REACTIVITY RATIOS AND UV SPECTRAL CHARACTERISTICS
OF COPOLYMERS OF VINYL OR ISOPROPENYL DERIVATIVES
OF 2-(2-HYDROXYPHENYL)-2H-BENZOTRIAZOLES*

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Dedicated to Dr M. Lazár on the occasion of his 60th brithday.

The preparation of polymeric UV stabilizers by copolymerization of polymerizable UV stabilizers like 2-(2-hydroxy-5-vinylphenyl)-2H-benzotriazole (2H5V) and 2-(2-hydroxy-5-isopropenyl-phenyl)-2H-benzotriazole (2H5P) with styrene (S), methyl methacrylate (MMA), and butyl acrylate (BA) was studied. Copolymerization parameters for six pairs of monomers, i.e. 2H5V–S, 2H5V–MMA, 2H5V–BA, 2H5P–S, 2H5P–MMA, and 2H5P–BA and UV spectra of the 2H5P copolymers were determined. The effect of stiffness of the polymer chain on UV spectra of copolymers studied is discussed.

One of the most serious shortcomings of low molecular weight stabilizers is that significant amounts are often lost from the polymer before they fulfil their function because of volatilization during fabrication or because of exudation, leaching or solvent extraction during the use.

One solution of this problem is to build the stabilizer molecules into the polymer chains[1]. Such a polymeric stabilizer mixed with a polymer cannot readily be removed from the polymer[2]. Introduction of the stabilizer molecules into the polymer chains may be done in several ways: through the attachment of the stabilizer functionality to the reactive end groups of the polymer or oligomer-endcapping[3], substituting a reactive stabilizer onto the polymer chain[4], by grafting the vinyl derivative of the stabilizer to the polymer chain[5,6] or by copolymerization of the vinyl or acrylic derivative of the stabilizer with a suitable vinyl monomer[7-14].

In this paper, we describe the preparation of effective polymeric UV stabilizers by copolymerization of polymerizable UV stabilizers; 2-(2-hydroxyphenyl)-2H--benzotriazoles with vinyl- or isopropenyl groups in the 5 position of the phenol ring were copolymerized. We selected common vinyl monomers as comonomers when expected good compatibility with a large number of polymers.

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EXPERIMENTAL

Materials

The polymerizable ultraviolet absorbers 2-(2-hydroxy-5-vinylphenyl)-2H-benzotriazole (2H5V) and 2-(2-hydroxy-5-isopropenylphenyl)-2H-benzotriazole (2H5P) were synthesized as described previously[5,8].

Styrene (S) (Aldrich Chemical Co.), methyl methacrylate (MMA) (Eastman Kodak Co.) and butyl acrylate (BA) (Polysciences, Inc.), were washed twice with 5% aqueous sodium hydroxide solutions and twice with water to remove the polymerization inhibitor; the monomers after drying over anhydrous sodium sulfate were distilled twice under reduced pressure immediately before use.

2,2'-Azobis(isobutyronitrile) (AIBN) (Aldrich Chemical Co.) was recrystallized three times from dry methanol and dried for 24 hours at 7 Pa at room temperature.

