

Photosensitive copolymers of styrene with 4-vinylbenzyl selenocyanate: synthesis and comparison with similar copolymers

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The copolymer poly (VBSe-*co*-ST), containing photolabile selenocyanato groups, was prepared by the free-radical copolymerization of styrene (ST) with the new monomer 4-vinylbenzyl selenocyanate (VBSe). Alternatively, the copolymer poly (VBBr-*co*-ST), containing 4-vinylbenzyl bromide (VBBr), was treated with KSeCN to give poly (VBSe-*co*-ST); the copolymer poly (VBT-*co*-ST), containing 4-vinylbenzyl thiocyanate (VBT) units, was obtained in a similar way. The photocrosslinking of these copolymers was investigated under 248 nm excimer laser irradiation. Poly (VBSe-*co*-ST) was found to be about four times more photosensitive than poly (VBBr-*co*-ST) or poly (VBT-*co*-ST). Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

In previous papers we reported the synthesis and ultra-violet (u.v.) photocrosslinking of polymers containing photolabile thiocyanato groups^{1,2}. The copolymer poly (VBT-*co*-ST) of 4-vinylbenzyl thiocyanate (VBT) with styrene (ST) was investigated as a negative resist material under deep-u.v. (248 nm) irradiation². Results from experiments with benzyl thiocyanate as a low-molecular-weight model compound provided information about the chemical reactions which occur in the resist material under irradiation. It was concluded that the photochemistry of thiocyanates (as pseudohalides) is similar to the radiation chemistry of halides, e.g. chlorides^{3,4}.

Selenocyanates are also regarded as pseudohalides, but in general their chemistry has attracted much less attention than that of thiocyanates. Michels *et al.*⁵ described the synthesis of modified styrene-divinylbenzene resins containing selenocyanatophenyl groups. However, the photochemical properties of these cross-linked materials were not considered.

Suzuki *et al.*⁶ reported that substituted benzyl selenocyanates are converted into the corresponding isoselenocyanates under u.v. irradiation. The photo-reaction observed proceeded with moderate yields (up to 40%) and represents an alternative to the classical synthesis of isoselenocyanates from the corresponding isocyanides and elemental selenium⁷. For the mechanism of the photoreaction, both a concerted pathway and a radical mechanism via benzyl and selenocyanato radicals have been discussed⁸. Regarding the analogous photo-isomerization of thiocyanates to the corresponding isothiocyanates⁹, which is known to occur via radical

intermediates, it is likely that radicals are formed by a cleavage of the C–Se bond of the selenocyanate. Thus we expected polymers containing photolabile selenocyanato groups to be u.v.-photocrosslinkable via a radical mechanism.

To our knowledge, 4-vinylbenzyl selenocyanate (VBSe) has not yet been described in the literature. The present paper describes the synthesis of the VBSe monomer and the copolymerization of VBSe with styrene (ST) to give poly (VBSe-*co*-ST) (*Figure 1*). In addition, the copolymer poly (VBBr-*co*-ST) was prepared from 4-vinylbenzyl bromide (VBBr) and ST. It was then treated with KSeCN to give poly (VBSe-*co*-ST) or with NH₄SCN to give poly (VBT-*co*-ST). The photosensitivity of poly (VBSe-*co*-ST) under 248 nm irradiation was compared to that of the copolymers poly (VBBr-*co*-ST) and poly (VBT-*co*-ST).

Furthermore, reactions of the isoselenocyanato groups in the irradiated poly (VBSe-*co*-ST) and the isothiocyanato groups in the irradiated poly (VBT-*co*-ST) with amines were carried out. Selenourea or thiourea groups, respectively, were formed.

EXPERIMENTAL

Measurements

The weight-average molecular weight M_w and the polydispersity index *PDI* were determined by size exclusion chromatography with polystyrene gel columns (10³, 10⁴ and 10⁶ Å, size 5 μm, tetrahydrofuran (THF) as eluent) using a Viscotec Model 200 differential refractometer/viscometer as the detector (universal calibration).

