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Functional Polymers. XXVI.* Co- and Terpolymers Involving Methacrylates, N-Vinylpyrollidone, and Polymerizable Ultraviolet Stabilizers and Antioxidants

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ABSTRACT

2(2-Hydroxy-5-isopropenyl)2H-benzotriazole and 2(2-hydroxy-5-vinylphenyl)2H-benzotriazole, both of which are well-established polymerizable ultraviolet stabilizers, have been co- and terpolymerized with N-vinylpyrrolidone, 1,1,1-tris(trimethylsiloxy)-methacrylato-propylsilane, and various methacrylate esters. Additionally, 4-isopropenyl-2,6-ditertiarybutyl phenol was co- and terpolymerized with these monomers as such to provide polymer compositions stable against autoxidation or in combination with the 2(2-hydroxy-5-isopropenylphenyl)2H-benzotriazole to provide stability against autoxidation and photooxidation. The polymerizations resulted in insoluble polymers from which the ultraviolet stabilizer or the antioxidant could not be extracted or

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leached out. The stabilized polymers had water absorption behavior similar to that of co- and terpolymers without the incorporation of the polymerizable stabilizers.

INTRODUCTION

In recent years the preparation of polymerizable stabilizers, particularly of ultraviolet (UV) absorbers, has been the focus of increased attention [1, 2]. Much of the work has concentrated on polymerizable derivatives of 2(2-hydroxy-phenyl)2H-benzotriazole due to their superior efficiency for UV absorbing and energy dissipation of these compounds. Attention has been focused on the synthesis of polymerizable UV stabilizers of the 2(2-hydroxyphenyl)2H-benzotriazole family which are styrene derivatives [3-7]. Other recent work has concentrated on the synthesis and polymerization of polymerizable 2,6-ditertiarybutyl phenol derivatives which can act as stabilizers against autoxidation [8-10]. These polymerizable stabilizers once incorporated into the polymer backbone, result in long-lasting UV and oxidative stability [11].

Many polymeric materials that are available would benefit from polymer bound, nonleachable stabilizers to protect them from the harmful effects of increased temperature in the presence of some oxygen while the polymer is being fabricated or from the effects of UV light and oxygen while the polymeric material is aging.

Among these many polymeric materials are biomedical materials (for example, soft contact lenses). Early work on soft contact lenses was based on the work of Wichterle [12, 13]. O'Driscoll [14, 15] employed hydrophilic cross-linked methacrylic esters, particularly hydroxyethyl methacrylate (HEM) and N-vinylpyrollidone (NVP). Gaylord [16] improved on the important properties of the lens material and particularly the hydrophilicity of the lens material by using HEM and added silicon monomers (acrylates and methacrylates) to increase oxygen permeability. This conclusion was based on the fact that the characteristic necessary to have useful contact lenses is oxygen permeability in order to avoid the possible growth of anaerobic bacteria between the eye and the lens material. Ultimately, contact lens materials were developed that were co- or terpolymers, including polysiloxanylalkyl methacrylates); these as well as terpolymers of methacrylates or acrylates with NVP were investigated.

A patent by Chang [17] on "Hydrophilic, Soft and Oxygen Permeable Copolymer Compositions" describes materials for the production of soft contact lenses, artificial eyes, or other prosthetic devices. It claims a composition or compositions that have the characteristics of increased hydrophilicity, softness after hydration, and oxygen permeability; the patent examples describe most prominently compositions containing NVP in 30 to 50%, the silicon monomer, 3MS, in 25 to 50%, about 12 to 30% of MMA, and a small amount, perhaps 2-3%, of EDM as cross-linking agent.

We can consequently see three stages in the development of materials with potential usefulness as soft contact lenses: (a) Hydrogels involving HEM cross-linked with ethylene dimethacrylate (EDM) to provide the proper insoluble polymer matrix for the basic lens material, (b) poly(siloxanyl)esters of methacrylates (3MS) as comonomers to provide oxygen permeability while maintaining all the other desirable properties of HEM hydrogels, (c) use of NVP in combination with or without HEM and other acrylates or methacrylates to provide the hydrophilic properties and poly(siloxanyl) esters of methacrylates for the proper combination of hydrophilicity and oxygen permeation of the material.

