

# A Comparative Study on Polymers Containing Different Ultraviolet Stabilizer Moieties

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## SYNOPSIS

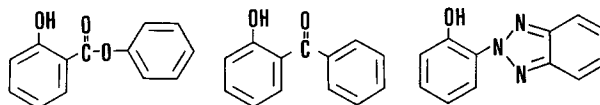
A number of styrene and methylmethacrylate copolymers containing different UV stabilizer units (benzophenone, phenylbenzotriazole, and naphthylbenzotriazole) fixed to the polymer backbone were characterized by UV spectroscopy and size exclusion chromatography. UV spectroscopy was found to be suitable for the determination of the copolymer composition and the stability of intramolecular hydrogen bonds, which are important for the performance of UV stabilizer molecules. The highest stability of the intramolecular hydrogen bond was obtained for phenylbenzotriazole containing polymers. Using size exclusion chromatography with refractive index and ultraviolet detection, it was shown that the UV stabilizer units were statistically distributed along the different molar mass fractions.

## INTRODUCTION

Polymeric materials, when used outdoors or in an environment rich in UV radiation, tend to undergo a process of degradation. Photochemical processes initiate specific reactions, for example, chain cleavage, crosslinking, peroxidation, and elimination of small molecules. Whatever the reaction is, it ultimately leads to the deterioration of the physical, mechanical, and esthetic properties of the polymer.

Therefore, polymeric materials must be stabilized by ultraviolet stabilizers. Several types of UV stabilizers are available, including ultraviolet screening agents, quenchers, and antioxidants. The most commonly used ultraviolet stabilizers are ultraviolet screens. These molecules can absorb the damaging ultraviolet radiation and are then capable of returning the photoexcited stabilizer molecule to the

ground state by dissipating the excess energy in the form of vibrational energy:



For many years these low molar mass organic compounds were simply mixed with the polymers during processing. Thus they were not chemically bound to the polymers and shared the disadvantages of limited compatibility, volatility, and leaching from the polymer surface.<sup>1</sup>

In recent years there have been different approaches to overcome the diffusion problem by chemically incorporating the stabilizer into the polymer in order to improve long-time stability.<sup>2-5</sup> One of the most economic ways appears to be the preparation of polymeric UV stabilizers which can be compounded with virgin polymers.<sup>6-8</sup> The advantage of this approach is that a masterbatch polymer can be prepared that is compounded in different ratios with the virgin polymer, depending on the final use of the product. Although polymers containing

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UV stabilizer moieties of different chemical structure were prepared and tested, a comparison in terms of the interrelationship between chemical structure and photochemical activity is not available yet. As a first step towards this goal, an adequate characterization of the fine chemical structure of the polymers is necessary.

Therefore, we made it the objective of the present work to prepare polymers with high amounts (20–60 mol %) of UV stabilizer units and compare them in terms of copolymer composition, molar mass distribution, and light absorption behavior.

## EXPERIMENTAL

The synthesis of the UV stabilizer monomers was described elsewhere.<sup>9,10</sup> Methyl methacrylate and styrene were distilled twice immediately before use. Methylene chloride, ethanol, THF, and chloroform were analytical or spectroscopical grade. AIBN was recrystallized from dry methanol.

The absorption spectra were recorded on a Shimadzu spectrophotometer UV-160 using chloroform as solvent. Microanalyses (C, H, N) were carried out at the wet chemistry section, Central Analytical Laboratory, Kuwait Institute for Scientific Research (KISR).

The GPC measurements were carried out on a Waters high performance gel permeation chromatograph LC 244, equipped with RI and UV (313 nm) detectors. Column systems consisting of Ultrastayragel columns, 30 cm × 7.8 mm I.D., were used. The flow rate was 1 mL/min, 50–150 μL of 2% polymer solutions in THF were injected using a WISP Model 710B sample processor (Waters). Data processing was carried out on a Waters Model 730 data model with GPC option. The calibration was based on monodisperse polystyrene calibration samples (Waters) in the molar mass range of 10<sup>3</sup>–10<sup>6</sup> Dalton.

