PVP–Br_2 toward acetylenedicarboxylic acid may also bear some analogy to the solubilization process reported for cross-linked 4-vinylpyridine–ethylene dimethylacrylate resins.[34]

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Thermal Loss of Ultraviolet Absorbers from BPA-Polycarbonate

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ABSTRACT: The thermal loss from BPA-polycarbonate films of 15 UV absorbers from 4 generic classes of chemical compounds was determined at 125 and 190 °C, temperatures well above and below the glass transition temperature of the resin. The loss rates at 190 °C for all of the UV absorbers were rapid, with diffusion coefficients ranging from 0.3×10^{-8} to about 60×10^{-8} cm²/s. While several UV absorbers were lost only very slowly at 125 °C, others were not lost at all. These results were correlated with the UV absorbers' molar volumes as determined by density measurements. UV absorbers with molar volumes of 230 cm³/mol or less were lost and those with molar volumes of at least 260 cm³/mol were not.

Introduction

Most organic polymers degrade when they are exposed to ultraviolet light. Since degradation can reduce both the aesthetic and physical properties of polymers, various methods have been used to improve their UV stability. A common approach has been to use UV absorbers as bulk additives for polymers. In most cases, UV absorbers function by preferentially absorbing damaging UV radiation and dissipating the energy harmlessly. Their effectiveness depends on numerous factors including absorptivity, compatibility, stability, and distribution within the polymer. Above all, their effectiveness is dependent upon their concentration in the polymer, especially near the surface. It is critical, therefore, for polymers to have effective concentrations of UV absorbers after processing and long-term use.

Concentration changes of UV absorbers in polymers may be due to either chemical or physical losses. Chemical losses result from thermal, photooxidative, and oxidative reactions. Billingham and Calvert have outlined a model for the physical losses of additives from polymers.[1] According to their model, three parameters are required to allow prediction of loss under all conditions: the

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