None of the authors of these compositions mentions the necessity or desirability of protecting the polymer composition against oxidative, photo (ultraviolet) degradation, oxidative photodegradation, or generally the need for screening the ultraviolet light in such compositions.

It is normally accepted that methacrylates do not need to be stabilized against autoxidation or photooxidation. New and more carefully conducted studies have revealed that methacrylates as well as acrylates are subject to oxidation or photooxidation; however, only when the methacrylate-containing material is exposed for longer periods of time to the environment [18]. Photostabilizers and perhaps even antioxidants would then be needed. Water also seems to play a part in this degradation process.

For some applications the screening of the ultraviolet light is also desirable. Ultraviolet absorbers of a permanent nature must be used, especially when the ultraviolet light (even the near-ultraviolet light) is dangerous to the body (for example, the eye) if the light is not screened and can penetrate. Contact with the human eye when it is exposed for long periods of time can lead to photooxidative changes. It was suggested that the photooxidation might involve tryptophan units [19]. It was also found that ascorbic acid [20] inhibits this photooxidation of tryptophan in the eye. These findings seem to suggest that ascorbic acid acts as a ultraviolet stabilizer/antioxidant for the eye. Additional stabilization in lens materials as afforded by stabilized contact lenses would be most essential, especially for those people who have had their lens removed.

It should also be mentioned that while ultraviolet stabilizers or antioxidants of the low molecular weight category are usually phenols, by the very nature of this structure it can potentially cause irritations or allergic reactions. Recent work has suggested that polymeric materials of the same basic chemical structure and functionality (as contrasted to low molecular weight compounds) are nonallergenic [21].

It was the objective of this work to incorporate 2(2-hydroxy-isopropenylphenyl)2H-benzotriazole (2H5P), 2(2-hydroxy-5-vinylphenyl)-2H-benzotriazole (2H5V), and 4-isopropenyl-2,6-diteryiarybutyl phenol (4ITP) into co- and terpolymers with NVP, various acrylates, methacrylates, and 3MS.

EXPERIMENTAL

Materials

3-Methacryloxypropyltrimethoxysilane (3MS) (Petrarch Sustem) and O-trimethylsilyl acetate (OTA) (Petrarch Systems), and tetraethyleneglycoldimethacrylate (TEGDM) (Pfaltz and Bauer) were used as received.

Ethyl methacrylate (EMA) (Aldrich Chemical Co.), methyl methacrylate (MMA) (Aldrich Chemical Co.), isobutyl methacrylate (IMA) (Pfaltz and Bauer), and 2-ethylhexyl methacrylate (EHM) (Pfaltz and Bauer) were washed twice with 5% aqueous sodium hydroxide and twice with distilled water to remove the inhibitor. After drying over magnesium sulfate, they were distilled under nitrogen at reduced pressure.

N-Vinylpyrrolidone (NVP) (Aldrich Chemical Co.) was distilled at 10 mmHg under nitrogen.

Azobisisobutyronitrile (AIBN) (Aldrich Chemical Co.) was recrystallized three times from absolute methanol and dried for one day at 0.05 mmHg at room temperature.

2(2-Hydroxy-5-isopropenylphenyl)2H-benzotriazole (2H5P) [6] and 4-isopropenyl-2,6-ditertiarybutyl phenol (4ITP) [10] were prepared in our earlier work on ultraviolet stabilizers. 2(2-Hydroxy-5-vinylphenyl)2H-benzotriazole (2H5V), previously made and kept stabilized with picric acid, was recrystallized twice from absolute methanol and once from n-hexane to remove the picric acid stabilizer. It was then dried for one day at 0.05 mmHg at room temperature.

Measurements

Ultraviolet spectra were recorded on a Beckman MVI spectrometer. The samples were measured in the form of solutions in n-hexane (HPCL Grade, Fischer Scientific Co.). The solutions were obtained from the extraction of the polymers with n-hexane under dry nitrogen in a Soxhlet extractor for one day.

All polymers were placed for one week in a 93% relative humidity chamber. The polymers were predried under vacuum at 100°C and 0.5 mmHg for two days. The water uptake at 93% humidity was done in a desiccator by exposing the polymer samples to a saturated aqueous potassium nitrate solution atmosphere for at least one week [20].