Infra-red (i.r.) spectra were recorded with a Bomem M100 FT i.r. spectrometer. The u.v. absorbance of the

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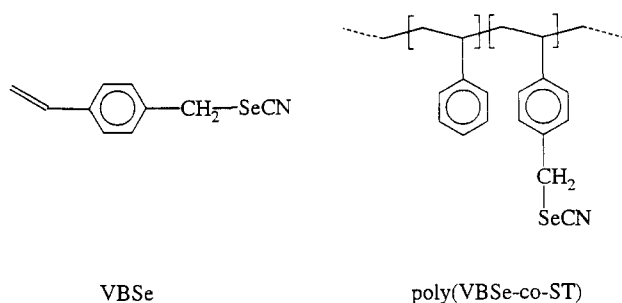


Figure 1 Structures of 4-vinylbenzyl selenocyanate (VBSe) and poly (VBSe-co-ST)

polymer films at 248 nm was recorded with a Hewlett Packard HP 8452A spectrometer. ^1H nuclear magnetic resonance (n.m.r.) spectroscopic measurements were carried out with a Bruker 300 MHz spectrometer.

The thickness r of each polymer film was determined interferometrically by using a Perkin-Elmer Lambda 9 u.v.-vis-n.i.r. spectrometer. The data were found to be in good agreement with ellipsometric measurements (Plasmos SD 2300 ellipsometer).

A KrF excimer laser (Lambda Physik LPX 105i; 10 Hz pulse frequency) was used as the 248 nm light source for photocrosslinking.

Synthesis of low-molecular-weight compounds

4-Vinylbenzyl selenocyanate (VBSe) was prepared from 4-vinylbenzyl bromide (VBBBr)¹⁰. In this reaction 1.36 g (6.90 mmol) of VBBBr were dissolved in 2 ml of *N,N*-dimethylformamide (DMF) and added dropwise to a solution of 1.50 g (10.4 mmol) of KSeCN in 10 ml of DMF. After addition of 20 mg of 2,6-di-*tert*-butyl-*p*-cresol (BHT) the mixture was stirred for 150 min at 20° in the dark. During the reaction time argon was bubbled through the solution. The solution was then poured into 500 ml of water (at 0°C) and extracted with methylene chloride (three times, using 50 ml portions in each). The collected methylene chloride extracts were washed with water, dried over sodium sulfate and concentrated *in vacuo*. The oily residue was chromatographed in a silica gel column using a mixture of *n*-heptane and ethyl acetate (10:1(vol: vol)) as eluent. After evaporation of the solvent, crystals were obtained; recrystallization from ethanol yielded 0.45 g (2.0 mmol) of 4-vinylbenzyl selenocyanate, m.p. 68–70°C. I.r. (KBr pellet): 2146 (–SeCN), 1626, 1508, 1405, 1190, 1106, 989, 915, and 841 cm^{-1} . ^1H n.m.r. (CDCl_3) δ : 4.20 (s, –CH₂–, 2H), 5.27 (d, =CH₂, 1H), 5.74 (d, =CH₂, 1H), 6.68 (d of d, –CH=, 1H), and 7.30–7.33 (aromatic, 4H) ppm.

Benzyl selenocyanate was synthesized following the method of Suzuki and co-workers⁶.

Copolymerization of VBSe with styrene (ST) to give poly (VBSe-co-ST) (polymer I)

In this reaction 0.27 g (1.2 mmol) of VBSe, 0.5 g (4.8 mmol) of styrene and 11.8 mg (0.07 mmol) of azoisobutyronitrile (AIBN) were dissolved in dry toluene to give a total volume of 1.5 ml. The solution was degassed by three freeze–thaw–freeze cycles and after sealing, the vessel was then thermostated at 60°C using a water bath (exclusion of light). After 360 min reaction time the polymerization reaction was terminated by

Table 1 Composition, weight-average molecular weight M_w and polydispersity index PDI of the copolymers I–VII

Polymer sample	Comonomer	Comonomer content (mol %)	M_w (g mol^{-1})	PDI
I	VBSe	24	10 000	1.28
II	VBBBr	13	52 000	1.78
III	VBBBr	24	50 000	1.67
IV	VBSe	13	58 000	1.82
V	VBSe	24	65 000	1.87
VI	VBT	12	53 000	1.78
VII	VBT	22	52 000	1.70

rapid cooling. The solution was diluted with toluene (1:1) and slowly precipitated with 50 ml of methanol. After reprecipitation from methanol the polymer was dried *in vacuo* to constant weight (yield 90 mg). I.r. (film on NaCl disc): 2148 cm^{-1} . ^1H n.m.r. (CDCl_3) δ : 4.13 (–CH₂–SeCN) ppm. Elemental analysis of the polymer yielded 2.55 wt% nitrogen and 14.3 wt% selenium, which corresponded to a mole ratio of VBSe:ST = 0.24:0.76. The values for M_w and PDI are given in Table 1.

