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Electrical degradation of polymers of styrene and substituted styrenes. 2

A. Gustafsson[1], T. Reitberger[2], and U. W. Gedde[1,*]

[1]Department of Polymer Technology, Royal Institute of Technology, S-100 44 Stockholm, Sweden
[2]Department of Nuclear Technology, Royal Institute of Technology, S-100 44 Stockholm, Sweden

SUMMARY

Different substituted styrene monomers (p-amino styrene (p-AS), p-dimethylamino styrene (p-DMAS), p-trifluoromethyl styrene (p-TFMS), p-phenoxy styrene (p-PhOS), p-benzyloxy styrene (p-BeOS) and p-chloromethyl styrene (p-ClMS)) were copolymerized with styrene. Homopolymers were produced of monomers p-PhOS and p-butoxy styrene (p-BuOS). Thin films of the polymers were subjected to external partial discharges in air and the time to breakdown was measured. The stability of the polymers towards partial discharges is discussed with reference to radical formation and segmental mobility.

INTRODUCTION

Electrical degradation of polymer insulations is frequently induced by partial discharges (PD). These PD's produces a variety of aggressive species, e.g. energetic electrons and ions, ozone and UV radiation (1) which interact with the polymer and cause radical formation, chain scission, crosslinking and the formation of volatile species leading to surface roughening and to the growth of electrical trees (2). The degradation of a number of different homo- and copolymers of styrene and substituted styrenes subjected to external PD was reported in a previous paper (3), and the stability towards PD was discussed with reference to radical formation and segmental mobility. It was also demonstrated that the size of the aromatic system is a positive factor in obtaining polymers which are more stable towards PD and high electric fields. Styrene copolymers containing larger aromatic moieties, p-phenyl styrene and 2-vinyl naphthalene, were found to be more resistent towards PD than unsubstituted polystyrene also at low concentrations of the diaromatic monomer (3). This paper is an extension of the work on styrene polymers and includes a series of not previously studied co- and homopolymers of styrene monomers.

EXPERIMENTAL

p-Dimethylamino benzaldehyde, p-benzyloxy benzaldehyde and p-phenoxy benzaldehyde were purchased from Aldrich and p-amino styrene (p-AS) and p-chloromethyl styrene (p-ClMS) was respectively were obtained from Polyscience and Kodak. p-Trifluoromethyl styrene (p-TFMS) supplied by Prof. Jan Bergman, Department of Organic Chemistry, Royal Institute of Technology, Stockholm. Styrene (S), activated with neutral Al_2O_3, solvents, initiators and the Wittig reagents were used as received (Merck & Aldrich). p-Dimethylamino styrene (p-DMAS), p-phenoxy styrene (p-PhOS) and p-benzyloxy styrene (p-BeOS) were synthesized from the corresponding aldehydes using Wittig reagents (4). The yields of the monomers after the Wittig