Microanalyses (C, H, N, Si) were done at the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, Massachusetts.

Preparations

Monomer Synthesis

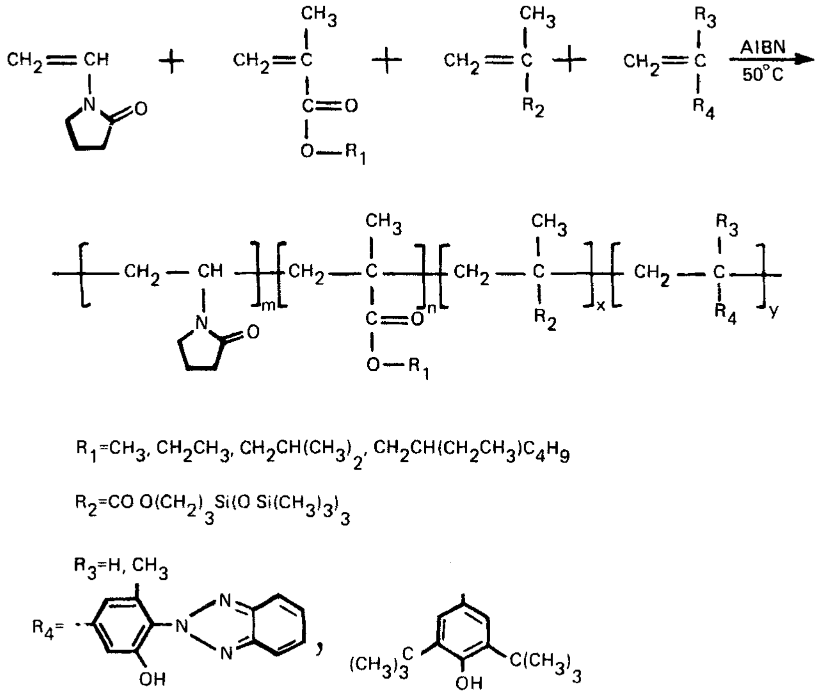
1,1,1-Tris(trimethylsiloxy)methacrylatopropyl silane (3MS). This monomer was prepared by the method of Gaylord. To a cooled, stirred mixture of 3-methacryloxypropyltrimethoxy silane (21.9 g, 0.088 mol) and O-trimethylsilylacetate (35 g, 0.27 mol) was added 4.3 mL of ethyl sulfuric acid–prepared by adding 14 g of concentrated sulfuric acid to a cooled mixture of 7 g of absolute ethanol and 10 mL of distilled water. After two days stirring at room temperature under dry nitrogen, the oily layer was separated and washed with sodium bicarbonate solution, water, and dried over anhydrous sodium sulfate. After distillation at 42°C and 0.25 mmHg to remove ethyl acetate, the monomer was stored in the refrigerator.

Polymerizations

Terpolymerization of Methyl Methacrylate (MMA), N-Vinylpyrrolidone (NVP), 1,1,1-Tris(trimethylsiloxy)methacrylatopropyl Silane (3MS), and 2(2-Hydroxy-5-vinylphenyl)2H-benzotiazole (2H5V). A 20-mL polymerization tube was charged with AIBN (30 mg, 0.18 mmol), MMA (0.94 g, 9.4 mmol), NVP (0.98 g, 8.8 mmol), 3MS (0.99 g, 2.4 mmol), and 2H5V (30 mg, 0.13 mmol). After three freeze-thaw cycles at 0.05 mmHg pressure to degas the homogenous mixture, the tube was sealed and allowed to react for 40 h at 50°C followed by 10 h at 100°C. The tube was opened, the solid clear plug extracted under dry nitrogen in a Soxhlet extractor with n-hexane, and then dried under vacuum of 0.05 mmHg for one day to give the terpolymer in quantitative yield. All other polymerizations described in Table 1 were carried out similarly.

Analysis: Calculated for $-\!\!(C_5H_8O_2)_{\overline{0.45}}(C_6H_9N_3O_3)_{\overline{0.42}}(C_{16}H_{38}O_5Si_4)_{\overline{0.12}}(C_{14}H_{11}N_3O)_{\overline{0.01}}$: C, 56.9%; H, 8.4%; N, 4.5%; Si, 8.8%. Found: C, 56.1%; H, 8.5%; N, 4.4%; Si, 7.4%.