Copolymerization of 4-vinylbenzyl bromide (VBBBr) with styrene (ST) to give poly (VBBBr-co-ST) (polymers II and III)

The free-radical copolymerization of VBBBr and ST to give poly (VBBBr-co-ST) was carried out by following a procedure similar to that described above. Polymer II was obtained from the reaction of 0.71 g (3.60 mmol) of VBBBr, 3.37 g (32.4 mmol) of ST and 0.16 mmol of AIBN in 10 ml of toluene (60°C, 300 min); in the case of polymer III, 1.45 g (7.40 mmol) of VBBBr, 2.7 g (26 mmol) of ST and 0.14 mmol of AIBN were used (60°C, 600 min). The polymers were precipitated with excess methanol, reprecipitated with methylene chloride/methanol (three times) and dried *in vacuo*. The VBBBr content was calculated from elemental analysis data (polymer II; 13 mol%; polymer III; 24 mol%) and found to be in good agreement with ^1H n.m.r. spectroscopic data. The values for M_w and PDI are presented in Table 1.

Conversion of poly (VBBBr-co-ST) into poly (VBSe-co-ST) (polymers IV and V)

In a typical reaction, 0.5 g of polymer II were dissolved in 10 ml of DMF, and 0.3 g (2.08 mmol) of KSeCN in 5 ml of DMF were added dropwise. After 24 h stirring (argon atmosphere, exclusion of light), the polymer IV that was obtained was precipitated with methanol and purified as described above. In the same way, polymer III was converted into polymer V. Elemental analysis showed that the conversion of the bromomethyl groups into selenocyanatomethyl groups was at least 99%. The values for M_w and PDI are presented in Table 1.

Conversion of poly (VBBBr-co-ST) into poly (VBT-co-ST) (polymers VI and VII)

As an example, 0.2 g of polymer II were dissolved in 10 ml of DMF, and then 137 mg (1.8 mmol) of NH_4SCN dissolved in 1.5 ml of DMF were added. After 24 h stirring the resulting polymer VI was precipitated with methanol and purified by reprecipitation from DMF/methanol (twice) and finally from methylene chloride/

methanol. The conversion of polymer III into polymer VII was achieved in a similar way. Elemental analysis data showed that ca. 92% of the bromomethyl groups had been transformed into thiocyanatomethyl groups. The values obtained for M_w and PDI are presented in *Table 1*.

Photocrosslinking

Films were spin-cast from chloroform solution onto CaF_2 plates, dried *in vacuo* and irradiated under nitrogen². The light intensity (248 nm) was 4.2 mJ per pulse and per cm^2 (8.7×10^{-9} mol photons per pulse and per cm^2) as determined by ferrioxalate actinometry¹¹. Sol/gel analysis was performed by immersion of the irradiated films in methylene chloride as the solvent (25°C, 10 min). After drying *in vacuo* the insoluble fraction W was calculated from the i.r. absorbance of the polymer films at 1452 and 1493 cm^{-1} before and after development.

RESULTS AND DISCUSSION

Synthesis of the copolymers

The free-radical copolymerization of VBSe with styrene (ST) at 60°C using AIBN as the initiator yielded a material (polymer I in *Table 1*) which was readily soluble in methylene chloride, DMF, THF and other organic solvents. Elemental analysis showed that the polymer had a composition almost identical with that of the monomer feed (20 mol% VBSe and 80 mol% ST). The ¹H n.m.r. spectrum of poly (VBSe-co-ST) showed a single signal at $\delta = 4.13$ ppm in the region $\delta = 2-6$ ppm, indicating that no considerable isomerization or decomposition of the selenocyanato group had occurred during the polymerization reaction.

The average molecular weight of this polymer was fairly low ($M_w = 10\,000$). This was unexpected, because under similar experimental conditions the copolymerization of both 4-vinylbenzyl thiocyanate (VBT)² and 4-vinylbenzyl bromide (VBBBr) with ST yielded copolymers with significantly higher average molecular weights. Poly (VBT-co-ST), containing 25 mol% of VBT units, was obtained with $M_w = 67\,000$, and for poly (VBBBr-co-ST), containing 24 mol% VBBBr units (polymer III in *Table 1*), an M_w of 50 000 was found.