Copolymerization Procedure

2H5V or 2H5P were copolymerized with the S, MMA and BA. The polymerization procedure was the same in all cases: A 5-ml polymerization tube was charged with AIBN ($1-1.5$ mg, $0.006-0.009$ mmol), the comonomer (S, MMA or BA) ($0.5-1.0$ g, $5-10$ mmol) and 2H5V or 2H5P ($0.05-0.5$ g, $0.2-2$ mmol). The total amount of monomer mixture was $0.8-1.2$ g ($8-12$ mmol). No solvent was used. After degassing the polymerization mixture by three freeze--thaw cycles under nitrogen, the polymerization tube was sealed at 0.05 mm and placed in a constant temperature bath at 50°C. The polymerization was allowed to proceed for 4 to 8 hours, so that the conversion did not exceed 5%. The tube was then opened, the mixture diluted with chloroform and the copolymer precipitated by pouring the solution into methanol. The copolymer was isolated by filtration, placed into methanol (50 ml) for 12 hours in order to remove any unreacted monomer (2H5V or 2H5P). After filtration the copolymer was washed with methanol and dried in a drying pistol (56°C, 6.7 Pa).
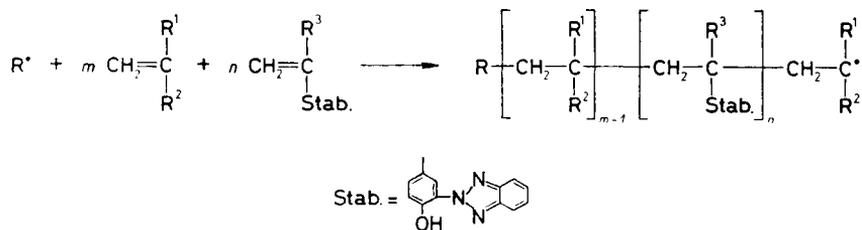
Measurements

Ultraviolet absorptions were measured in chloroform (Spectrograde, Lachema) on a Specord UVIS (made in the G.D.R.) spectrometer in a double beam servo mode. The sample solutions having the concentration of monomer units of 2H5V or 2H5P about $1 . 10^{-4}$ mol dm^{-3} were measured in quartz cells which had a 1.0 cm optical path length. The maximum absorbances and corresponding wavelength were determined by dialing in the wavelength and recording the absorbance value presented on the digital display.

RESULTS AND DISCUSSION

The copolymerization of three monomers, styrene (S), methyl methacrylate (MMA), and butyl acrylate (BA) with the polymerizable UV absorbers, viz. 2-(2-hydroxy-5--vinylphenyl)-2H-benzotriazole (2H5V) and 2-(2-hydroxy-5-isopropenylphenyl-2H--benzotriazole (2H5P) was studied. For six pairs of monomers, i.e. 2H5V–S, 2H5V--MMA, 2H5V–BA, 2H5P–S, 2H5P–MMA and 2H5P–BA the copolymerization parameters were determined. A general scheme illustrates the copolymerization of

these monomer pairs initiated by a radical initiator (generated from the thermal dissociation of 2,2'-azobis(isobutyronitrile)) (see Scheme 1).

$$R^{\bullet} + m\ CH_2{=}\underset{R^2}{\overset{R^1}{C}} + n\ CH_2{=}\underset{Stab.}{\overset{R^3}{C}} \longrightarrow R{-}\left[CH_2{-}\underset{R^2}{\overset{R^1}{C}}\right]_{m-1}\left[CH_2{-}\underset{Stab.}{\overset{R^3}{C}}\right]_{n}{-}CH_2{-}\underset{R^2}{\overset{R^1}{C^{\bullet}}}$$

Stab. = 2-(2-hydroxyphenyl)benzotriazole

Monomer pair, no.	1	2	3	4	5	6
R^1	H	CH_3	H	H	CH_3	H
R^2	C_6H_5	$COOCH_3$	$COOC_4H_9$	C_6H_5	$COOCH_3$	$COOC_4H_9$
R^3	H	H	H	CH_3	CH_3	CH_3

SCHEME 1

Although copolymers of 2H5V and 2H5P with some comonomers have been prepared earlier[7-14], this copolymerization has not been studied from the point of view of determining the copolymerization parameters for the pairs of polymerizable ultraviolet absorbers and the three comonomers mentioned. Also, UV spectra of the 2H5P copolymers were determined[15,16].

The copolymerization of monomers 2H5V and 2H5P with S, MMA, and BA was carried out without solvent because such conditions would be used under conditions of practical application. This approach has the disadvantage because both 2-(2--hydroxyphenyl)benzotriazole monomers in the comonomers S, MMA and BA have a relatively low solubility at the polymerization temperature of 50°C. The solubility of 2H5V in S, MMA, and BA varies between 15 and 20 mole % at 50°C. The solubility of 2H5P in these monomers is little lower, i.e. about 10 mole % at 50°C (ref.[17]). On the other hand, a 10—20 mole % content of a 2-(2-hydroxyphenyl)-benzotriazole structure in the copolymer would be sufficient for the application of these copolymers as polymeric UV absorbers for commodity polymers. Higher contents of the stabilizer unit would raise compatibility problems. The copolymerization parameters had to be determined from a relatively narrow concentration region of 2H5V or 2H5P in the comonomer mixtures; this limitation influenced the accuracy of their determination.

