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Synthesis and photochemical reactions of functional organotin macromolecules

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The alternating copolymers of allyl chloroacetate (ACA) and allyl propionate (AP) with maleic anhydride (MA) and their organotin derivatives were synthesized by radical copolymerization in the presence of benzoyl peroxide as initiator in benzene at 70°C and by the polymer-analogous reaction of anhydride-containing copolymers prepared with hexa-*n*-butyldistannoxane, respectively, and all were characterized. The alternating copolymers of monoallyl maleate (MAM) and tri-*n*-butylstannylallyl maleate (TBSAM) with styrene (St) and MA were also synthesized by radical copolymerization in methylethylketone in the presence of benzoyl peroxide at 60°C. Photochemical reactions and structure–property correlations in the synthesized copolymers containing Sn, O=C, Cl and C=C (side-chain allyl or vinylene groups) were studied by using u.v.-irradiation with monochromatic light at 405 nm, Fourier transform infrared (*FT*i.r.) spectroscopy, differential thermal analysis (d.t.a.) and thermogravimetric analysis (t.g.a.). It is shown that unlike anhydride-containing copolymers which decompose easily upon u.v.-irradiation, the organotin derivatives cross-link under similar conditions. It is explained that the relatively low values of the quantum efficiency, $\varphi_{crl} = 0.035–0.11$ mol Einstein^{-1}, of the photochemical conversion and the high photosensitivity, $S = 6.8–21.6$ cm^2 J^{-1}, for the organotin copolymers is provided by coordination-bound organotin fragments with sensitive $CH_2–Sn$ groups which transfer readily to the intermolecular carboxylate form under the conditions of photooxidation. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: synthesis; photochemical reaction; photosensitivity)

INTRODUCTION

The photochemistry of functional polymers in the solid state is an important area of polymer science and technology. These polymers are applied widely as functionalized resists in microlithography. The synthesis and examination of photoreactive and photosensitive functional polymers have received considerable attention during recent years due to their important role as highly sensitive resist systems in microelectronic technology. The results obtained in this field have been summarized and discussed in many review articles[1–5].

In recent years, we have developed several new photosensitive, E-beam- and X-ray-sensitive polymer resist materials, the advantages of which over conventional resists lie in their speed and high sensitivity[6–8].

In early publications some attention has been focused on the study of photochemical reactions and lithographical properties of organosilicon[9–11] and organotin[12–15] polymer resists of the positive and negative type, respectively. It was shown that the pentacoordinated state of the tin atom in organotin epoxy-oligomers and carboxylate copolymers is the main reason for both the formation and photocross-linking reactions of their macromolecules[12–15].

The ever-increasing attention paid to organotin functional polymers may be attributed to their unique properties and the possibility to develop novel materials with specified characteristics.

In this study some results on the synthesis, photochemical reactions and structure–property correlation in polyfunctional film-forming polymers such as alternating copolymers of allyl chloroacetate (ACA) and allyl propionate (AP) with maleic anhydride (MA) and their organotin derivatives, alternating monoallyl maleate (MAM)–styrene (St), MAM–MA, tri-*n*-butylstannylallyl maleate (TBSAM)–St and TBSAM–MA copolymers, are discussed. The presence of highly u.v.-sensitive functional groups and bonds such as Sn–C, O=C, Cl–C and C=C (side-chain allyl or vinylene groups) and also coordination-bound fragments ($-C{=}O\ldots SnR_3$) in macromolecules of synthesized copolymers allowed us to develop the study of the photochemical reaction of functional macromolecules as an important objective of polymer photochemistry.

EXPERIMENTAL

Materials

The initial monomers such as ACA, AA and St, purified by distillation twice just before use, have the following characteristics: ACA: b.p. 84.5°C/0.65 kPa, $d_4^{20} = 1.1468$, $n_D^{20} = 1.4460$; AP: b.p. 45°C/0.69 kPa, $d_4^{20} = 1.0365$, $n_D^{20} = 1.4720$; St: b.p. 25.5°C/0.65 kPa, $d_4^{20} = 0.9058$, $n_D^{20} = 1.5468$.

MA was recrystallized from benzene and sublimed twice *in vacuo*; m.p. 52.8°C.

MAM was synthesized by the incomplete esterification of MA with allyl alcohol using a known method[16]; $d_4^{20} = 1.1517$, $n_D^{20} = 1.4708$.