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[*] Corresponding author

synthesis were about 70% and after the distillation about 40-50%. All monomers were distilled before use: *p-DMAS:* 109-111°C at 5 mbar, *p-PhOS:* 115-117°C at 4 mbar and *p-BuOS:* 87-88°C at 4 mbar. p-BeOS was recrystallized from hot ethanol. ^{1}H-NMR ($CDCl_3$, 250 MHz Bruker spectrometer) and gas chromatography (Varian 3400 GC) on the synthesized monomers verified pure products; *p-DMAS:* δ (ppm) = 7.40 (d, 2H, aromatic), 6.77 (d, 2H, aromatic) 6.75 (q, 1H, vinyl), 5.65 (d, 1H, vinyl), 5.11 (d, 1H, vinyl), 3.03 (s, 6H, $-N[C\underline{H}_3]_2$); *p-PhOS:* δ (ppm) = 7.0–7.5 (m, 9H, aromatic), 6.71 (q, 1H, vinyl), 5.68 (d, 1H, vinyl), 5.24 (d, 1H, vinyl); *p-BeOS:* δ (ppm) = 7.35–7.50 (m, 7H, aromatic), 6.94 (d, 2H, aromatic), 6.67 (q, 1H, vinyl), 5.61 (d, 1H, vinyl), 5.14 (d, 1H, vinyl), 5.09 (s, 2H, CH_2); *p-BuOS:* δ (ppm) = 7.34 (d, 2H, aromatic), 6.85 (d, 2H, aromatic) 6.67 (q, 1H, vinyl), 5.60 (d, 1H, vinyl), 5.11 (d, 1H, vinyl), 3.96 (t, 2H, $-O-C\underline{H}_2-$), 1.76 (m, 2H, $-O-CH_2-C\underline{H}_2-CH_2$), 1.50 (m, 2H, $-CH_2-C\underline{H}_2-CH_3$), 0.98 (t, 3H, $-CH_3$); *p-TFMS:* δ (ppm) = 7.61 (d, 2H, aromatic), 7.52 (d, 2H, aromatic) 6.78 (q, 1H, vinyl), 5.88 (d, 1H, vinyl), 5.47 (d, 1H, vinyl).

All the monomers (except p-BuOS) were suspension polymerized in water at 80°C for 9 h with gelatine (1 wt-% of water) as emulsifier and with 0.5 mol-% AIBN as initiator. The copolymer composition was studied by elemental analysis (Table 1).. p-BuOS was polymerized cationically in air at room temperature with BF_3OEt_2 as initiator; 5.0 g of the monomer was dissolved in CH_2Cl_2 (0.5 M) and 0.1 mol-% of the initiator was added (dissolved in CH_2Cl_2, 280 mM) during stirring which immediately gave a viscous solution. The solution was precipitated in a 10 times volume excess of methanol.

The copolymer reactivity ratios found were for p-AS ($r_S/r_{p\text{-}AS}$ = 0.41/0.22 (5)), p-DMAS ($r_S/r_{p\text{-}DMAS}$ = 1.01/0.84 (6)), p-PhOS ($r_S/r_{p\text{-}PhOS}$ = 1.38/0.94 (7)) and p-ClMS ($r_S/r_{p\text{-}ClMS}$ = 0.72/1.31 (8)). These show that the polymerizations give approximately random or alternating sequences of the monomers.

Table 1. Copolymer compositions from elemental analysis

Monomer feed		Calculated					Found					Copolymer
[mole-%]		C	H	N	O	Cl	C	H	N	O	Cl	composition
S/p-AS	80/20	0.897	0.077	0.026			0.907	0.078	0.022			83.5/16.5
S/p-DMAS	80/20	0.895	0.080	0.025			0.896	0.081	0.025			79.9/20.1
S/p-TFMS	80/20	0.836	0.067				0.825	0.067				77.4/22.6
S/p-PhOS	80/20				0.026					0.030		76.3/23.7
S/p-BeOS	80/20				0.026					0.034		71.3/28.7
S/p-ClMS	80/20					0.062					0.041	87.9/12.1

All polymers were purified by dissolution in appropriate solvents, filtrated and precipitated in cold methanol and dried to constant mass in vacuum. The polymers were analysed by size exclusion chromatography (Waters system with five µ-Styragel® columns; solvent: THF, 30°C, polystyrene standards) and, after compression moulding at 150°C to yield films of thicknesses 250±10 µm, by differential scanning calorimetry (Perkin-Elmer DSC-7; heating rate: 10 °C/min) and dielectric spectroscopy (Hewlett Packard 4284 LCR meter; 25°C, 1000 Hz). Data for molar mass, glass transition temperature and room temperature dielectric permittivity of the synthesized polymers are presented in Table 2. All polymers were tested by a dynamic mechanical spectrometer (Polymer Laboratories DMTA) between -155°C and 50°C at 10 Hz. The samples were subjected to tensile strains of 0.1 % (11 µm amplitude). All polymers were optically clear and exhibited only one glass transition indicating a single-phase morphology.