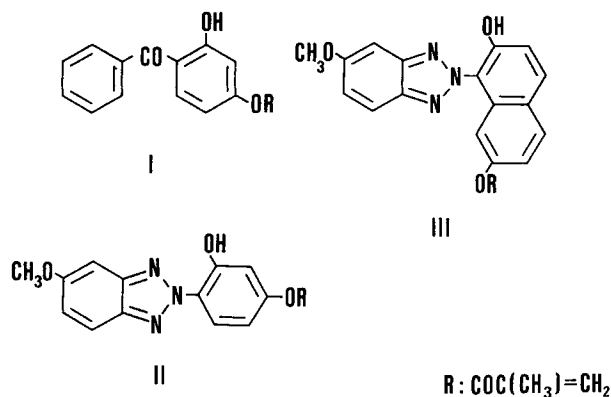
Homopolymerizations were achieved in dichloromethane solution using AIBN in glass tube. The homogenous mixture was degassed by three freeze-thaw cycles. The tube was sealed at 0.02 mm Hg and placed in a constant temperature bath at 60°C. After 5 days the tube was opened and the solution was added dropwise with stirring to ethanol (200 mL). The suspension was allowed to settle for 1 h and filtered. The solid polymer was dissolved in dichloromethane and precipitated again from ethanol, collected by filtration, washed with ethanol (60 mL), and dried under reduced pressure for 2 days.

Procedures for the copolymerization with styrene (St) and methyl methacrylate (MMA) were similar to the homopolymerization process. The amounts

of materials used for the polymerization are presented in Table I. The yields in all cases were 50–60%.

## RESULTS AND DISCUSSION

Three UV stabilizer monomers of different chemical structure were used in the present study, a benzophenone I, a phenylbenzotriazole II and a naphthylbenzotriazole III.



**Table I** Summary of the Polymerization Experiments

Sample	Comonomer Amount		
	UV (mmol)	MMA/St (mmol)	[UV] (mol %)
Poly-I	5.00	—	100.0
20% I/St	1.43	5.74	19.9
40% I/St	2.28	3.43	39.9
60% I/St	2.84	1.90	59.9
20% I/MMA	1.46	5.87	19.9
40% I/MMA	2.31	3.48	39.9
60% I/MMA	2.87	1.92	59.9
Poly-II	5.00	—	100.0
20% II/St	1.35	5.39	20.0
40% II/St	2.08	3.12	40.0
60% II/St	2.54	1.69	60.0
20% II/MMA	1.38	5.52	20.0
40% II/MMA	2.10	3.16	39.9
60% II/MMA	2.55	1.70	60.0
Poly-III	5.00	—	100.0
20% III/St	1.26	5.06	19.9
40% III/St	1.88	2.83	39.9
60% III/St	2.25	1.50	60.0
20% III/MMA	1.29	5.16	20.0
40% III/MMA	1.90	2.86	39.9
60% III/MMA	2.26	1.51	59.9

**Table II** Amount of UV Stabilizer Units in the Copolymers (Calculated from Microanalysis)

Polymer	[UV] <sub>0</sub> <sup>a</sup> (mol %)	[UV] <sub>p</sub> <sup>b</sup> (mol %)	Polymer	[UV] <sub>0</sub> (mol %)	[UV] <sub>p</sub> (mol %)
I/St	19.9	27.3	I/MMA	19.9	21.0
	39.9	42.3		39.9	43.2
	59.9	61.6		59.9	64.2
II/St	20.0	40.6	II/MMA	20.0	25.5
	40.0	59.5		39.9	48.1
	60.0	90.4		60.0	80.0
III/St	19.9	32.8	III/MMA	20.0	22.7
	39.9	51.1		39.9	52.1
	60.0	82.2		59.9	74.7

<sup>a</sup> [UV]<sub>0</sub> = initial concentration in the monomer mixture.

<sup>b</sup> [UV]<sub>p</sub> = final concentration in the polymer.

These monomers were copolymerized with styrene (St) and methyl methacrylate (MMA) in different ratios, resulting in copolymers of different composition. The amount of incorporated UV stabilizer was calculated from the nitrogen content, obtained by C, H, N microanalysis. For comparison the same information was obtained from the extinction coefficients of the homo- and copolymers using UV spectroscopy, and it was found that they are in good agreement.