TBSAM was synthesized by the condensation of MAM with hexa-*n*-butyldistannoxane using a known method [16]; b.p. 180–182°C/0.47 kPa, $d_4^{20} = 1.1517$, $n_D^{20} = 1.4708$.

Hexa-*n*-butyldistannoxane (HBDS) was purified by

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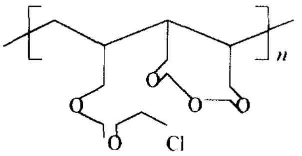
distillation *in vacuo*; b.p. 186.5–187°C/0.39 kPa, d_4^{20} = 1.1715, n_D^{20} = 1.4862.

Benzoyl peroxide (BP) as initiator was purified by precipitation twice from chloroform with methanol; m.p. 106°C.

Synthesis of copolymers

Copolymerization of ACA and AP with MA was carried out in benzene at 70°C in the presence of BP initiator (0.5%) in a nitrogen atmosphere. Reaction of MAM and TBSAM with St and MA was carried out in methylethylketone (MEK) at 60°C in the presence of BP (0.1–0.5%) in a nitrogen atmosphere.

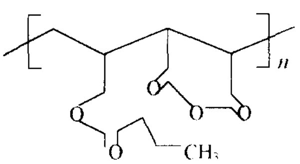
The copolymers synthesized have the following characteristics:



(I)

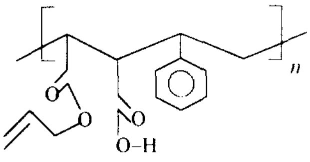
Aca–MA copolymer (I). Softening point 85–88°C, $[\eta]_{in}$ 0.17 dl g^{-1} in MEK at 20°C, acid number 499 mg KOH g^{-1}, Cl 14.76%.

*FT*i.r. spectra (film), cm^{-1}: ν_{CH2} 2925 (as) and 2850 (s), ν_{C-O-C} 1020, $\nu_{C=O}$ 1840 and 1780 (anhydride), ν_{C-Cl} 680.



(II)

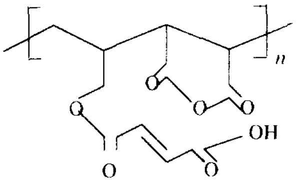
AP–MA copolymer (II). Softening point 120–123°C, $[\eta]_{in}$ 0.22 dl g^{-1} in MEK at 20°C, acid number 560 mg KOH g^{-1}.



(III)

MAM–St copolymer (III). Softening point 305°C, $[\eta]_{in}$ 0.14 dl g^{-1} in MEK at 20°C, acid number 220 mg KOH g^{-1}, unsaturation (allyl) 28.6%.

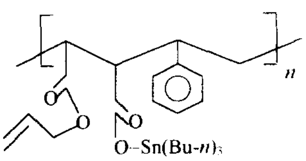
*FT*i.r. spectra (film), cm^{-1}: $\nu_{CH=}$ 3080 and 3025 (vinyl), ν_{CH2} 2940, $\nu_{C=O}$ (ester group) 1735, ν_{C-C} 1605 (benzene ring), $\nu_{C=O}$ 1710, δ_{C-O} (–COOH) 1380, ν_{C-C} 1650 (allyl), ν_{C-O-C} 1210, δ_{CH2} 995 and 930, $\delta_{CH=}$ 770 and 705 (benzene ring).



(IV)

MAM–MA copolymer (IV). Softening point 300–305°C, $[\eta]_{in}$ 0.07 dl g^{-1} in MEK at 20°C, acid number 660 mg KOH g^{-1}, unsaturation (vinylene) 31.5%.

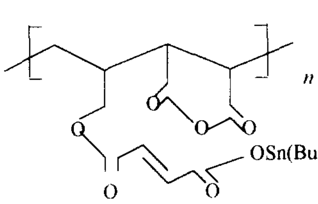
*FT*i.r. spectra (film), cm^{-1}: $\nu_{CH=}$ 3080, ν_{CH2} 2960 and 2855, $\nu_{C=O}$ (ester group) 1730, ν_{C-O} (anhydride) 1845 and 1775, ν_{C-O} 1715, ν_{C-O-C} 1215 and 1180, δ_{CH2} 990 and 930.



(V)

TBSAM–St copolymer (V). Softening point 97–100°C, $[\eta]_{in}$ 0.09 dl g^{-1} in MEK at 20°C, unsaturation (allyl) 23.8%, Sn 22.2%.