Terpolymerization of N-Vinylpyrrolidone (NVP), 1,1,1-Tris(trimethylsiloxy)methacrylatopropyl silane (3MS), Ethyl Methacrylate (EMA), and 2(2-Hydroxy-5-isopropenylphenyl)2H-benzotriazole (2H5P). A 20-mL polymerization tube was charged with AIBN (34 mg, 0.21 mmol), NVP (0.98 g, 8.8 mmol), 3MS (0.99 g, 2.4 mmol), EMA (0.91 g, 8.0 mmol), and 2H5P (30 mg, 0.21 mmol). After three freeze-thaw cycles at 0.05 mmHg pressure to degas the homogeneous mixture, the tube was sealed and allowed to react for 40 h at 50°C followed by 10 h at 100°C. The tube was opened, the solid clear plug extracted one day in a Soxhlet extractor with n-hexane, and the polymer was then dried at 0.05 mmHg for one day and gave a quantitative



SCHEME 1.

yield of terpolymer. All other polymerizations described in Table 2 were performed similarly.

Analysis: Calculated for $-(C_4H_9NO)_{0.45}-(C_{16}H_{38}O_5Si_4)_{0.12}-(C_6H_{10}O_2)_{0.41}-(C_{15}H_{13}N_3O)_{0.01}$: C, 58.0%; H, 8.5%; N, 4.5%; Si 9.0%. Found: C, 56.6%; H, 8.8%; N, 4.6%; Si, 7.6%.

Terpolymerization of N-vinylpyrrolidone (NVP), 1,1,1-Tris(trimethylsiloxy)methacrylatopropyl Silane (3MS), 2-Ethylhexyl Methacrylate (EHM), and 4-Isopropenyl-2,6-ditertiarybutyl phenol (4ITP): A 20-mL polymerization tube was purged with dry, oxygen-free nitrogen for 30 min and under this inert gas flow was charged with AIBN (30 mg, 0.18 mmol), NVP (0.98 g, 8.8 mmol), 3MS (0.99 g, 2.4 mmol), EHM (0.88 g, 4.4 mmol), and 4ITP (43 mg, 0.17 mmol). After three freeze-thaw cycles at 0.05 mmHg pressure to degas the homogeneous mixture, the tube was sealed and allowed to react for 60 h at 50°C followed by 10 h at 100°C. The tube was opened, the solid, clear plug extracted for one day in a Soxhlet extractor with n-hexane, dried under vacuum at 0.05 mmHg for one day, and gave a quantitative yield of polymer.

RESULTS AND DISCUSSIONS

Copolymerizations and terpolymerizations with one or a combination of more than one ultraviolet polymerizable stabilizers and/or polymerizable antioxidants have been carried out with methacrylate esters, NVP, and 3MS. 2H5P and 2H5V as polymerizable ultraviolet stabilizers and 4ITP as a polymerizable antioxidant were used. The copolymerizations were accomplished according to the general reaction scheme for the copolymerization of stabilizers in terpolymer compositions. Previous experience in our laboratory on polymerizable 2(2-hydroxyphenyl)2H-benzotriazoles, the copolymerization of 2H5V [3-5] and 2H5P [6] grafting of 2H5V [23], and copolymerizations with 4ITP [10] as well as the utilization of other polymerizable stabilizers, particularly those of methyl vinylsalicylates [24], have shown that polymerizations can be carried out effectively. The free phenolic hydroxyl group present in the polymerization mixture does not inhibit the polymerization if oxygen is rigorously excluded from the reaction mixtures. As a consequence, all our polymerizations had to be performed in sealed tubes after thorough degassing by several freeze-thaw cycles and at pressures of below 0.05 mmHg. It appears that 4ITP is particularly sensitive to the presence of traces of oxygen in the polymerization mixture, and careful flushing of the polymerization tubes with inert gas was necessary prior to charging.