The results are summarized in Table II. The data show, that the monomers I, II, and III have different reactivities in the copolymerization reaction. In the case of the benzophenone I the amount of UV stabilizer in the polymer [UV]<sub>p</sub> is close to the initial concentration [UV]<sub>0</sub>. Both the phenylbenzotriazole II and the naphthylbenzotriazole III exhibit a sig-

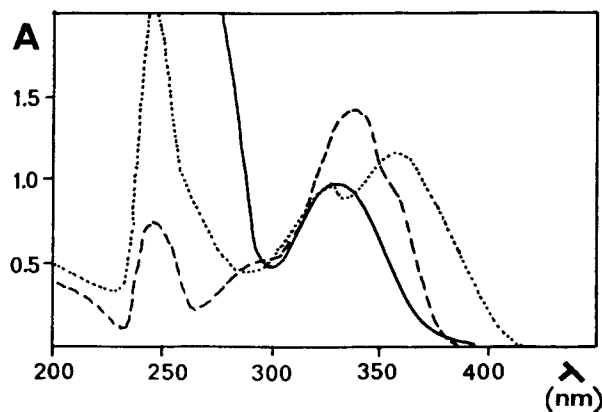
nificantly higher reactivity, which is documented by higher [UV]<sub>p</sub> compared to the monomer feed.

An important indication for the performance of any UV stabilizer is its UV spectroscopical behavior. The UV spectra of the homopolymers Poly-I, Poly-II, and Poly-III are presented in Figure 1 and the extinction coefficients, determined at the peak maxima are:

$$\text{Poly-I: } \epsilon = 0.567 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1} \\ (\lambda_{\text{max}} = 332.0 \text{ nm})$$

$$\text{Poly-II: } \epsilon = 2.174 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1} \\ (\lambda_{\text{max}} = 339.0 \text{ nm})$$

$$\text{Poly-III: } \epsilon = 1.329 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1} \\ (\lambda_{\text{max}} = 359.0 \text{ nm}) \\ \epsilon = 1.112 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1} \\ (\lambda_{\text{max}} = 327.5 \text{ nm})$$



**Figure 1** UV spectra in CHCl<sub>3</sub> of Poly-I (0.05 mg/mL) (—), Poly-II (0.02 mg/mL) (---), and Poly-III (0.03 mg/mL) (···).

It can be seen that Poly-II exhibits the highest extinction coefficient, followed by Poly-III and Poly-I. For the appropriate copolymers absorption maxima close to the homopolymers were obtained. However, for the systems II/MMA and III/MMA slight bathochromic and hypsochromic shifts respectively were obtained when going from higher to lower amounts of UV stabilizer units. For the lowest amounts (20% UV/MMA) the absorption maxima were close to the absorption maxima of the styrene copolymers (see Table III).

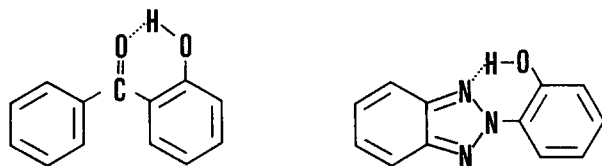
This behavior indicates that there exist certain interactions between the benzotriazole units in the

**Table III** Ultraviolet Absorption Maxima for UV Stabilizer Containing Polymers

Polymer	$\lambda_{\max}$ (nm)	Polymer	$\lambda_{\max}$ (nm)
Poly-II	339.0	Poly-III	359.0
60% II/MMA	341.3	60% III/MMA	358.0
40% II/MMA	342.3	40% III/MMA	356.8
20% II/MMA	344.5	20% III/MMA	356.8
60-20% II/St	344.5	60-20% III/St	356.0

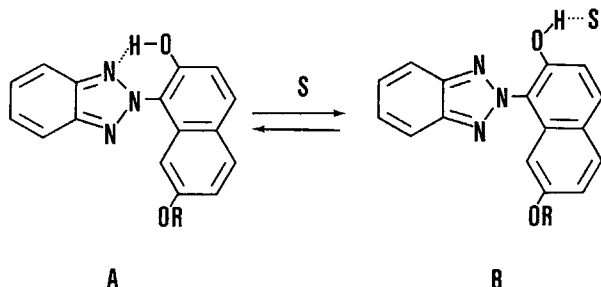
copolymers. The lower the amount of these units and, therefore, the larger the distance between them, the weaker will be the interaction. In the case of the styrene copolymers, this interaction is suppressed because of the bulkiness of the styrene units.