*FT*i.r. spectra (film), cm^{-1}: $\nu_{CH=}$ 3080 (phenyl) and 3025, ν_{CH2} 2930 and 2855, ν_{CH3} 2955 and 2870, $\nu_{C=O}$ (ester group) 1735, ν_{C-O-C} 1210, δ_{CH2} 995 and 930, $\nu_{C=C}$ (allyl) 1640, δ_{CH} 770 and 705 (monosubstituted benzene), ν_{Sn-O} 960, ν_{Sn-C} 552.



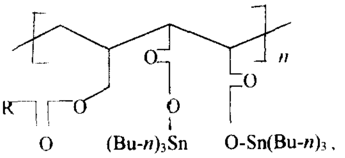
(VI)

TBSAM–MA copolymer (VI). Softening point 100–103°C, $[\eta]_{in}$ 0.06 dl g^{-1} in MEK at 20°C, unsaturation (vinylene) 18.9%, Sn 21.9%.

*FT*i.r. spectra (film), cm^{-1}: $\nu_{CH=}$ 3080, ν_{CH2} 2960 and 2855, ν_{C-O-C} 1210 and 1180, $\nu_{C=O}$ 1845 and 1780, δ_{CH2} 995 and 930, $\nu_{C=O}$ (–COOCH$_2$–) 1735, $\nu_{C=O}$ (–C=O...SnR$_3$) 1575, $\nu_{C=C}$ (–CH=CH–) 1650, ν_{Sn-C} 650 (as) and 535 (s).

Synthesis of organotin polymer-analogues

Organotin derivatives of ACA–MA and AP–MA copolymers were synthesized by condensation of anhydride-containing copolymers with HBDS in the heterogeneous phase in benzene at 40°C.The organotin polymer-analogues synthesized have the following characteristics:



where R = CH$_2$Cl and *n*-Pr

ACA–MA–Sn polymer-analogue. Softening point 70–72°C, $[\eta]_{in}$ 0.09 dl g^{-1} in MEK at 25°C, Sn 13.02%, Cl 9.82%.

AP–MA–Sn polymer-analogue. Softening point 108–110°C, $[\eta]_{in}$ 0.11 dl g^{-1} in MEK at 25°C, Sn 22.03%.

Organotin derivatives with different contents of tin (2.80–22.03%) have the following typical absorption bands of *FT*i.r. spectra: ν_{CH2} 2970 (s) and 2925 (as), ν_{CH3} 2960 (as) and 2855 (s), $\nu_{C=O}$ 1845 and 1770 (free anhydride group), $\nu_{C=O}$ 1745 (–COOCH$_2$Cl), $\nu_{C=O}$ 1650 (–COOSnR$_3$), $\nu_{C=O}$ 1580 (–OC=O···SnR$_3$), ν_{Sn-Bu} 1150, ν_{C-Cl} 800 and 695, ν_{Sn-C} 615 (as), ν_{Sn-C} 575 (–OC=O···SnR$_3$), ν_{Sn-C} 525 (s).

Methods

I.r. spectra of copolymer films before and after phototreatment were recorded by a Nicolet 510 *FT*i.r. spectrometer in the 4000–400 cm^{-1} range with a resolution of 2 cm^{-1}.

Thermogravimetric analysis (t.g.a.) and differential thermal analysis (d.t.a.) of copolymers before and after u.v.-irradiation were carried out with a derivatograph of the Paulik–Erday system in air at a heating rate 5°C min^{-1}.

An Osram-Ultra Vitalux E 27 u.v. high-pressure lamp (480 W) and monochromatic wavelength of 405 nm (actinometer with potassium ferrioxalate) served as sources of u.v.-irradiation. Thin polymer films (15–20 μm) formed from the solution in the presence or absence of 1,9-dibromoanthracene (DBA) as sensitizer (E_T = 168 and E_S = 294 kJ mol^{-1}[17]) on KBr optic crystals were exposed to u.v.-

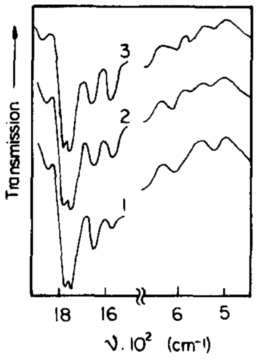


Figure 1 Fragments of the *FT*i.r. spectra of the organotin derivative of the ACA–MA copolymer (Sn 21.92% and Cl 6.45%) (1) before and after u.v.-irradiation for (2) 30 and (3) 60 min

irradiation in a special box. The distance between the source and the films was kept at 15 cm.