The electrical testing involved exposure of the 250±10 µm films (compression moulded at 120–170 °C depending on glass transition temperature), after they had been single-side coated with evaporated Al, to external partial discharges (PD) by applying an AC-voltage of 4.0 kV at 1000 Hz in air at 23°C. The time to breakdown was measured by an attached clock and the acquired data were fitted to the Weibull distribution function (3,9).

Table 2. Chain structure, thermal transitions and dielectric constant of produced polymers.

Polymer	M_n	M_w	T_g [°C]	ε
PS[a]	39 000	77 000	103	2.79
P(S-*stat*-p-AS) (0.165)[b]	27 000	52 000	116	2.99
P(S-*stat*-p-DMAS) (0.201)[b]	31 000	74 000	116	2.97
P(S-*co*-p-TFMS) (0.226)[b]	54 000	129 000	109	2.81
P(S-*stat*-p-PhOS) (0.237)[b]	54 000	144 000	104	2.95
P(S-*co*-p-BeOS) (0.287)[b]	35 000	80 000	91	3.14
P(S-*stat*-p-ClMS) (0.121)[b]	16 000	67 000	111	3.44
P(p-PhOS)	78 000	331 000	91	2.93
P(p-BuOS)	239 000	411 000	57	3.62

(a) Values from ref. 3.

(b) Molar content of substituted styrene monomer in copolymer.

RESULTS AND DISCUSSION

All the polymers studied exhibited similar unimodal Weibull distributions (3,9), which indicates that the samples were free from large defects and voids. Table 3 presents a summary of the Weibull parameters based on the time to breakdown data, with 95% confidence limits of the scale parameter ($t_{0.63}$) indicating the time when 63% of the samples have failed, and the shape parameter (b), which is a measure of scatter in the breakdown data. Table 3 shows that all the substituted styrene monomer units studied have a deleterious effect on the stability towards PD. All the different substituted styrenes are discussed in the following with reference to radical formation and segmental mobility. The influence of the substituents on the electron density is reflected by the Hammett constants (σ_p) taken from Jaffé (10).

Table 3. Weibull parameters from PD-experiments (time to breakdown data).

Polymer	n[a]	$t_{0.63}$ (h)	$t_{0.63}$ (h) (95%)	b	b (95%)
PS[c]	24	17.3	16.1–18.2	7.1	5.7–10.6
P(S-*stat*-p-AS) (0.165)[b]	19	13.4	12.1–14.8	5.8	3.6–8.0
P(S-*stat*-p-DMAS) (0.201)[b]	17	15.4	13.9–17.0	6.0	3.6–8.2
P(S-*co*-p-TFMS) (0.226)[b]	18	14.1	13.0–15.3	7.1	4.3–9.7
P(S-*stat*-p-PhOS) (0.237)[b]	18	15.4	14.0–16.8	6.4	4.0–8.8
P(S-*co*-p-BeOS) (0.287)[b]	17	10.8	9.8–11.9	6.1	3.7–8.4
P(S-*stat*-p-ClMS) (0.121)[b]	16	14.1	12.6–15.8	5.4	3.2–7.5
P(p-PhOS)	19	12.4	11.2–13.8	5.5	3.4–7.4
P(p-BuOS)	16	7.9	7.1–8.7	6.2	3.7–8.6

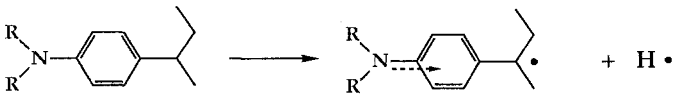
(a) Number of data points.

(b) Molar content of substituted styrene monomer in copolymer.

(c) Data from ref. 3.