It is known that the high photostability of the UV stabilizers under study is related to the formation of intramolecular hydrogen bonds, which enable the compounds to dissipate radiation energy in a fast nonradiative way.<sup>11,12</sup>

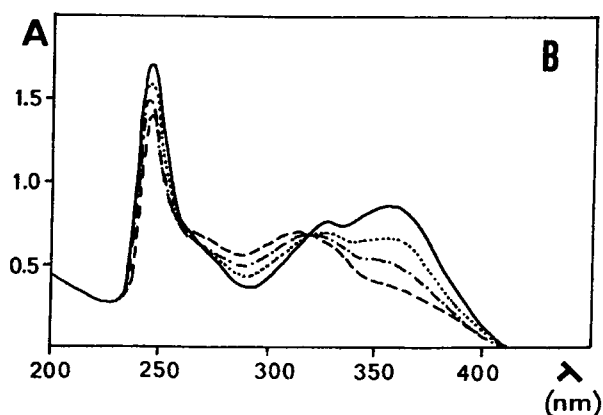
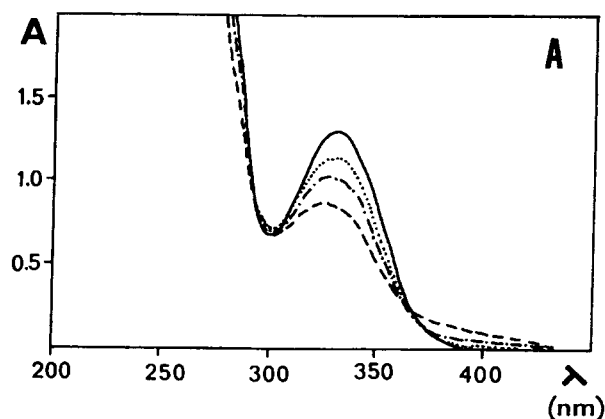


The formation of this type of hydrogen bonds in solution might be strongly influenced by the polarity of the solvent.<sup>13</sup> Therefore, the stability of the intramolecular hydrogen bond can be determined measuring the UV spectra in solvents of different polarity.<sup>14</sup>

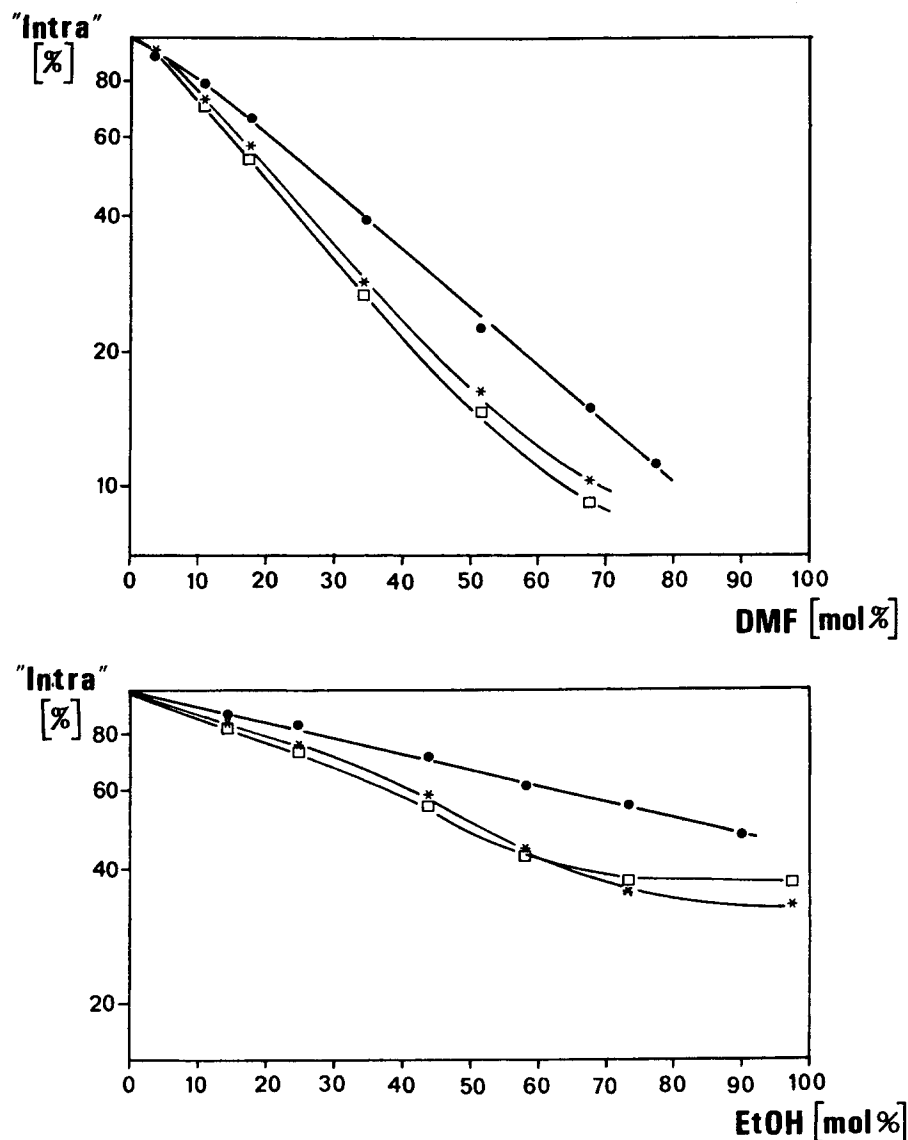
If polar solvents were added stepwise to a polymer solution in a nonpolar solvent, the absorption spectrum changed dramatically (see Fig. 2). The main absorption peak was progressively suppressed, and new peaks appeared at lower wavelengths. These changes in the absorption spectra were the result of the transformation of the UV stabilizer molecule from an intramolecularly hydrogen-bonded state to an intermolecularly hydrogen-bonded state.