The photosensitivity of the copolymers was measured by using a radiation thermoelement RTE-10 with $I^{ab} = 1.377 \times 10^{-10}$ Einstein s^{-1}.

RESULTS AND DISCUSSION

Alternating anhydride-containing copolymers and their organotin derivatives

The *FT*ir study of the structure of the ACA–MA copolymer and its organotin derivatives (*Figure 1*), with different degrees of transformation after u.v.-irradiation, shows that the essential decrease of the CH_2 (in the butyl substitute of the tin atom) band intensity and the increase of the C=O absorption bands 1650 and 1580 cm^{-1} (in ($C{=}O\cdots SnR_3$) take place. Simultaneously, the intensity of the Sn–C band at 525 cm^{-1} decreases and a new band at 575 cm^{-1} related to the pentacoordinated state of the tin atom in the organotin carboxylate fragment appears. The intensity of this band increases with irradiation time.

Visual illustration of the changes in the *FT*ir spectra of the organotin macromolecules exposed to u.v.-irradiation is presented in *Figure 2*. The intensity ratio between typical absorption bands (m^{2925} and m^{2855}) and the least changing band (m^{1360}) is used to illustrate the changes in the spectra. The change Δm ($m_0 - m_t$) at the initial irradiation stage can serve as a parameter for characterization of photochemical conversions into the organotin copolymer during absorption of radiation energy. As is evident from *Figure 2*, the photocross-linking reaction rate increases with a decrease in the tin content from 27.8 to 8.1% in ACA–MA–Sn polymer-analogues. This can be explained by an increase in the probable formation of photosensitive coordination-bound organotin fragments in copolymers with a low content of tin. Organotin derivatives of the AP–MA copolymer were used as model polymers containing no Cl-substitute (*Figure 2*, straight lines 7 and 8). It is seen that the presence of the Cl-substitute in the macromolecules also speeds up the photochemical conversion of copolymers. Polymer-analogues containing both Cl-substitute and tin have a greater tendency to photocross-linking compared with the organotin derivatives.

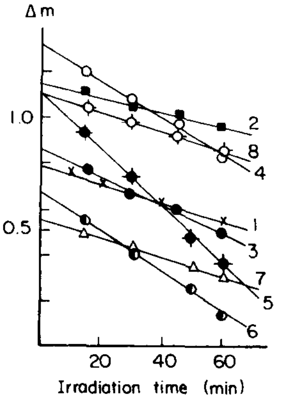


Figure 2 Plot of the absorption change, Δm (1360) *versus* u.v.-irradiation time for bending bands of organotin derivatives of (1–6) ACA–MA and (7 and 8) AP–MA copolymers: (1, 3, 5 and 7) 2855, (2, 4, 6 and 8) 2925 cm^{-1}. $\Delta m = \log A(2855 \text{ or } 2925)/\log A(1360)$

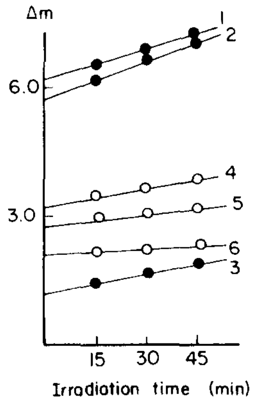


Figure 3 Plot of the absorption change, Δm (1450) *versus* u.v.-irradiation time for bending bands of (1–3) ACA–MA and (4–6) AP–MA copolymers: (1 and 4) 1770, (2 and 5) 1740, (3) 790 and (6) 1125 cm^{-1}

In the case of the ACA–MA and AP–MA alternating copolymers exposed to u.v.-irradiation, the degradation processes accompanied by an increase in the absorption band intensities of 1770 and 1740 ($\nu_{C=O}$), 790 (ν_{C-Cl}) and 1125 cm^{-1} (δ_{CH3}) (*Figure 3*) are dominant.

Quantum efficiency (φ) is the most important parameter for the characterization of photochemical reactions of functional polymers. Values of φ for studying photochemical reactions of copolymers were determined by the well-known actinometric method by using potassium ferrioxalate which has high sensitivity towards monochromatic light at 405 nm.