During the copolymerization of 2H5V and of 2H5P with S at 50°C we obtained the composition of the copolymer as a function of the feed composition (Tables I and II). The composition of the copolymers were calculated from elemental nitrogen analysis in the copolymer samples. The conversion of copolymers prepared did not

exceed 5%. As control, we determined the content of 2-(2-hydroxyphenyl)benzo-
triazole unit in the copolymers by UV spectroscopy (Table II). The values of the

TABLE I

Copolymerization of styrene (M_1) with 2-(2-hydroxy-5-vinylphenyl)-2H-benzotriazole (M_2) at
50°C initiated with 2,2'-azobis(isobutyronitrile), 0·1 wt. %. The composition of copolymer
(indexes of monomer units correspond to indexes of monomers) was found out from nitrogen
content

[M_1]	[M_2]	Conversion %	N %	[U_1]	[U_2]
mole %				mole %	
97·8	2·2	1·3	1·24	96·8	3·2
95·2	4·8	3·8	2·17	94·2	5·8
94·6	5·4	1·9	2·91	92·1	7·9
93·5	6·5	3·9	2·93	92·0	8·0
86·6	13·4	2·4	5·25	84·4	15·6
85·9	14·1	5·0	6·04	81·5	18·5
84·8	15·2	3·9	5·89	82·1	17·9
75·9	24·1	1·1	7·50	75·6	24·4

TABLE II

Copolymerization of styrene (M_1) with 2-(2-hydroxy-5-isopropenylphenyl)-2H-benzotriazole
(M_2) at 50°C initiated with 2,2'-azobis(isobutyronitrile) 0·1 wt. %. The composition of copolymer
was found out from nitrogen content

[M_1]	[M_2]	Conversion %	N %	[U_1]	[U_2]
mole %				mole %	
98·2	1·8	2·6	0·7	98·3	1·7
97·6	2·4	3·6	0·8	97·9	2·1
97·0	3·0	2·6	1·1	97·0	3·0 (2·7)[a]
96·4	3·6	1·2	1·2	97·0	3·0
95·0	5·0	3·2	1·8	95·2	4·8
93·9	6·1	4·1	2·1	94·5	5·5
93·1	6·9	3·4	2·2	94·1	5·9
91·9	8·1	3·9	2·6	92·9	7·1 (7·2)[a]
88·9	11·1	1·0	3·2	91·0	9·0

[a] UV determination.

TABLE III

Copolymerization of methyl methacrylate (M_1) with 2-(2-hydroxy-5-vinylphenyl)-2H-benzo-triazole (M_2) at 50°C initiated with 2,2′-azobis(isobutyronitrile) 0·1 wt. %; the composition of copolymer was found out from nitrogen content

[M_1]	[M_2]	Conversion %	N %	[U_1]	[U_2]
mole %				mole %	
97·4	2·6	5·4	2·5	93·6	6·4 (6·5)[a]
95·4	4·6	2·9	3·7	89·9	10·1
95·0	5·0	3·1	4·4	87·6	12·4
94·1	5·9	4·1	4·8	86·3	13·7 (13·5)[a]
91·0	9·0	1·1	6·4	80·6	19·4
90·6	9·4	1·1	6·7	79·5	20·5
87·3	12·7	1·0	7·6	75·9	24·0
84·2	15·8	1·1	8·7	71·2	28·8
82·6	17·4	2·4	9·3	68·3	31·7
80·6	19·4	4·0	9·7	66·2	33·8 (31·2)[a]

[a] UV determination.