As for the polymers of III, it could be shown that when ethanol or another polar solvent was added stepwise to a solution of the polymer in a nonpolar solvent (chloroform), an isosbestic point was obtained (see Fig. 2). This indicated that, there exists a simple equilibrium between intramolecular (A) and intermolecular (B) hydrogen bonds, which is shifted to form B when the polarity of the solvent is increased. As far as the same spectra were obtained for chloroform and toluene, in this case a fully intramolecular hydrogen-bonded state was assumed. Assuming a fully intermolecular hydrogen-bonded state in ethanol or DMF, via a multicomponent analysis the ratio of both states could be estimated for solvent mixtures. The calculated amount of form A in the solution vs. the concentration of the polar solvent is shown in Figure 3. It is evident from the



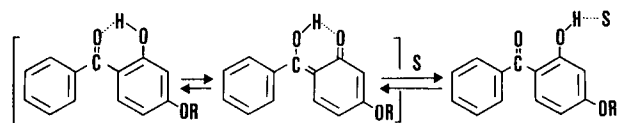
**Figure 2** UV spectra of polymers in solvents of different polarity: A: 20% I/MMA,  $\text{CHCl}_3/\text{DMF}$ : (—) 100/0; (···) 50/50; (-·-·) 33/67; (- - -) 7 : 93. B: 40% III/St,  $\text{CHCl}_3/\text{EtOH}$ : (—) 100/0; (···) 83/77; (-·-·) 67/33; (- - -) 33/67.



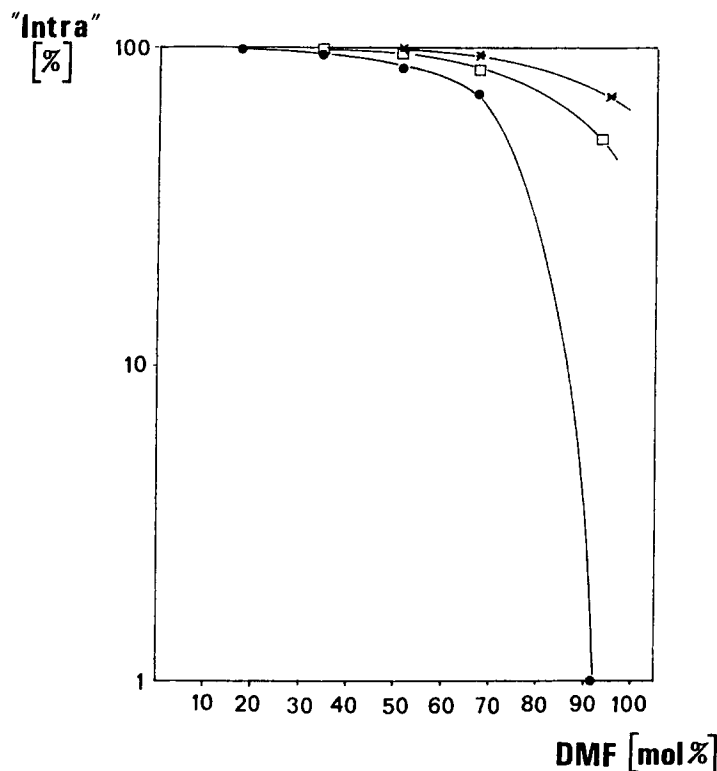
**Figure 3** Stability of the intramolecular hydrogen bond in solvents of different polarity: (○) Poly-III; (\*) 20% III/MMA; (□) 20% III/St.

curves, that there exists a direct dependence of the amount of intramolecular hydrogen bonding on the amount and the polarity of the cosolvent.