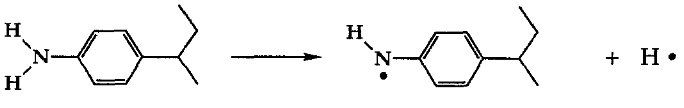
p-AS and p-DMAS

In accordance with ref. 3, polystyrene substituted with strongly electron-donating amino groups (σ_p= –0.66 (p-AS), σ_p= –0.60 (p-DMAS)) shows a low resistance towards PD due to stabilization of the resulting benzyl radical (Reaction 1). The latter reacts further with oxygen which propagates the degradation (11).



(1)

Tanigaki et al. (12) have also suggested hydrogen removal from the amino group (Reaction 2) which enhances the production of radicals. This may explain why the amino group is more deleterious towards PD exposure than the dimethylamino group (Table 3). Since electron-donating substituents lower the ionization potential (13) of the aromatic nucleus, a cation radical may be formed (Reaction 3) which decomposes to a radical and a proton (Reaction 4). The same ionization process is proposed to give the stabilizing effect in polymers containing so-called "voltage stabilizers". These compounds are considered to thermalize energetic electrons when they are added to the polymer (14).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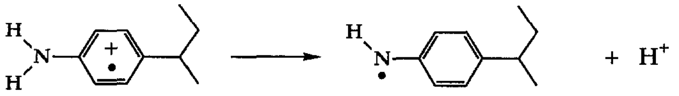
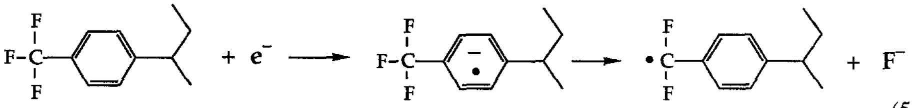

(4)

p-TFMS

It was shown in the previous paper (3) that halogen-containing styrene polymers show low PD-resistance. It was proposed that electrons were attached to the aromatic nucleus causing the formation of a halogen anion. The same behaviour is proposed for the electron-withdrawing p-trifluoromethyl substituent ($\sigma_p = 0.55$), Reaction 5. The primary radical formed presumably abstracts a hydrogen atom according to Reaction 6.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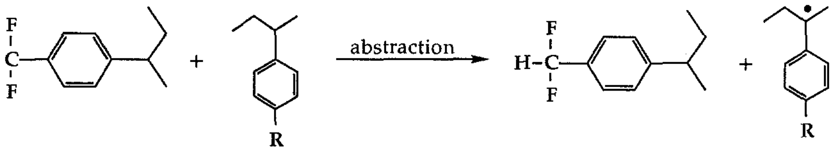
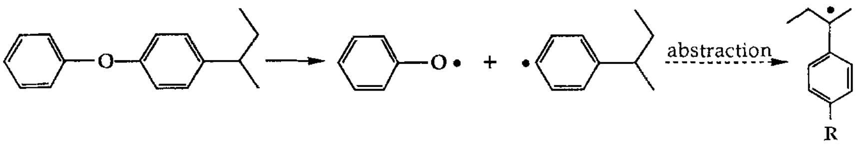


(6)

p-PhOS

p-PhOS has about the same Hammett constant ($\sigma_p = 0.03$) and segmental mobility as the unsubstituted styrene (Table 4). The negative influence of the phenoxyl substituent on the PD resistance can be explained neither by an increased stabilization of the benzyl radical nor by a higher segmental mobility (3). One possible explanation might be that relatively stable phenoxyl radicals are formed, Reaction 7. Both primary radicals may react further by abstracting hydrogen atoms to form benzyl type radicals as in Reaction 6.



(7)

The phenoxyl radical formed shows electron affinity and may also trap an electron to give a phenolate anion, Reaction 8.