TABLE IV

Copolymerization of methyl methacrylate (M_1) with 2-(2-hydroxy-5-isopropenylphenyl)-2H--benzotriazole (M_2) at 50°C initiated with 2,2′-azobis(isobutyronitrile) 0·1 wt. %; the composition of copolymer was found out from nitrogen content

[M_1]	[M_2]	Conversion %	N %	[U_1]	[U_2]
mole %				mole %	
97·7	2·3	3·6	2·1	94·6	5·4 (5·8)[a]
97·6	2·4	2·0	2·2	94·4	5·6
97·2	2·8	2·0	2·4	93·9	6·1
96·1	3·9	2·2	3·3	90·9	9·1 (9·8)[a]
95·4	4·6	1·5	3·6	90·2	9·8 (9·9)[a]
93·6	6·4	2·6	4·4	87·6	12·4
93·4	6·6	2·2	4·5	87·3	12·7
90·8	9·2	2·4	5·0	85·3	14·7
89·3	10·7	1·3	6·1	81·5	18·5

[a] UV determination.

TABLE V

Copolymerization of butyl acrylate (M_1) with 2-(2-hydroxy-5-vinylphenyl)-2H-benzotriazole (M_2) at 50°C initiated with 2,2′-azobis(isobutyronitrile) 0·1 wt. %; the composition of copolymer was found out from nitrogen content

[M_1]	[M_2]	Conversion %	N %	[U_1]	[U_2]
mole %				mole %	
97·1	2·9	3·9	4·23	85·5	14·5
96·3	3·7	3·9	5·00	82·5	17·5
95·5	4·5	4·3	5·61	80·0	20·0
94·8	5·2	1·7	6·40	76·6	23·4
93·9	6·1	2·5	6·85	74·6	25·4
93·2	6·8	2·3	7·09	73·5	26·5
91·0	9·0	1·8	8·35	67·5	32·5
90·4	9·6	4·5	8·34	67·5	32·5
90·1	9·9	1·2	8·59	66·3	33·7
86·3	13·7	2·5	9·77	60·1	39·9

TABLE VI

Copolymerization of butyl acrylate (M_1) with 2-(2-hydroxy-5-isopropenylphenyl)-2H-benzotriazole (M_2) at 50°C initiated with 2,2′-azobis(isobutyronitrile) 0·1 wt. %; the composition of copolymer was found out from nitrogen content

[M_1]	[M_2]	Conversion %	N %	[U_1]	[U_2]
mole %				mole %	
98·0	2·0	2·1	3·9	86·6	13·4
97·4	2·6	1·8	4·8	87·8	17·2
96·1	3·9	2·3	5·9	78·6	21·4
95·8	4·2	2·2	6·3	76·6	23·4
94·4	5·6	3·8	7·1	72·6	27·4
94·2	5·8	3·3	7·0	73·2	26·8
92·5	7·5	2·4	7·8	69·1	30·9
91·3	8·7	3·1	8·3	66·5	33·5
91·3	8·7	3·6	8·2	66·9	33·1
89·9	10·1	3·0	8·6	64·9	35·1
89·3	10·7	4·2	8·7	64·2	35·8

copolymer composition found by this method are in good agreement with the values obtained by elemental nitrogen analysis.

Copolymerization curves for 2H5V and 2H5P with MMA and BA were obtained in a similar way (Tables III—VI).

TABLE VII

Copolymerization parameters for vinyl monomers (M_1): styrene (S), methyl methacrylate (MMA), butyl acrylate (BA) with benzotriazoles (M_2): 2-(2-hydroxy-5-vinylphenyl)-2H-benzotriazole (2H5V) and 2-(2-hydroxy-5-isopropenylphenyl)-2H-benzotriazole (2H5P), respectively at 50°C