Table 1 shows the terpolymerization experiments of 2H5V with NVP, 3MS, and MMA. The 2H5V content in all those polymerization mixtures and presumably in the terpolymers was between 0.6 and 1.1 mol%. In three cases MMA was the third monomer at 45 mol% with about 42 mol% NVP and 12 mol% as the terpolymer. In one case, TEGDM was the cross-linking monomer present at 2 mol% in the comonomer mixture and in another case 2H5V was left out of the polymerization mixture. Other third monomers in these polymerizations included EMA at 41 mol%, IMA at 36 mol%, and EHM at 30 mol% in the mixture of the monomers and presumably in the terpolymer, in addition to 11-14 mol% of 3MS and about 0.7 mol% of 2H5V. The amount of NVP in these three terpolymer compositions ranged from 45 to 50 mol% of the total comonomer compositions.

Table 2 shows the terpolymerization experiments involving 2H5P. Here again MMA was used in two cases at 45 mol% with 42 mol% of NVP, 3MS at 11%, and 2H5P at 0.6 mol%. In one of the copolymerization mixtures TEGDM was used at 2.2 mol% as the cross-linking comonomer.

In addition, three more compositions were made where MMA was replaced by other acrylic monomers. NVP was at 35 to 55 mol% while the amount of 3MS in the polymer was 12 to 15 mol%. Amounts of the 2H5P in the comonomer mixture were 0.6 to 0.8 mol%. In the case where EMA was the comonomer, it was used at 41 mol%, IMA at 35 mol%, and EHM at 28 mol%. One series of polymerization ex-

TABLE 1. Terpolymerization Experiments Involving 2(2-Hydroxy-5-vinylphenyl)2H-benzotriazole[a]

	MMA		NVP		3MS		Other comonomer			2H5V	
Experiment	g	mol%	g	mol%	g	mol%	Type	g	mol%	g	mol%
Ia	-	-	0.98	77	0.99	21	-	-	-	0.030	1.1
Ib	0.94	45	0.98	42	0.99	12	-	-	-	0.030	0.6
Ic	0.94	44	0.98	41	0.99	11	TEGDM	0.16	2.2	0.030	0.6
Id	-	-	0.98	45	0.99	12	EMA	0.91	41	0.030	0.65
Ie	-	-	0.98	49	0.99	14	IMA	0.89	36	0.030	0.7
If	-	-	0.98	57	0.79	12	EHM	0.88	30	0.024	0.65
Ig	0.94	45	0.98	42	0.99	12	-	-	-	-	-

[a] Terpolymerization conditions: Initiator, AIBN, 1.0 mol%; temperature/time, 50°C/40 h, 100°C/10 h; sealed tube; pressure, 0.05 mmHg.

TABLE 2. Terpolymerization Experiments Involving 2(2-Hydroxy-5-isopropenylphenyl)2H-benzotriazole[a]

	MMA		NVP		3MS		Other comonomer			2H5P	
Experiment	g	mol%	g	mol%	g	mol%	Type	g	mol%	g	mol%
IIa	0.94	45	0.98	42	0.99	12	-	-	-	0.030	0.6
IIb	0.94	44	0.98	41	0.99	11	TEGDM	0.16	2.2	0.030	0.6
IIc	-	-	0.98	45	0.99	12	EMA	0.91	41	0.030	0.6
IId	-	-	0.98	49	0.99	14	IMA	0.89	35	0.030	0.7
IIe	-	-	0.98	55	0.99	15	EHM	0.88	28	0.030	0.8

[a] Terpolymerization conditions: Initiator, AIBN, 1.0 mol%; temperature/time, 50°C/41 h, 100°C/10 h; sealed tube; pressure, 0.05 mmHg.

periments also included terpolymerization of NVP and MMA with the polymerizable antioxidant, 4ITP, which was used in 0.6 to 1.1 mol%.

In three cases MMA was used at 45 mol% with 42 mol% of NVP and 12 mol% of 3MS. In one of the terpolymers 0.7 mol% 4ITP was incorporated. In another experiment in addition to 0.7 mol% 4ITP, 2H5P was also used as monomer; this polymerization was designed to impart both resistance to thermal oxidation (antioxidant) and resistance to photooxidation (ultraviolet stabilizer) into the polymer.

In one case TEGDM was used in 2.3 mol% as termonomer and cross-linking agent in addition to 4ITP. In three experiments NVP was used at a level of 45 and 55 mol% and 3MS at 12 to 15 mol%. MMA was replaced by EMA (41 mol%), EHM (25 mol%), EMA (41 mol%) and 2H5P (0.6 mol%) in addition to the 4ITP used as the polymerizable antioxidant (Table 3).