(8)

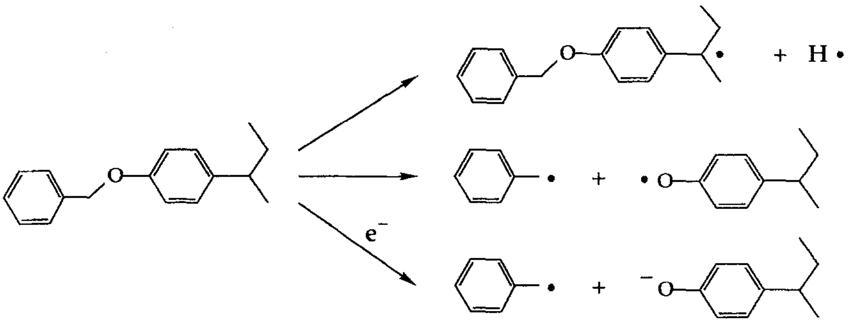
Table 4. Dynamic mechanical data at 10 Hz.

Polymer	log E (23°C)	log E(–150°C)	E (23°C)/E(–150°C)
PS[a]	9.304	9.393	0.81
P(S-*stat*-p-AS) (0.165)[b]	9.344	9.439	0.80
P(S-*stat*-p-DMAS) (0.201)[b]	9.356	9.448	0.81
P(S-*co*-p-TFMS) (0.226)[b]	9.382	9.308	0.84
P(S-*stat*-p-PhOS) (0.237)[b]	9.268	9.363	0.80
P(S-*co*-p-BeOS) (0.287)[b]	9.112	9.248	0.73
P(S-*stat*-p-ClMS) (0.121)[b]	9.310	9.414	0.79
P(p-PhOS)	9.148	9.274	0.75
P(p-BuOS)	9.074	9.517	0.36

(a) From ref. 3.
(b) Molar content of substituted styrene in copolymer.

p-BeOS

The deleterious influence of the electron-donating benzyloxy substituent ($\sigma_p = -0.42$) may be ascribed to the facile formation of benzyl radicals according to Reaction 1 (Reaction 9). It is also possible that bond scission in the pendant group may occur giving two stabilized radicals, Reaction 10. A dissociative electron attachment may also occur, Reaction 11.



(9)

(10)

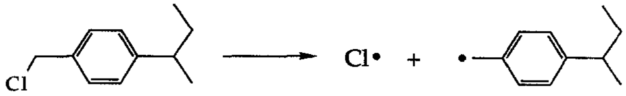
(11)

The benzyloxy group increases the segmental mobility of the polymer (Table 4). Therefore, the recombination of formed radicals by cage effects may be reduced and, consequently, the degradation may be promoted. The low stability towards PD is clearly demonstrated in Table 3. Note that the copolymer contains only ~29% p-BeOS-units.

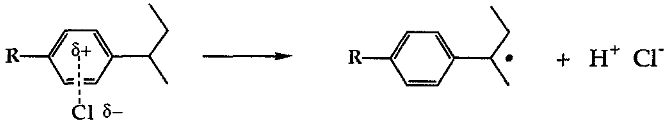
p-ClMS

The influence of the chloromethyl group was as expected. It has been shown for corresponding low molar mass analogs that chlorine is to a great extent removed during irradiation (12) producing benzyl radicals in the pendant group and free chlorine atoms, Reaction 12 (15). The latter may add to aromatic rings and give rise to benzyl radicals in the main chain, Reaction 13.

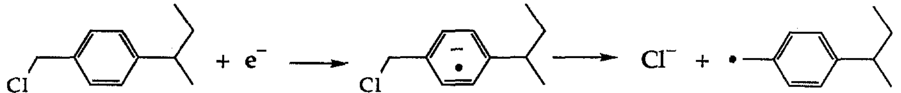
The electron-withdrawing character ($\sigma_p = 0.18$) may also promote the dissociative electron attachment (cf. Reaction 5) shown in Reaction 14.



