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Magnetic field effect on the photocrosslinking of a butadiene-styrene copolymer modified by benzoyl or phenylacetyl groups

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SUMMARY

A butadiene-styrene copolymer was partially modified by Friedel-Crafts reaction of phenyl groups with benzoyl chloride or phenylacetyl chloride. The resulting benzoylphenyl and phenylacetylphenyl groups served as photosensitizers for a subsequent crosslinking by u.v. irradiation. The extent of crosslinking was measured by sol/gel analysis. Crosslinking was carried out without magnetic field and with magnetic field of flux density 1.0 Tesla. The experiments with magnetic field yielded about 5% less soluble polymer, corresponding to a higher crosslink degree. The data were evaluated by statistical methods.

INTRODUCTION

Chemical reactions in magnetic fields have been investigated more frequently in recent years. Investigation in a magnetic field has become a method for the study of reaction pathways and diffusion processes and for isotope enrichment. Until now such measurements were preferably effected with low molecular substances (1), but the influence of magnetic fields is also interesting for polymers (2).

Our previous investigations were concerned with the influence of a magnetic field on the crosslinking of 1,4-polybutadiene by thermolysis of dibenzoyl peroxide or bis(2,4-dichlorobenzoyl) peroxide (3-5). The crosslink yield decreased by 2 to 5% in magnetic fields of 1.0 Tesla. Further measurements dealt with the photocrosslinking of polybutadiene or styrene-butadiene copolymer containing dispersed low molecular substances (phenanthrene, aromatic ketones) as photosensitizers without and with a magnetic field (3,6). Here the crosslinking was up to 15% more effective in a field of 1.0 Tesla. The results could be explained by radical pair theory (7) in both cases. Similar work was carried out by Morita et al. (8) with bromo- and chloromethylated polystyrene and 2,4-diisopentylthioxanthone as photosensitizer within the scope of investigations concerning photoresists.

In this paper we report experiments where the photosensitive groups benzoylphenyl (R_1) or phenylacetylphenyl (R_2) are bound covalently to polymers. Such polymers were prepared by Friedel-Crafts reactions of phenyl groups of a butadiene-styrene copolymer (SBR) with corresponding acid chlorides; the substitution was mainly in p-position. In the following, polymers containing R_1 are abbreviated BP-SBR and polymers containing R_2 are referred to as DB-SBR.

$$-C_6H_4-CO-C_6H_5 \qquad R_1$$

$$-C_6H_4-CO-CH_2-C_6H_5 \qquad R_2$$

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EXPERIMENTAL

Materials

Styrene-butadiene copolymer (SBR-E-53024, Goodyear) with 10 wt% styrene was purified by repeated precipitation with methanol from a solution in CH_2Cl_2. Benzoyl chloride, phenylacetyl chloride and $AlCl_3$ were applied as p.A. substances. CCl_4 and toluene were refluxed over P_2O_5 and distilled.

Modification of the polymer

For example, a solution of 150 mg of SBR in 50 ml of CCl_4 was added to a solution of 0.10 mmol of the acid chloride and 0.14 mmol of $AlCl_3$ in 10 ml of CCl_4 at 20°C. The reaction was stopped by addition of methanol after 20 min. The modified polymers were purified by repeated dissolution in CH_2Cl_2 followed by precipitation with methanol, dried in vacuo and kept in the dark under nitrogen at 5°C. The degree of modification (mmol keto groups in 100 g polymer) could be varied by different amounts of acid chloride or $AlCl_3$.

Photocrosslinking and crosslinking measurement

Polymer foils (thickness ca. 35 µm) on glass plates were crosslinked by u.v. irradiation with a 150 W high pressure mercury lamp at a distance of 80 cm as described elsewhere (5). The crosslinked products were characterized by determination of the polymer fraction soluble in toluene. For this the polymer foils were removed from the glass plates after reaction, weighed (G_v) and extracted with 15 ml of toluene for 3 days at 20°C. The remaining insoluble polymer was dried for 24 hr in vacuo at 40°C and weighed again (G_n). The soluble fraction G is

$$G\ (\%) = (G_v - G_n) * 100 / G_v$$

Spectra

i.r. Spectra of polymer foils were recorded with a Perkin-Elmer 684. The u.v. instrument was a Perkin-Elmer 550 SE. The content of keto groups (essentially R_1 or R_2) in the polymer was determined by comparison of the i.r. or u.v. absorption with that of calibration solutions of the corresponding low molecular substances (benzophenone or deoxybenzoin) and the unmodified polymer in CH_2Cl_2.