Table 4 shows the calculated and found amounts of carbon, hydrogen, silicon, and nitrogen by elemental analyses of our complicated polymeric compositions.

In all cases after isolation of the polymers and extraction with n-hexane in the Soxhlet extractor for two days and drying the polymers at 0.05 mmHg, it was found that the polymerizable stabilizers were incorporated quantitatively. To verify that 2H5V and 2H5P had been incorporated, the polymers were extracted in a Soxhlet extractor for two days with n-hexane and the extract was analyzed for the presence of extractable monomeric ultraviolet stabilizers by ultraviolet spectrophotometry. In no instance was any ultraviolet absorbing compound found in the extract to indicate that 2H5V or 2H5P had been extracted from the polymer. It should be remembered that 10^{-5} mol/L concentrations are normal for the measurement of the ultraviolet spectra of 2(2-hydroxyphenyl)2H-benzotriazoles, and concentrations of 10^{-6} to 10^{-7} mol/L are easily detectable.

To verify that ultraviolet stabilizers of low molecular weight could be extracted from polymers obtained by polymerizations of this type, 2H5P and poly-NVP were mixed in acetone solution, the solvent was then removed under reduced pressure, and the remaining mixture was extracted in the Soxhlet extractor for two days with n-hexane as had been done for the polymers containing the polymerizable stabilizer (2H5P was used in concentrations between 0.1 and 1.0%). Strong absorption measured in the ultraviolet at 310 and 340 nm clearly indicated the presence of 2H5P in the extract from the physical mixture, demonstrating that the low molecular weight ultraviolet stabilizer could readily be extracted with n-hexane by Soxhlet extraction from a polymer when not bound to the polymer backbone.

Some cross-linking had occurred in all polymers, not only in the presence of TEGDM, possibly as a consequence of the presence of phenolic hydroxyl groups acting as effective chain transfer agents in bulk polymerizations.

On the other hand, in separate work in this laboratory [25] the copolymerization of 2(2-hydroxy-4-acryloxy(methacryloxy)phenyl)2H-benzotriazole [BDHA(M)] with styrene, MMA, and n-butyl acrylate

TABLE 3. Terpolymerization Experiments Involving 4-Isopropenyl-2,6-ditertiarybutyl phenol[a]

	MMA		NVP		3MS		Other comonomer			4ITP	
Experiment	g	mol%	g	mol%	g	mol%	Type	g	mol%	g	mol%
IIIa	0.94	45	0.98	42	0.99	12	-	-	-	0.034	0.7
IIIb	0.94	44	0.98	41	0.99	11	TEGDM	0.16	2.3	0.029	0.6
IIIc	-	-	0.98	45	0.99	12	EMA	0.91	41	0.038	0.8
IIId	-	-	0.98	55	0.99	15	EHM	0.88	28	0.043	1.1
IIIe	0.94	45	0.98	42	0.99	11	2H5P	0.029	0.57	0.035	0.7
IIIf	-	-	0.98	45	0.99	12	EMA 2H5P	0.91 0.028	41 0.56	0.028	0.6

[a] Terpolymerization conditions: Initiator, AIBN, 1.0 mol%; temperature/time 50°C/60 h, 100°C/10h; sealed tube; pressure, 0.05 mmHg.

TABLE 4. Selected Elemental Analyses of Polymers

	C		H		Si		N	
Sample[a]	Theoretical	Found	Theoretical	Found	Theoretical	Found	Theoretical	Found
Ia	55.5	53.1	8.6	8.6	13.0	11.6	6.6	6.0
Ib	56.9	56.1	8.4	8.5	8.9	7.4	4.5	4.4
If	61.8	62.8	9.2	9.6	7.9	5.1	4.9	5.6
Ig	56.7	56.2	8.4	8.8	9.0	8.6	4.9	3.8
IIa	56.8	56.2	8.4	8.5	8.0	7.5	4.5	4.5
IIc	58.0	56.6	8.5	8.0	9.0	7.6	4.5	4.6
IIe	60.7	59.1	9.4	9.3	9.1	7.9	4.5	4.8

[a] Sample designations as in Tables 1-3.