It is likely that during the copolymerization of ST with VBSe, VBT or VBBBr, chain transfer reactions occur, in which the benzylic methylene group acts as a hydrogen donor. The substituents at the benzylic group (SeCN, SCN or Br) should have some effect on the hydrogen-donor properties of the methylene group. This would lead to different values of the chain transfer constant, C_s , and different average molecular weights of the copolymers. Comparing the similar M_w values of poly (VBT-co-ST) and poly (VBBBr-co-ST), it seems that the substituents Br and SCN exert similar effects. It can therefore be expected that with SeCN as the substituent the chain transfer constant of the benzylic methylene group will also be similar.

The low average molecular weight of poly (VBSe-co-ST) must be due to other causes. We suspect that the decomposition products of VBSe, which are formed before or during the polymerization procedure, are involved in chain transfer reactions. For the chain transfer constants (C_s s) of selenium compounds only few data are available. For example, the C_s of dibenzyl-

diselenide is reported to be 2.0 (dibenzyl disulfide: $C_s = 0.02$)¹². Chain transfer reactions induced by decomposition products would give a reasonable explanation for the low average molecular weight of poly (VBSe-co-ST) (polymer I).

The polymer analogous reaction of styrene copolymers containing 4-vinylbenzyl bromide as the comonomer (poly(VBBBr-co-ST)) with KSeCN is a convenient alternative route to obtaining poly (VBSe-co-ST). This reaction does not lead to a significant increase in the average molecular weight M_w of the polymer. As described previously² the synthesis of poly (VBT-co-ST) can be achieved by the free-radical copolymerization of the monomers 4-vinylbenzyl thiocyanate (VBT) and ST. The reaction of poly (VBBBr-co-ST) with NH_4SCN is a more convenient route to poly (VBT-co-ST). However, due to the lower nucleophilicity of thiocyanate anions compared with selenocyanate anions^{13,14} the conversion was not complete (ca. 92%).

A comparison of the photocrosslinking data obtained for different polymers is best achieved with materials of a similar average molecular weight M_w . Thus the samples of poly (VBSe-co-ST) and poly (VBT-co-ST) which were investigated under u.v. irradiation were prepared from portions of the same poly (VBBBr-co-ST) batch as described in the Experimental section.

Irradiation of benzyl selenocyanate in solution

The photoreactions of benzyl halides^{3,4} and benzyl thiocyanate⁹ in solution are well known, but no information could be obtained about the photochemical processes which occur during the photolysis of selenocyanates. We irradiated a solution of benzyl selenocyanate (0.14 mol l⁻¹) in benzene-d₆ and identified a number of reaction products by means of ¹H n.m.r. spectroscopic analysis. Benzyl isoselenocyanate, benzyl isocyanide and 1,2-diphenylethane were the main products. The photoproducts observed can easily be explained by the reaction pathway shown in *Figure 2*, which is based on radical reactions.

Photocrosslinking

The irradiation of a poly (VBSe-co-ST) film (polymer V) with 248 nm u.v. light leads to significant changes in the i.r. spectrum (see *Figure 3*). In the spectrum of the unirradiated film the bands at 2149 and 1192 cm^{-1} originate from the $-\text{CH}_2-\text{SeCN}$ group (benzyl selenocyanate⁶: 2145 and 1190 cm^{-1}). After irradiation these bands disappeared and a broad, intense band at 2145 cm^{-1} and another band at 1337 cm^{-1} were observed. The comparison with the i.r. spectroscopic data of benzyl isoselenocyanate⁶ (2140 and 1345 cm^{-1}) indicates that in the polymer photoisomerization also occurs. The broad band observed at around 2145 cm^{-1} is