The experimental findings of the optical density of thin polymer films in the absorption region of the C=O group, of the molar extinction coefficient of irradiated and non-irradiated films, and the intensities of absorbed light at 405 nm made it possible to determine the quantum efficiency for the photocross-linking (φ_{crl}) and photodestruction (φ_{dst}) processes using the following equations:

$$\varphi_{crl} = \frac{\Delta n}{I_n^{ab}t} \cdot \frac{C_0(D_0 - hD_t)}{D_t I_n^{ab} t} \qquad (1)$$

$$\varphi_{dst} = \frac{\Delta n}{I_n^{ab}t} \cdot \frac{C_0(hD_0 - D_t)}{D_t I_n^{ab} t} \qquad (2)$$

where C_0 is the initial concentration (mol), h is the thickness of the films (cm), D_0 and D_t are the optical densities of the films before and after irradiation, respectively, t is the exposition time (s), and $I_n^{ab} = 0.2066 \times 10^{-10}$ is the difference between the 405 nm absorption on the KBr crystal with coating and the pure crystal.

For quantitative appraisal of the sensitivity of the copolymers exposed to 405 nm monochromatic light in the absence and presence of sensitizer DBA, the method of solubility differentiation of thin films in a solvent (MEK organotin copolymer or water for anhydride-containing copolymers) was used. The photosensitivity (S) of the films

Table 1 Quantum efficiency of photochemical reaction (φ) and photosensitivity (S) of ACA–MA and AP–MA alternating copolymers and their organotin derivatives

Copolymer	Sn (%)	Cl (%)	φ_{crl} (mol Einstein^{-1})	Photosensitivity (cm^2 J^{-1})[a]	
				S_0	S_{DBA}
ACA–MA	0.00	15.66	0.06[b]	5.6	7.7
ACA–MA–Sn	27.81	4.23	0.13	10.4	20.6
ACA–MA–Sn	21.92	6.45	0.18	13.2	25.0
ACA–MA–Sn	13.06	8.12	0.27	24.2	38.5
ACA–MA–Sn	8.13	12.34	0.32	50.0	89.7
ACA–MA–Sn	2.82	14.25	0.12	8.6	10.7
AP–MA	0.00	0.00	0.07[b]	7.3	10.2
AP–MA–Sn	14.61	0.00	0.19	9.6	17.0

[a] Values of S_0 and S_{DBA} characterize the photosensitivity of the copolymers and their organotin derivatives determined in the absence and presence of 3% 1,9-dibromoanthracene (DBA) as a sensitizer, respectively

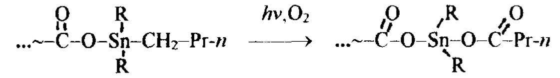
[b] These values characterize the photodegradation reaction (φ_{dst})

was determined by the more rapid and greater solubility in the developer of the non-exposed surface parts with the preservation of the photorelief of necessary height by the following known equation[20]:

$$S = 1/It \tag{3}$$

where I is intensity of the activated irradiation with λ = 405 nm (J cm^{-2}) and t is exposition time (s).

The values of φ_{crl}, φ_{dst} and S obtained are presented in *Table 1*. These values ($\varphi < 1$) suggest the domination of the photochemical cross-linking reactions in the presence of O_2. On the other hand, the organotin macromolecules, in contrast to the ACA–MA or AP–MA copolymers, inhibit peroxide formation and favour other reactions essential for photooxidation:



$$\ldots\sim\!\!-\overset{\overset{\displaystyle O}{\|}}{C}-O-\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle R}{|}}{Sn}}-CH_2-Pr\text{-}n \xrightarrow{h\nu, O_2} \ldots\sim\!\!-\overset{\overset{\displaystyle O}{\|}}{C}-O-\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle R}{|}}{Sn}}-O-\overset{\overset{\displaystyle O}{\|}}{C}-Pr\text{-}n \tag{4}$$

The quantum efficiency of the photochemical conversion and the photosensitivity of the organotin copolymers are strongly dependent on the content of tin in the copolymers with maximum values of φ_{crl} and S at 8–13% of tin (*Table 1*).

Thus, the addition of organotin groups in the anhydride-containing copolymer by the polymer-analogous reaction prevents the destruction processes because of the tendency of these groups to coordination-bound formation with electron-donor substitutes of macromolecules, on the one hand, and stimulates the proceeding of photocross-linking reactions primarily in the side-chain fragments, on the other.