(BA) was studied with AIBN on the initiator. In copolymerizations involving BA, insoluble gels (of apparently cross-linked polymers) were observed. When the copolymerization was carried out in very dilute solutions, no gels were found. As the concentration of BA increased, increasing amounts of gel were found. Complete gelation was observed when the BA polymerization was carried out in bulk. The amount of gel did not seem to depend on the amounts of BDHA or BDHM present in the comonomer feed. No insoluble gels were found in solution homopolymerizations of BDHA or BDHM or in copolymerization with St and MMA.

We have not unequivocally solved the problem of why all our polymers were insoluble, but it should be remembered that all our polymerizations were carried out in the bulk. It is in these cases that cross-linking can readily occur.

The determination of the incorporation of the polymerizable ultraviolet stabilizers had to be done by examining the extractables (long-term Soxhlet extraction with n-hexane) rather by the normally more accurate determination of the stabilizer content in the (cross-linked and insoluble) polymers.

We have shown in the past in copolymerizations involving 2H5P, 2H6V, but particularly 4ITP that cross-linking (chain transfer) does not occur when the co- or terpolymerizations were carried out in solution or emulsion; even in bulk, cross-linking occurred only in isolated cases.

The nonextractability and nonleachability of a stabilizer, whether it is an ultraviolet absorber or an antioxidant, or for that matter a flame retardant, is very essential from both the viewpoint of stabilization and because of the possible or real biological or toxicological effects of low molecular weight stabilizers. Monomeric materials that can be leached out from the polymeric matrix in contact with the human body, especially when the compounds belong to the category of the aromatic phenols or amines, can pose a potential health hazard or, even more importantly, could cause allergic reactions.

An important feature of hydrogels is the appropriate absorption of the correct amount of water. It was important for our polymer compositions to ascertain that the water absorption was not diminished significantly when our millicomponent polymers contained polymerbound antioxidants or ultraviolet stabilizers. In actual fact, the water absorption of the polymers containing these polymerized stabilizers was very similar to those of polymers without stabilizers. This result is not surprising since the amount of stabilizer is very small, as only about 1 mol% of the stabilizer was used in our polymer compositions.

The amount of water gain was measured after the polymeric materials were exposed for 1 week to 93% relative humidity. The water uptakes of the various polymers are significant but only of relative value. As expected, the water uptake value is directly related to the amount of NVP incorporated into the polymer. When the total polymer contained 77 mol% NVP (in addition to the other comonomer components), the

TABLE 5. Characterization of Selected Polymers for Water Uptake

Sample[a]	Weight gain[b]
Ia	28.2
Ib	12.1
If	20.6
Ig	12.8
IIa	15.5
IIc	14.2
IIe	13.0
III a	13.2
IIIb	9.7
IIIc	12.4

[a] Sample designations as in Tables 1-3.
[b] Values reported as total weight percent gain after one week in 93% relative humidity.

water uptake was almost 30%; at 57 mol% NVP, the water uptake was slightly more than 20%.

When the comonomer composition contained 42-45 mol% of NVP, the weight gain of the water uptake was between 12 and 15%. The water uptake is somewhat lower in more highly cross-linked systems of similar composition as in the case of IIIb (Table 5) which has TEGDM as a cross-linking agent. This polymer, although it has 45% NVP, has a water uptake of only 9.7%. Another apparent exception is the case where the methacrylate polymer is more hydrophobic, such as with 2-ethylhexyl methacrylate as the comonomer. Even higher amounts of NVP comonomer keep the water uptake of the polymer at a low level (13 to 15%).

In conclusion, 2H5V, 2H5P, and 4ITP have been successfully incorporated into co- and terpolymers which also include NVP, methacrylate esters, MMA, and 3MS. These polymers have monomeric ultraviolet absorbers and antioxidants completely incorporated into the polymer as judged by long-term Soxhlet extraction with n-hexane. It has been demonstrated that a mixture of poly-NVP with low molecular weight ultraviolet stabilizers, especially 2H5P (mixtures prepared by solution blending), can be easily separated and the low molecular weight stabilizer extracted under these conditions.

It has also been shown that polymers having polymerizable ultraviolet absorbers or polymerizable antioxidants show water absorptions similar to polymers without them (control); the water absorption could be directly related to the amount of NVP or other hydrophilic monomers in the polymers.

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