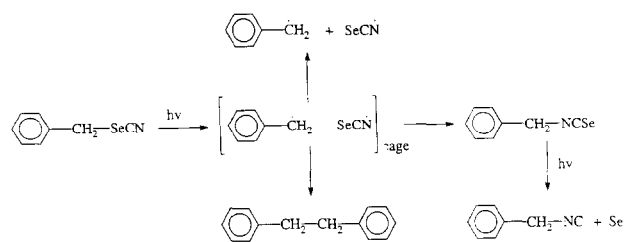


Figure 2 Photochemical reactions of benzyl selenocyanate

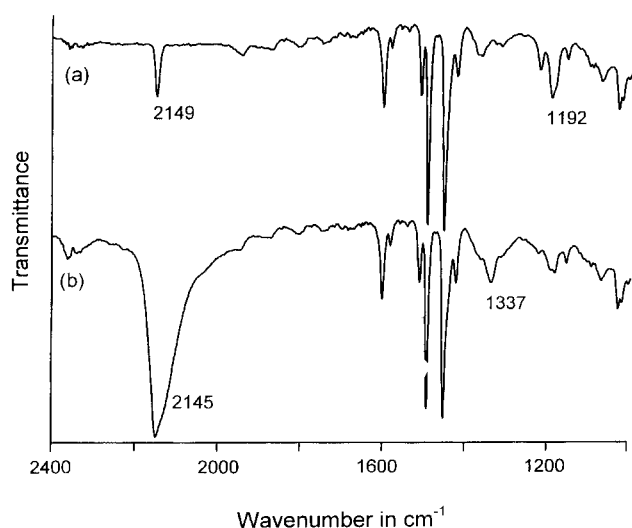


Figure 3 FTIR spectra of a poly (VBSe-co-ST) film: (a) before irradiation; (b) after irradiation

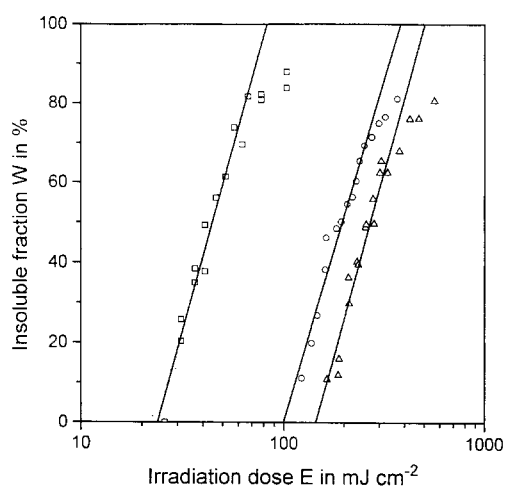


Figure 4 Photocrosslinking of the various copolymers: (○) poly (VBBr-co-ST), polymer II; (□) poly (VBSe-co-ST), polymer IV; (Δ) poly (VBT-co-ST), polymer VI. The insoluble fraction W is shown as a function of the irradiation dose E .

assigned to the asymmetric vibration mode ν_{as} of the NCSe group¹⁵.

Poly (VBSe-co-ST) became crosslinked under u.v. light and prolonged irradiation caused a yellow colouring. In Figures 4 and 5 the sol/gel curves (insoluble fraction W versus irradiation dose E) of the polymers II–VII are shown.

The photosensitivity of the polymers is expressed in terms of the gel dose E_g (mJ cm^{-2}), which is obtained by extrapolation of the sol/gel curves to $W = 0$. The quantum efficiency Φ of intermolecular crosslinking as a measure of the intrinsic reactivity of a photoreactive polymer was calculated according to the following equation^{16,17}:

$$\Phi = rd / FM_w E_g \quad (1)$$

where r is the film thickness in m, d the density of the polymer in kg m^{-3} , F the fraction of light absorbed at 248 nm, M_w the average molecular weight in kg mol^{-1} and E_g the gel dose in mol photons per m^2 . In this calculation the density of polystyrene ($d = 1050 \text{ kg m}^{-3}$)

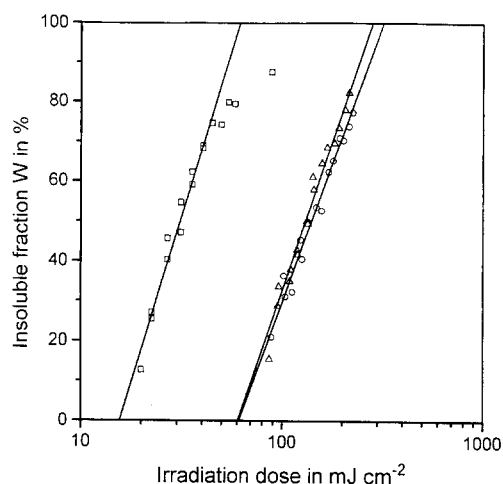


Figure 5 Photocrosslinking of the various copolymers: (○) poly (VBBr-co-ST), polymer III; (□) poly (VBSe-co-ST), polymer V; (Δ) poly (VBT-co-ST), polymer VII. The insoluble fraction W is shown as a function of the irradiation dose E .