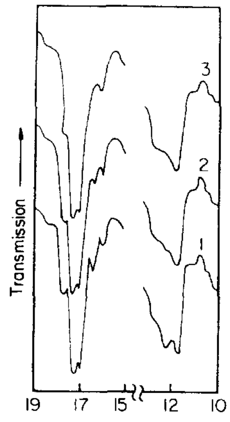


Figure 4 Fragments of the *FT*i.r. spectra of the MAM–St copolymer (1) before and after u.v.-irradiation for (2) 40 and (3) 90 min

Unsaturated organotin copolymers and their organic analogues

The MAM–St, TBSAM–St, MAM–MA and TBSAM–MA alternating copolymers containing photosensitive and reactive double bonds of the allyl (donor) and vinylene-maleate (acceptor) type, with carbonyl and organotin carboxylate groups in the side-chain, also readily undergo photocross-linking upon u.v.-irradiation with light at 405 nm.

Cross-linking of copolymers was studied by *FT*i.r. spectroscopy at various stages of exposure with u.v.-light. Considerable changes in the MAM–St copolymer absorption bands at 1778 and 1710 (C=O), 1650 (C=C) and 1215 cm^{-1} (C–O) after exposure to u.v.-irradiation have been observed (*Figure 4*).

The changes in typical absorption bands of MAM–St and TBSAM–St copolymer films exposed to u.v.-irradiation during various times are presented in *Figure 5*. The decrease in the relative intensities of the carbonyl, allyl and α-methylene (CH_2–Sn) bands and the disappearance of the 1650 cm^{-1} (C=C) band have been observed; in addition, the exposed portions of films became insoluble in organic solvents. The changes observed in the spectra suggest the formation of cross-linked fragments with participation of photosensitive side-chain allyl and CH_2–Sn groups.

Analogous decreases of typical band intensities have been observed in the *FT*i.r. spectra of MAM–MA (*Figure 6*) and TBSAM–MA (*Figure 7*) alternating copolymers exposed to u.v.-irradiation under similar conditions.

In the *FT*i.r. spectra of TBSAM–MA organotin copolymer film exposed to u.v.-light at various stages (10–60 min), the gradual decrease of the absorption band of the CH_2–Sn group (ν^{as}_{CH} 2920 and ν^{s}_{CH} 2855 cm^{-1}) and the C=C

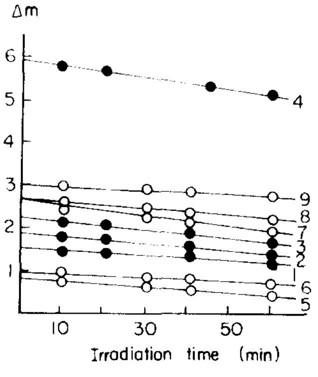


Figure 5 Plot of the absorption change, Δm (1490) *versus* u.v.-irradiation time for bending bands of (1–4) MAM–St and (5–8) TBSAM–St copolymers: (1 and 6) 990, (2 and 5) 930, (3 and 7) 1650, (4) 1710, (8) 1730 and (9) 2925 cm^{-1}

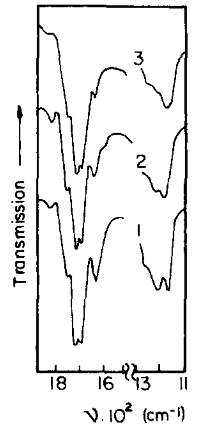


Figure 6 Fragments of the *FTi.r.* spectra of the MAM–MA copolymer (1) before and after u.v.-irradiation for (2) 30 and (3) 60 min

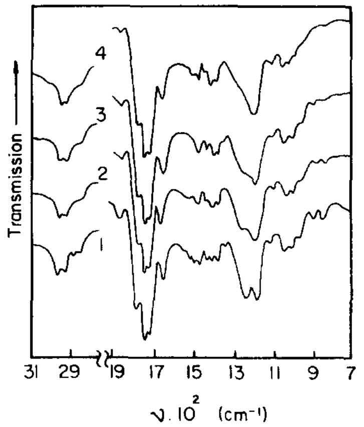


Figure 7 *FTi.r.* spectra of the TBSAM–MA copolymer (1) before and after u.v.-irradiation for (2) 15, (3) 30 and (4) 60 min

bond (δ_{CH}= 960 and 825 cm^{-1}) and simultaneous decreases of most typical bands have been observed. The changes observed indicate that the photocross-linking of the macromolecules proceeds through photodimerization of the side-chain maleate double bounds and photooxidation of the CH_2–Sn bonds in the tri-*n*-butylstannyl groups (*Figure 8*).

