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Copolymers from 1-Phenyl-2-(3-vinylphenylthio)-diazen and Styrene and Grafting with Acrylonitrile

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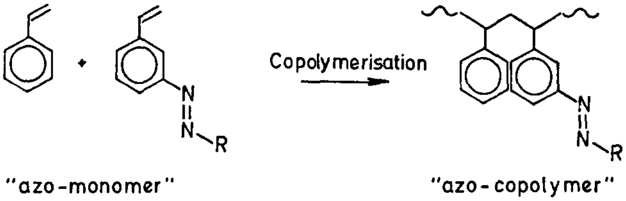
Summary

A new azo monomer (2) was synthesized and copolymerized with styrene. The resulting azo copolymer could be used as an initiator for the acrylonitrile polymerisation yielding grafted copolymers. Quantitative treatment of the grafting experiments leads to the conclusion that the intermediate thiyl radicals show less reactivity towards monomers than phenyl radicals.

1. Introduction

It is an important condition for controlled synthesizing of graft copolymers to prepare a backbone polymer with a defined number of possible grafting positions. One type of potential grafting positions of increasing interest are thermally instable azo groups, available through copolymerizing of "azo monomers" with ordinary monomers (KERBER et al. 1976; 1978; NUYKEN et al. 1979; in press)



favourably under such conditions, that the copolymer composition is similar to that of the monomer mixture (NUYKEN et al. 1979; in press). In the following chapters a new azo monomer will be described which fulfils this condition almost entirely in case of copolymerisation with styrene.

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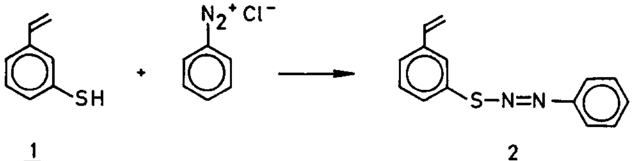
2. Synthesis of the azo monomer 2

1-phenyl-2-(3-vinylphenylthio)-diazen (2) was synthesized by coupling 3-vinylbenzenethiol (1) (HOFINGER 1979) with benzenediazonium chloride.



1 2

3. Copolymerisation of 2 with styrene

3.1. in bulk

At 50°C 2 operates as monomer and as initiator so that the copolymerisation of styrene/2 is affected without any additional initiator. Copolymer composition differs only relatively little from that of the starting monomermixture (TABLE 1)

TABLE 1: bulk copolymerisation of 2 (0,5 mol %) with styrene (99,5 mol %) at 50°C

polymerisation time h	2 mg	styrene g	conversion a) weight %	2 in copolymer b) mol %	$10^{-3}\ \bar{M}_n$ c)
1	103	8.57	3.6	0.61	28
3	100	8.67	10.6	0.74	30
6	104	8.59	19.1	0.49	34
15	95	8.20	35.7	0.34	50

a) gravimetrically determined
b) uv-spectroscopically determined
c) membranosmometer

The decrease in the concentration of 2 in the copolymers with increasing conversion can be explained by partial thermolysis of azo groups. In accordance with this explanation the molecular weights increase resulting from some side chains initiated by thermolyzed azo groups of the copolymer

3.2. in emulsion

The results obtained are very similar to those of the mass copolymerisation. Again it was found that monomer and copolymer compositions closely resemble each other (TABLE 2).

TABLE 2: emulsion copolymerisation of **2** (0,5 mol %) and styrene (99,5 mol %) at 40°C

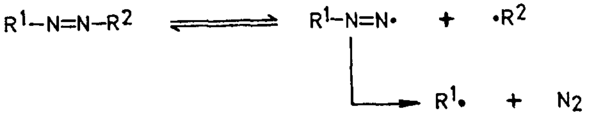
polymerization time h	**2** mg	styrene g	conversion[a] weight %	**2** in copolymer[b] mol %	$10^{-3}\cdot\bar{M}_w$ [c]
4	86	7.30	4.7	0.58	61
16	72	6.18	17.7	0,53	108

a) gravimetrically determined
b) uv-spectroscopically determined
c) light scattering

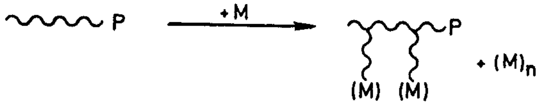
4) grafting with acrylonitrile

4.1. general remarks

Thermolysis of unsymmetric azocompounds R^1-N=N-R^2 generates 3 types of radicals (KERBER et al. 1974)