When the same procedure was carried out for polymers of I, the intensity of the absorption band decreased with increasing polarity of the solvent, but a new absorption peak was not obtained. It was assumed that in nonpolar solvent and equilibrium existed between the intramolecularly hydrogen-bonded keto and enol forms, which are characterized by a high absorptivity. In the polar solvent this equilibrium was destroyed and an intermolecularly hydrogen-bonded keto form was present, which should exhibit a lower absorptivity.



Comparing Figures 3 and 4, it can be seen that at the same concentration of the polar solvent the ratio of intra- to intermolecular hydrogen bond for polymers of I was always higher than for polymers of III. Under the same experimental conditions polymers of II did not exhibit any changes in the UV spectrum. From these results it can be concluded that the stability of the intramolecular hydrogen bond is the highest for phenylbenzotriazole con-



**Figure 4** Stability of the intramolecular hydrogen bond in DMF/CHCl<sub>3</sub> mixtures: (○) Poly-I; (□) 20% I/MMA; (\*) 20% I/St.

**Table IV** Molar Masses of UV Stabilizer Polymers Determined by SEC

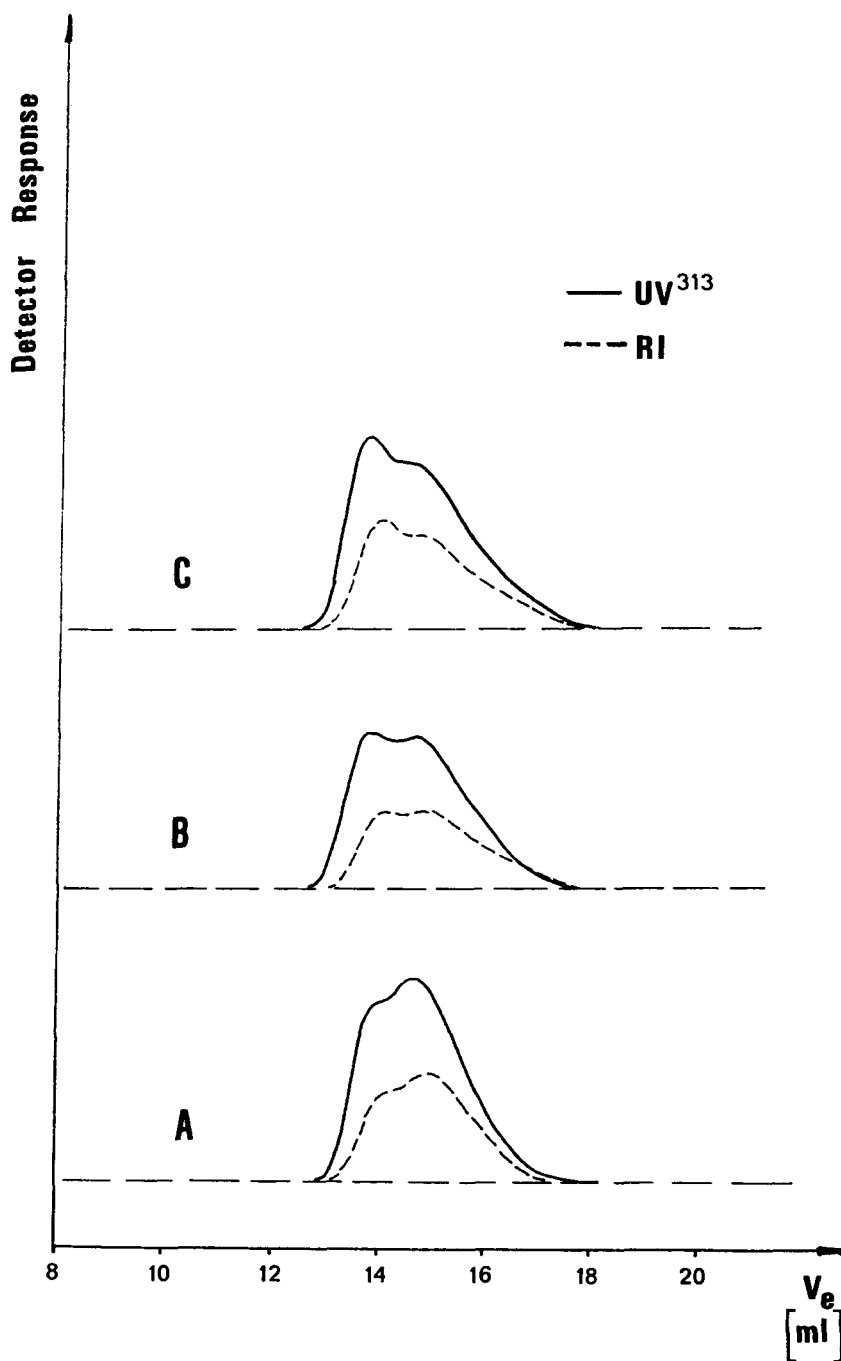
Sample	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
Poly-III	4.500	10.800	2.4
20% III/St	8.200	19.900	2.4
40% III/St	7.300	17.600	2.4
60% III/St	7.200	16.900	2.4
20% III/MMA	17.000	87.400	5.1
40% III/MMA	15.200	70.000	4.6
60% III/MMA	12.600	45.700	3.6
Poly-II	3.500	20.600	5.8
20% II/St	12.500	43.400	3.5
40% II/St	11.400	43.900	3.8
60% II/St	11.300	49.100	4.3
20% II/MMA	12.500	87.400	7.0
40% II/MMA	10.900	52.200	4.8
60% II/MMA	8.800	74.200	8.4
Poly-I	3.000	13.500	4.5
20% I/St	5.800	18.600	3.2
40% I/St	3.800	12.500	3.3
60% I/St	4.200	14.700	3.5
20% I/MMA	8.900	33.800	3.8
40% I/MMA	5.500	17.600	3.2
60% I/MMA	8.000	29.600	3.7