(12)



(13)

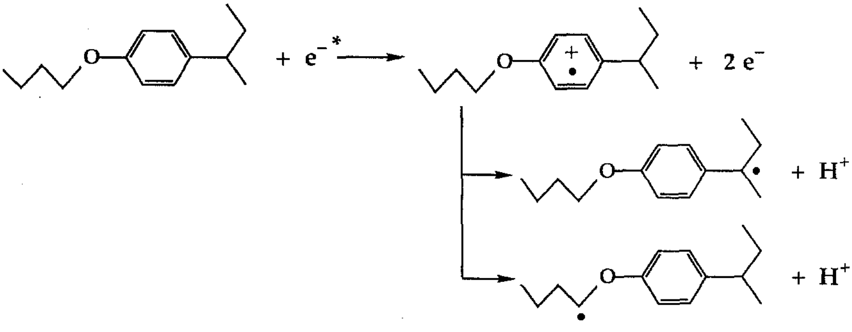


(14)

The chloromethyl substituent is very sensitive to radiation and p-ClMS-containing polymers are discussed as negative resists since crosslinks are easily produced by recombination of the radicals formed (12). The crosslinking may also explain why the number of p-ClMS units is significantly less in the polymer than is indicated by the composition of the monomers, Table 1.

p-BuOS

This homopolymer shows a high segmental mobility and a very low stability towards PD. The large decrease in modulus (Table 4) increases with the number of methylene units in the substituent (3). These strong sub-glass processes are shown in Figure 1. This higher segmental mobility inhibits radical recombination reactions by decreasing the cage effect. The electron-donating butoxy group ($\sigma_p = -0.32$) also contributes to the stabilization of benzyl radicals by the β-scission (cf. Reaction 1) which in turn increases the formation of radicals and hence the oxidative degradation. In the case of this electron-donating alkoxy group, ionization may also occur, Reaction 15.



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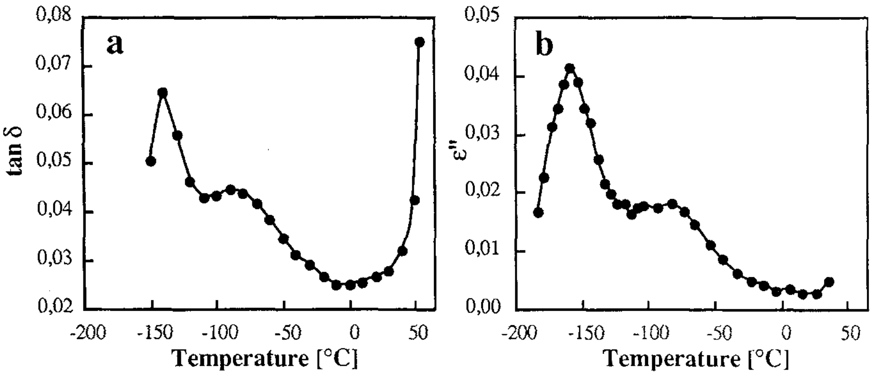

Figure 1. Loss data for P(p-BuOS) obtained by (a) dynamic mechanical thermal analysis at 10 Hz and (b) dielectric spectroscopy at 10 Hz (16).

CONCLUSION

This paper corroborates the results of our previous study that the overall stability of a given styrene polymer is controlled primarily by the stability of the polymer towards the formation of radicals. High segmental mobility decreases the probability of fast radical recombinations and this results in increased (oxidative) degradation. In the case of non-halogenic styrene polymers, data indicate that a dominant initiation reaction is the formation of a benzyl type radical or, where appropriate, the formation of a phenoxyl radical. Polymers with strong electron-donating substituents are more easily oxidized and show less stability against fragmentation, due to stabilization of the resulting benzyl radical. Electron-donating substituents in the aromatic ring also impart a lower ionization potential. Accordingly formation of radical cations is favoured, and these may decompose by elimination of protons to give, e. g. radicals of the benzylic type. Halogen-containing polymers generally show a very low stability towards partial discharges and the stability decreases with increasing electronegativity of the halogen. It is suggested that halogen atoms allow a dissociative electron-attachment reaction to occur. The resulting radical presumably produces a benzyl type radical by abstracting a hydrogen atom intermolecularly.

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