Monomer pair, No.	M_1	M_2	r_1	r_2
1	S	2H5V	0.71 ± 0.20	0.10 ± 0.50
2	MMA	SH5V	0.45 ± 0.01	1.18 ± 0.30
3	BA	2H5V	0.22 ± 0.00	2.09 ± 0.28
4	S	2H5P	1.07 ± 0.13	0.01 ± 0.12
5	MMA	2H5P	0.41 ± 0.03	0.03 ± 0.07
6	BA	2H5P	0.12 ± 0.01	0.76 ± 0.25

TABLE VIII

UV absorption maxima of 2-(2-hydroxy-5-vinylphenyl)-2H-benzotriazole (2H5V) and 2-(2--hydroxy-5-isopropenylphenyl)-2H-benzotriazole (2H5P) copolymers (chloroform): ε represents the value of molar decadic extinction coefficient of monomers or monomer units of 2H5V or 2H5P

Copolymer from monomer pair[a]	$\varepsilon \cdot 10^{-4}$, dm^3 cm^{-1} mol^{-1} (λ_{max}, nm)	References
2H5V[a]	1.23 (350), 1.74 (301)	8
2H5V[b]	1.34 (340), 1.35 (299)	8
2H5V–S	1.33 (342), 1.38 (299)	8
2H5V–MMA	1.59 (341), 1.47 (300)	8
2H5V–BA	1.71 (339), 1.50 (299)	8
2H5P–S	0.98 (343), 1.03 (303)	this work
2H5P–MMA	1.19 (338), 1.22 (299)	this work
2H5P–BA	1.60 (330) 1.54 (300)	this work
2H5P[c]	1.22 (349), 1.70 (301)	10

[a] UV measurement of the monomer, it has also a third UV absorption maxima at 268 nm, $\varepsilon = 1.86 \cdot 10^4$ dm^3 cm^{-1} mol^{-1}; [b] homopolymer; [c] UV measurement of the monomer.

Calculation of the copolymerization parameters for the monomers S, MMA, and BA with 2H5V and 2H5P respectively, was done according to the Kelen–Tüdös method[18] and the values of the parameters are listed in Table VII. A lower r_1 value expresses the higher rate of the addition of 2H5V to PBA propagating radical compared with PMMA and the PS propagating radical. On the other hand, higher r_2 value expresses a decreasing reactivity of BA towards the 2H5P propagating radical with respect to S and MMA.

The UV characterizations of all copolymers of 2H5P were carried out (Table VIII). The UV characterization of the copolymers of 2H5V had been determined earlier[8,10] but are also reported here.

Table VIII shows that the highest UV absorption maxima for both 2H5V and 2H5P comonomer units are in their copolymers with BA; the lowest extinction coefficients in UV absorption spectra are found in the copolymers of styrene. Because of slight differences in the exponents of the Mark–Houwink relation for polystyrene, poly(methylmethacrylate), and poly(butyl acrylate) in chloroform[19], we cannot ascribe the differences in the UV absorption maxima observed in the copolymers to differences in the coiling of the polymer molecules, which could affect the absorption spectra. The differences may be caused more by difference in the flexibility of the different polymer backbone chains or by difference in the size of the substituents of the comonomers, which may influence the planar arrangements of 2-(2--hydroxyphenyl)benzotriazole structure and their electronic overlap. Formation of the planar structure is caused by the formation of intramolecular hydrogen bond between hydroxyl group and the nitrogen atom of the benzotriazole ring followed by excitation. Ghiggino et al. and others[20,21] have found that the UV absorption maximum between 340 and 350 nm is caused by the intramolecular hydrogen bonded structure. The increase of the extinction coefficient of this UV absorption maximum of 2-(2-hydroxyphenyl)benzotriazoles in styrene copolymer over both types of methyl methacrylate to butyl acrylate copolymer (Table VIII) is in agreement with the increase of the flexibilities of the polymer chain in the particular sequence, with the decrease in the size of substituents in the comonomers. Smaller size of substituents with higher chain flexibility could favor the formation of the planar 2-hydroxyphenylbenzotriazole structures. It might be the reason why the change of the type of comonomer in the copolymerization from 2H5V or 2H5P leads to a change in the instensity of the absorption maxima or the extinction coefficients of the individual copolymers.

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