RESULTS AND DISCUSSION

Polymers BP-SBR were prepared with benzoyl chloride and had the following content of keto groups (mmol in 100 g polymer): 0.5, 1.3, 1.7 and 7.0. Polymers DB-SBR were received with phenylacetyl chloride, the content of keto groups being: 6.0, 8.0 and 13.0. i.r. Spectra of SBR, a BP-SBR and a DB-SBR are reproduced in Figure 1. In contrast to benzophenone the carbonyl band of BP-SBR does not appear at 1661 but at 1683 cm^{-1}. The carbonyl band of DB-SBR is also shifted to higher wave numbers compared with deoxybenzoin, namely from 1682 to 1707 cm^{-1}, as a result of the covalent bonding to the polymer chain. i.r. Spectra of the modified polymers were also taken after irradiation to investigate structural differences. With the band at 1490 cm^{-1} as reference, a decrease in the carbonyl band was found after irradiation. Otherwise no significant spectroscopic differences were found between irradiated and non-irradiated polymers.

For each polymer, at all reaction times (irradiation times) four experiments were carried out with 0 Tesla and four with 1.0 Tesla. Only mean values of G are considered in the following.

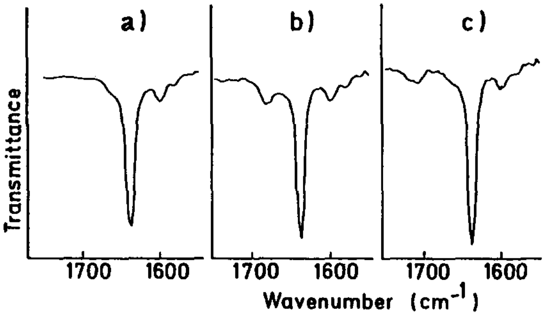

Figure 1. i.r. Spectra (1800-1200 cm^{-1}) of a) SBR, b) BP-SBR (7.0 mmol keto groups in 100 g polymer) and c) DB-SBR (8.0 mmol keto groups in 100 g polymer).

Table 1 gives a statistical evaluation for the experiments with BP-SBR (7.0 mmol keto groups in 100 g polymer) and differing reaction times with a flux density B = 0 Tesla and B = 1.0 Tesla; s denotes the standard deviation (in %). The difference E is calculated from

$$E\ (\%) = (G_{B=1.0} - G_{B=0}) * 100 / G_{B=0}$$

G is the soluble part of the samples in percent. The probability P, according to which the values received for 0 and 1.0 Tesla belong to different parent populations, is in most cases greater than 95% as shown by a Student's t test (9). Table 2 shows in the same way the evaluation

Table 1
Crosslinking of BP-SBR (7.0 mmol keto groups in 100 g polymer) at different reaction times without and with magnetic field; statistical evaluation of the polymer fraction G, soluble in toluene.

reaction time (min)	B = 0 Tesla		B = 1.0 Tesla		E (%)	P (%)
	G (%)	s (%)	G (%)	s (%)		
5	30.80	1.29	29.16	0.41	-5.30	97.5 - 99.0
15	23.27	0.22	22.76	0.76	-2.19	80.0 - 90.0
30	17.40	1.09	15.23	0.90	-10.99	99.5 - 99.9

Table 2
Crosslinking of DB-SBR (13.0 mmol keto groups in 100 g polymer) at different reaction times without and with magnetic field; statistical evaluation of the polymer fraction G, soluble in toluene.

reaction time (min)	B = 0 Tesla		B = 1.0 Tesla		E (%)	P (%)
	G (%)	s (%)	G (%)	s (%)		
10	80.10	0.58	79.12	0.32	-1.22	80.0 - 90.0
15	73.90	0.43	71.70	0.39	-2.98	99.9
30	60.95	0.63	59.70	1.04	-2.05	95.0 - 97.5
60	44.68	0.88	42.30	1.39	-5.33	97.5 - 99.0

for a DB-SBR (13.0 mmol keto groups in 100 g polymer). The relative difference between experiments with B = 0 Tesla and those with B = 1.0 Tesla is more obvious at longer reaction times for both polymers; at the beginning of the reaction the effect is in general ca. 2%, at the end between 5 and 10%.