On the basis of the experimental data of *Table 2*, φ_{crl} values were found by using equation (1). The quantum efficiency of photocross-linking (φ_{crl}) of the macromolecules was calculated from the changes in the optical density of the 2855, 1710 and 1210 cm^{-1} absorption bands. As is evident from the data of *Table 2*, the value of φ_{crl} is not very dependent on the change in the absorption band type.

In the case of water as solvent-developer for MAM–MA and TBSAM–MA copolymers, hydrolysis of the anhydride groups occurs and the free carboxyl groups formed increase the hydrophobic properties of the films, and consequently provide the rapid solubility of the thin layers of the photoresists. That is why anhydride-containing copolymers have higher photosensitivity compared with copolymers containing styrene units. Moreover, the addition of the sensitizer in the system studied essentially speeds up the cross-linking of the macromolecules and allows the photoresists formed to have high sensitivity (*Table 2*).

As is seen from the φ_{crl} values obtained (*Table 2*), the photocross-linking proceeds more easily the as compared with peroxide-formation and photooxidation reactions. The comparatively low value of φ_{crl} for the organotin copolymers (TBSAM–St and TBSAM–MAM) can also be explained by the increase in flexibility and photosensitivity of the macromolecules because of the side-chain tri-*n*-butylstannyl groups.

T.g.a. and d.t.a. methods were then used to study the photo- and thermal cross-linking of the alternating unsaturated MAM–St copolymer and its organotin analogue the TBSAM–St copolymer with allyl groups in the side-chain.

The results obtained are illustrated in *Figure 9*. These data show that the character of the t.g.a. and d.t.a. curves is different because exo-peaks at 160 and 140°C appear before the beginning of the thermal degradation processes, which may belong to the cross-linking reaction of the macromolecules in the isothermal conditions. This can be confirmed by the following interpretations of the data given in *Figure 9*: (1) on the d.t.a. curves the exo-peaks disappear before the phototreated (25°C, 60 min, curves 3 and 4) copolymers; (2) in the conditions noted above for the phototreated copolymers, there is an increase in polymer thermostability, which is also in agreement with data of the t.g.a. analysis; (3) the smaller weight loss of the phototreated copolymers (curves 3 and 4) compared with the pure copolymers (curves 1 and 2) confirms the cross-linked

Table 2 Experimental data for the determination of the quantum efficiency of the photochemical reaction (φ) and the photosensitivity (S) of MAM–St, TBSAM–St, MAM–MA and TBSAM–MA alternating copolymers

Parameter	Copolymer			
	MAM–St	TBSAM–St	MAM–MA	TBSAM–MA
Density (g cm^{-3})	1.101	1.078	1.184	1.205
Thickness of film (μm)	18.0	19.0	19.0	21.0
Concentration × 10^5 (mol g^{-1})	4.2	1.9	4.6	2.3
Initial optical density of absorption bands:				
D_0 (2855)	–	0.3148	–	0.0793
D_0 (1710)	0.5759	–	0.4742	–
D_0 (1210)	0.2253	0.2494	0.2409	0.2554
Optical density of absorption bands for time t:				
D_t (2855)	–	0.2840	–	0.0771
D_t (1710)	0.4824	–	0.3394	–
D_t (2855)	0.2062	0.2574	0.2508	0.2477
Exposure time to u.v.-light at 405 nm (s)	1800	1800	1800	1800
Photosensitivity				
S_0 (cm^2 J^{-1})	14.7	13.0	9.7	3.8
S_{DBA} (cm^2 J^{-1})	16.6	21.6	19.3	6.8
Quantum efficiency of photocross-linking, φ_{crl} (mol Einstein^{-1}):				
φ(2855)	–	0.087	–	0.035
φ(1710)	0.12	–	0.13	–
φ(1210)	0.16	0.11	0.09	0.054

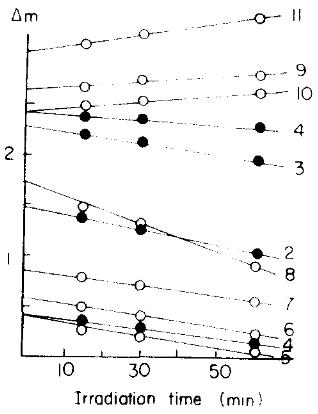


Figure 8 Plot of the absorption change, Δm (1475 or 1395) *versus* u.v.-irradiation time for bending bands of (1–4) MAM–MA and (5–8) TBSAM–MA copolymers: (1 and 5) 625, (2 and 8) 1215, (3) 1705, (4) 1730, (6) 2855, (7) 2920, (9) 1440, (10) 1415 and (11) 1460 cm^{-1}