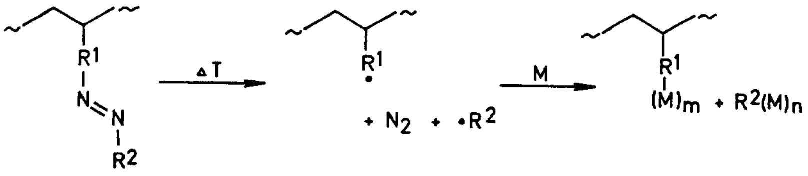
However, it seems reasonable to assume that the radicals R^1-N_2• are negligible because of their instability and therefore their short lifetime. From the radicals R^1• and R^2• one cannot expect without restrictions identical reactivity. One possibility to determine the differences in the reaction of these radicals is, among others (PRYOR 1966), the comparison of the characteristic quantities of grafting (FISCHER 1973) to polymer chains bearing either R^1• or R^2• radicals.



$$\text{success of grafting} \quad U_G\,[\%] = \frac{\text{grafted backbone P}}{\text{grafted} + \text{ungrafted backbone}} \cdot 100$$

$$\text{grafting efficiency} \quad \varepsilon\,[\%] = \frac{\text{grafted monomer M}}{\text{grafted monomer} + \text{Homopolymer } (M)_n} \cdot 100$$

$$\text{degree of grafting} \quad \pi\,[\%] = \frac{\text{weight grafted monomer M}}{\text{graft copolymer total weight}} \cdot 100$$



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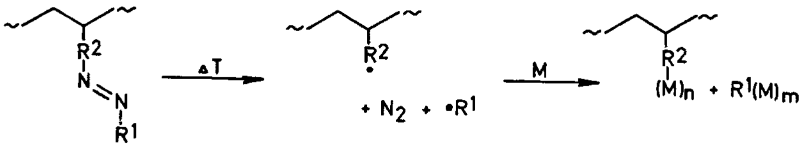
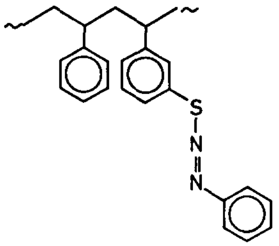
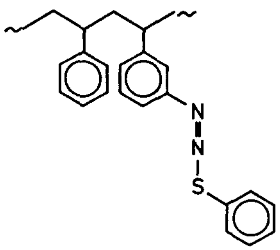


An example for such a posssibility is grafting of copolymers from 2/styrene and from 3/styrene



CP 2 / styrene



CP 3 / styrene

4.2. results

Samples of the copolymers were dissolved in toluene, acrylonitrile was added, and the mixture warmed up to 63°C and kept at this temperature for 10 half-life times of the initiator groups. Afterwards the polymer was seperated into ungrafted backbone (extraction with $CHCl_3$), homopolyacrylonitrile (extraction by $CH_3NO_2/H_2O/\Delta T$) and graftcopolymer (soluble in DMF) (TABLE 3)

TABLE 3: results of grafting of azo copolymers with acrylonitrile

CP	azogroups in copolymer mol %	monomer conversion weight %	ε weight %	U_G weight %	π weight %	HPAN weight %
3/styrene	0.42	43.5	56.1	80.5	70.0	43.9
2/styrene	0.49	57.6	36.2	68.5	71.8	63.9
3/styrene	0.70	50.1	56.4	78.5	74.3	43.6
2/styrene	0.74	56.0	28.2	80.5	62.3	71.8

High values for U_G are typical for the grafting of azo group containing copolymers. The π-values are certainly limited by the solubility of the grafted product (the reaction becomes heterogeneous with increasing conversion). The ε-values show greater variations. From these values it is quite obvious that the thiyl radicals (in CP 2/styrene fixed to the chain, in CP 3/styrene free moving) show less reaction towards acryliονitrile than phenyl radicals.

5. Experimental

1-phenyl-2-(3-vinylphenylthio)-diazen (2) and (3-vinylphenylazo)-phenylsulfid (3) were prepared analogous to methods already described (KERBER et al.1976; 1978; NUYKEN et al. 1979; in press)
analytical data of 2 (for 3: NUYKEN et al. 1979)

$C_{14}H_{12}N_2S$ (240,3):

calc.	C	69.97 %	H	5.03 %	N	11.65 %
det.	C	70.65 %	H	5.21 %	N	11.14 %

^{1}H-NMR (CDCl$_3$) δ (ppm) : 5,35 (d; $=CH_2$); 5,85 (d; $=CH_2$);
6,85 (dd, $-CH=$); 7,55 (m, $-C_6H_4-$, C_6H_5-)
IR(CHCl$_3$) ν (cm^{-1}) 3010 - 3060 (C-H, aromatic, olefinic)
1625 (C=C)
1590, 1565 (aromatic), 990 ($-CH=CH_2$)
UV(CHCl$_3$) λ_{Max} = 332 nm, ε = 9500 lmol^{-1} cm^{-1} (instabil)

The copolymerisation of 2 and styrene in bulk and emulsion were carried out analogous to those of 3 and styrene (NUYKEN et al. 1979). The grafting and separation of grafted products were performed as described previously (KERBER et al. 1976).

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