Figure 2 demonstrates the dependence of the soluble fraction G on the content of keto groups at 15 and 30 min reaction times for BP-SBR. Figure 3 presents the curves for DB-SBR at 30 and 60 min. As expected the percentage of the soluble part decreases with increasing ketone concentration. Figure 4 depicts the soluble part as a function of the reaction time for BP-SBR (1.7 mmol keto groups in 100 g polymer) and DB-SBR (8.0 mmol keto groups in 100 g polymer). Although the concentration of the keto groups was much smaller in BP-SBR compared with DB-SBR, the decrease of the soluble part was much quicker, corresponding to a greater crosslinking efficiency. The curves for 0 and 1.0 Tesla differ at all reaction times.

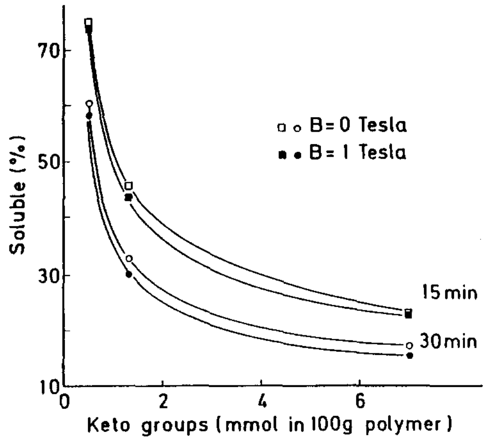

Figure 2. Crosslinking of BP-SBR; soluble fraction in toluene versus content of keto groups at 15 and 30 min reaction time, without and with (B = 1.0 Tesla) magnetic field.

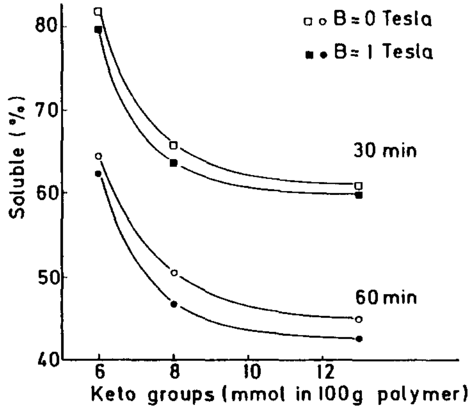

Figure 3. Crosslinking of DB-SBR; soluble fraction in toluene versus content of keto groups at 30 and 60 min reaction time, without and with (B = 1.0 Tesla) magnetic field.

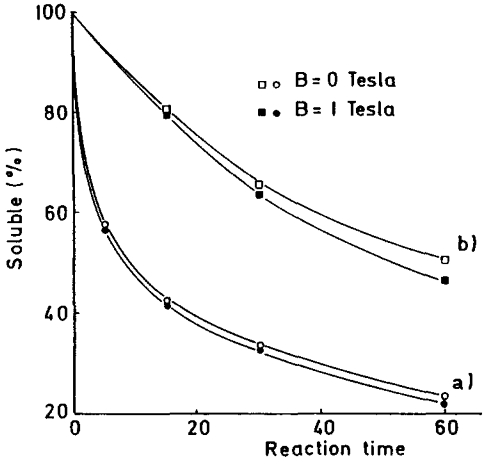

Figure 4. Crosslinking of a) BP-SBR (1,7 mmol keto groups in 100 g polymer) and b) DB-SBR (8.0 mmol keto groups in 100 g polymer); soluble fraction in toluene versus reaction time, without and with (B = 1.0 Tesla) magnetic field.

These results can be compared with those received with benzophenone or deoxybenzoin dispersed in SBR (6), showing that the magnetic field effect is smaller for photosensitive groups bound to the polymer. There are two possible explanations consistent with radical pair theory (7). First, the g factor of one component of the radical pair is changed because this component is now a polymer radical. Second, the mobility of the photosensitive entities is altered by fixing to a polymer backbone. Experiments attempting to distinguish between these possibilities will be described in a forthcoming paper.

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