Table 2 Photocrosslinking of the copolymers II–VII under 248 nm irradiation

Polymer sample	r^a (m)	F^b	E_g^c (mJ cm^{-2})	Υ^d	Φ^e
II	1.5	0.33	102	1.7	4
III	1.7	0.54	60	1.4	5
IV	1.3	0.30	24	1.9	16
V	1.8	0.63	15	1.7	15
VI	1.4	0.20	144	1.8	5
VII	1.9	0.38	63	1.5	8

^a Film thickness ($\times 10^7$)

^b Fraction of light absorbed at 248 nm

^c Gel dose

^d Contrast

^e Quantum efficiency of intermolecular crosslinking ($\times 10^3$)

was used. From the initial slope of the curves in Figures 4 and 5 the contrast γ was obtained according to equation (2); as follows:

$$\gamma = (dW/d \log E)_g \quad (2)$$

The data for r , F , E_g , γ and Φ are given in Table 2. For polymer IV (containing 13 mol% VBSe) a gel dose E of 24 mJ cm^{-2} was found, which corresponds to $\Phi = 16 \times 10^{-3}$. In the case of polymer V (containing ca. 24 mol% VBSe) the sensitivity was even higher ($E_g = 15 \text{ mJ cm}^{-2}$), but a similar Φ (15×10^{-3}) was observed.

The photosensitivity of poly (VBBr-co-ST) was determined in the same way. In the case of polymer II (13 mol% VBBr) E_g was found at 102 mJ cm^{-2} ($\Phi = 4 \times 10^{-3}$). For polymer III (24 mol% VBBr) E_g was 60 mJ cm^{-2} and Φ was 5×10^{-3} .

The samples of poly (VBT-co-ST) investigated here were polymer VI, containing 12 mol% VBT, and polymer VII, containing 22 mol% VBT. The gel dose E_g was 144 mJ cm^{-2} for polymer VI and 63 mJ cm^{-2} for polymer VII, which corresponded to the Φ values of 5×10^{-3} and 8×10^{-3} , respectively. These values for the quantum efficiency Φ are in acceptable agreement with results obtained for poly (VBT-co-ST) samples, which were prepared by the copolymerization of VBT and ST². The

photosensitivity of poly (VBT-co-ST) was similar to that of poly (VBBr-co-ST).

The contrast values (γ) which were obtained for the polymers II–VII varied between 1.4 and 1.9 (see Table 2). Such low values are typical for broad molecular-weight distributions as these are obtained by free-radical polymerization.

From the data for the quantum efficiency Φ and the gel dose E_g the following can be seen: the introduction of selenocyanatomethyl groups into polystyrene yields polymers which are markedly more photosensitive than polystyrenes bearing bromomethyl or thiocyanatomethyl groups. This was found both for the polymer samples II, IV and VI (13 mol% reactive comonomer) and for the polymer samples III, V and VII (ca. 24 mol% reactive comonomer).

Considering the photoreactions of benzyl selenocyanate (as a low-molecular-weight model compound) it is reasonable to assume that the crosslinking of poly (VBSe-co-ST) occurs *via* radical intermediates, as has been proposed for the analogous chloromethylated polystyrenes^{4,18}. A comparative investigation of the products which are formed during the photolysis of benzyl selenocyanate, benzyl bromide and benzyl selenocyanate will be published separately.

Reaction of irradiated poly (VBSe-co-ST) and poly (VBT-co-ST) with amines

During the irradiation of poly (VBSe-co-ST), isoselenocyanato groups are formed, which are well known to react with amines to give selenoureas¹⁹. In a similar manner the isothiocyanato groups which are formed in poly (VBT-co-ST) undergo addition reactions with amines to give thioureas²⁰.

In our studies 0.2 μm thick films of poly (VBSe-co-ST) (polymer V) and poly (VBT-co-ST) (polymer VII) were irradiated with a dose of 400 mJ cm^{-2} and subsequently immersed in a mixture of benzyl amine and THF (1:1, vol:vol) for 15 min. I.r. spectra which were taken after the irradiation of the films showed that in both cases the photoisomerization was almost complete. After treatment with benzylamine both the isoselenocyanate and the isothiocyanate band disappeared quantitatively and new i.r. bands appeared.

In poly (VBT-co-ST) the new bands were located at 960, 1273, 1377, 1543, and ca. 3300 cm^{-1} . A comparison with the i.r. spectrum of *N,N*-dibenzyl thiourea²¹, which shows bands at 960, 1280 (C=S), 1390, 1550, and 3310 (N–H) cm^{-1} , indicated the conversion of isothiocyanato

groups to thiourea groups. The spectroscopic changes in poly (VBSe-co-ST) were less clear, but it is likely that selenourea groups were formed in an analogous way.

These reactions with amines provide a possibility for the selective functionalization of irradiated zones.

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