taining polymers and the lowest for naphthylbenzotriazole containing polymers.

The molar masses of the polymers were determined by size exclusion chromatography. In a first set of experiments a Waters Ultrastyrigel linear column (set A) was used, the mobile phase was tetrahydrofuran and the calibration was based on monodisperse polystyrene. The results are presented in Table IV. They show that the molar mass of the copolymers decreased gradually with increasing amounts of UV stabilizer units. The lowest molar masses were obtained for the homopolymers. This indicates that the bulkiness of the UV stabilizer moiety effects the polymerization in terms of steric hindrance.

It is obvious that, besides the molar mass and the polydispersity, the chemical heterogeneity is an important parameter affecting the performance of the product.

In order to evaluate the chemical heterogeneity of the polymers, a second set of experiments was carried out using a column system Waters Ultrastyrigel linear + Ultrastyrigel 500 Å (set B) and a simultaneous refractive index and ultraviolet detec-

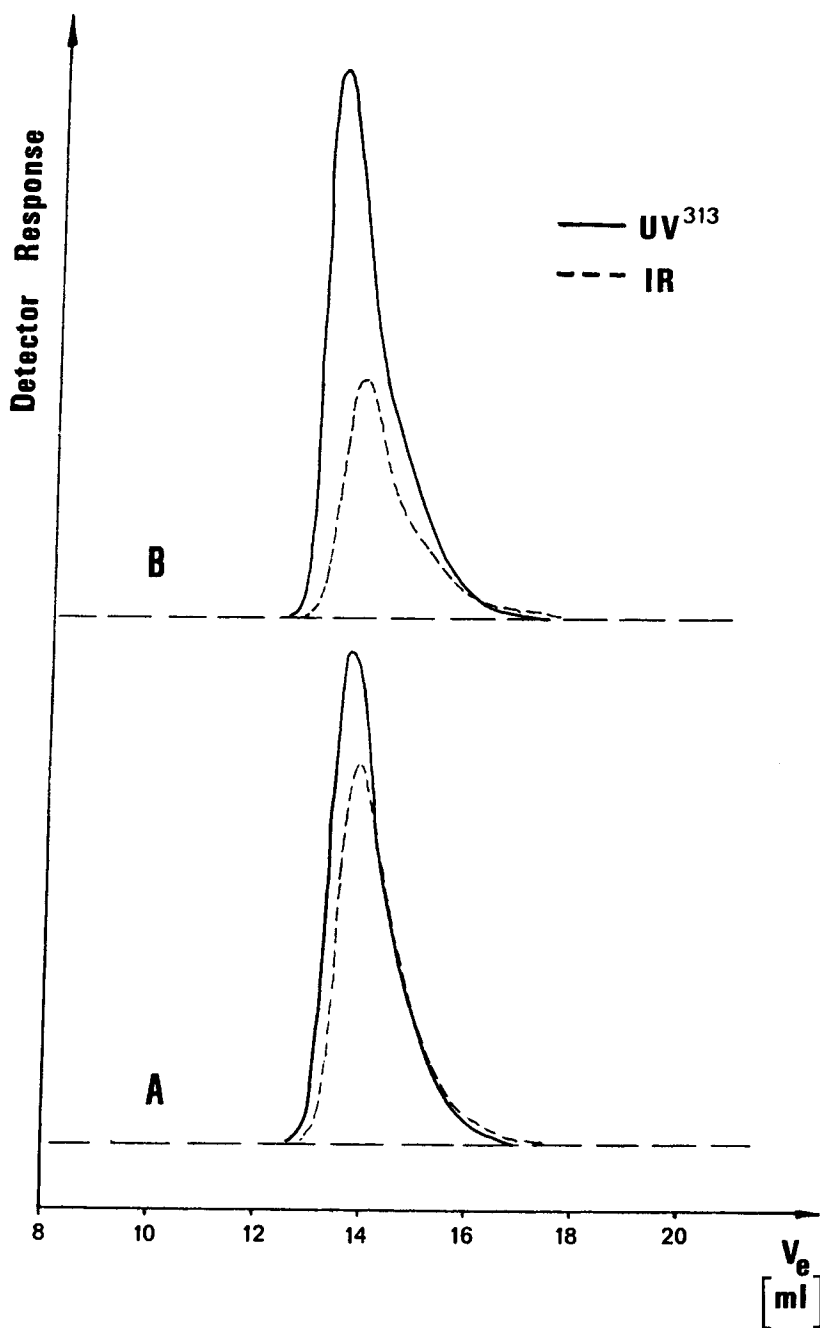


**Figure 5** SEC chromatograms of I/St copolymers using RI and UV detection: (A) 20% I/St; (B) 40% I/St; (C) 60% I/St.

tion at a wavelength of 313 nm. It is important to notice that at a detector wavelength of 313 nm only the UV stabilizer units absorb, i.e., are “visible” in the detector. The styrene and methyl methacrylate units are transparent at this wavelength. Therefore, the UV profile shows the distribution of only the UV stabilizer units along the molar mass ( $V_e$ ) axis.

The molar masses determined on set B using the RI detector for calculation, summarized for one type of polymers in Table V, showed that a very good agreement between the results from system A and system B was achieved.

Now, for the evaluation of the chemical heterogeneity of the copolymers different samples were