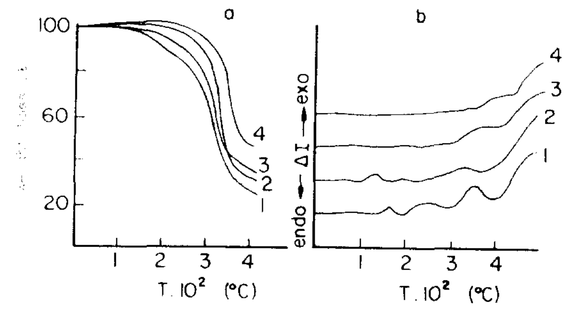


Figure 9 The curves of (a) t.g.a. and (b) d.t.a. of (1) MAM–St and (2) TBSAM–St copolymers (1 and 2) before and (3 and 4) after u.v.-irradiation

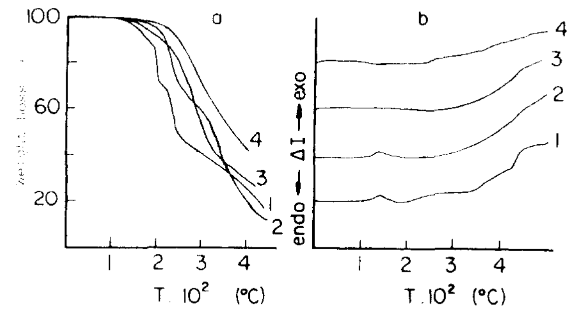


Figure 10 The curves of (a) t.g.a. and (b) d.t.a. of (1) MAM–MA and (2) TBSAM–MA copolymers (1 and 2) before and (3 and 4) after u.v.-irradiation for 60 min. Heating rate is 5°C min^{-1} in air

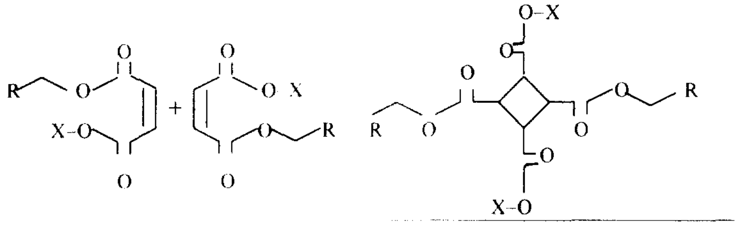
structure of the macromolecules as a result of intermolecular reactions of the allyl groups in the side-chain.

The copolymers easily undergo cross-linking by u.v.-irradiation as a consequence of which the films become insoluble.

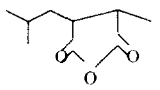
It is shown that the organotin TBSAM–St copolymer has higher thermostability than the MAM–St copolymer which can be explained by the stabilizing effect of the side-chain organotin carboxylate fragments of the macromolecules.

Analogous changes in the t.g.a. and d.t.a. curves (*Figure 10*) for the MAM–MA and TBSAM–MA copolymers are observed. In contrast to the copolymers with styrene units, the anhydride-containing unsaturated copolymers have low thermostability, which can be explained by the low molecular weight of these copolymers ($[\eta]_{in} = 0.06$–0.07 dl g^{-1}).

The exo-peaks at 135 and 145°C in the d.t.a. curves also disappear after exposure of the copolymer films to u.v.-irradiation; an increase in copolymer thermostability (curves 3 and 4) is observed. This is explained by the formation of cross-linked structures through photodimerization of the side-chain maleate double bonds by preservation of orbital symmetry during the reaction according to the following scheme:



where R is the macromolecular chain of



and X = H or $(n\text{-Bu})_3$Sn.

It is known that cyclobutane photosynthesis is a typical reaction for a 1,2-substituted ethylene such as poly(vinyl cinnamate) and its analogues[18,19]; the high activity of cinnamoyl derivatives in the photodimerization reaction was explained.

The formation of cyclobutane cross-linked fragments in macromolecules of MAM–MA and TBSAM–MA copolymers is confirmed by the data of the *FT*i.r. analysis (*Figure 8*): (1) the disappearance of the maleate double bond absorption bands and (2) the increase in the intensity of the *tert*-CH band (in the CH–CO group) at 1460–1400 cm^{-1}.

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