**Figure 6** SEC chromatograms of II/St copolymers using RI and UV detection: (A) 20% II/St; (B) 60% II/St.

measured using (1) the RI detector and (2) the UV<sup>313</sup> detector in the calculation mode. The SEC curves obtained from both detectors are presented in Figures 5 and 6. In all cases the obtained profiles were similar, except that the UV curves are slightly shifted towards higher elution volumes, as has to be expected.

The corresponding molar masses are summarized in Table VI. As can be seen from the data, there is a good agreement between the results derived from the RI and UV signal. Therefore, it can be concluded that in all copolymer samples the UV stabilizer units are statistically distributed along the different molar mass fractions.



**Table V Molar Masses of Polymers Containing III, Determined Using Different Column Sets (RI Detection)**

Polymer	Set A			Set B		
	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
20% III/St	8.200	19.900	2.4	10.600	24.100	2.3
40% III/St	7.300	17.600	2.4	8.800	19.100	2.2
60% III/St	7.200	16.900	2.4	7.600	16.700	2.2

## CONCLUSIONS

The present study was aimed at the determination of microstructural parameters of polymers, containing different types of UV stabilizer moieties. It was shown that important parameters affecting the performance of the UV stabilizer polymer, such as the molecular and chemical heterogeneity and the strength of the internal hydrogen bond, can be determined using size exclusion chromatography and UV spectroscopy, respectively. These parameters have to be correlated with the photostability of the products in forthcoming investigations.

**Table VI Molar Masses of Copolymers Determined Using Set B with RI and UV<sup>313</sup> Detection**

Polymer	RI		UV <sup>313</sup>	
	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
20% I/St	9.600	2.6	10.400	2.8
40% I/St	7.400	4.3	10.600	3.1
60% I/St	8.200	4.6	9.400	4.1
20% III/St	10.600	2.3	10.800	3.4
40% III/St	8.800	2.2	6.800	4.4
60% III/St	7.600	2.2	5.700	3.5
20% II/St	17.700	2.2	17.900	2.2
40% II/St	18.500	2.6	16.300	2.5

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Received September 20, 1989

Accepted March 21, 1990