

Light-sensitive elastomers modified by 4-(*N*-dimethylmaleimido)-benzenesulphenyl chloride

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New light-sensitive polymers were prepared by modification of four different elastomers with 4-(*N*-dimethylmaleimido)-benzenesulphenyl chloride (DMI-BSCI). Polydienes modified by DMI-BSCI form block copolymers. These polymers show a strong increase of the glass transition temperature T_g whereby the T_g increase of modified poly(octenamer) is much smaller. Higher modified polydienes have two T_g . Modified poly(octenamers) show a melting temperature dependence T_m on the content of *trans* double bonds which is characteristic of statistical copolymers. The ratio of rate constants with which *trans*- and *cis*-structures in poly(octenamer) are occupied by DMI-BSCI, is

$$k_{trans}/k_{cis}=0.34$$

(Keywords: unsaturated light-sensitive polymers; elastomers; dimethylmaleimide side groups; sulphenyl chloride; glass transition temperature; melting temperature)

INTRODUCTION

The addition of sulphenyl chlorides, mostly benzenesulphenyl chloride and its derivatives to the olefinic double bonds of polydienes has been studied by Cameron¹⁻⁴. These reactions are spontaneous and high saturation can be easily achieved. Depending on the conversion polydienes have different physical characteristics, e.g. glass transition temperature T_g , dielectric relaxation or morphology.

Polydienes are often used in light-sensitive coatings but their applications require a higher T_g . This is achieved by different modifications, e.g. by the cyclization through double bonds in the poly(isoprene) backbone⁵.

In this work some physico-chemical characteristics of new light-sensitive polymers are presented. These polymers are based on commercially available elastomers modified by 4-(*N*-dimethylmaleimido)-benzenesulphenyl chloride. The dimethylmaleimide (DMI) group is light-sensitive and dimerizes under the influence of the ultraviolet or—when sensitized—visible irradiation^{6,7}. More details about this behaviour were reported recently on polymers based on radical polymerization of methacrylates with pendant DMI groups⁸ and on the high photosensitivity of coatings based on such polymers⁹.

EXPERIMENTAL

The following elastomers have been used:

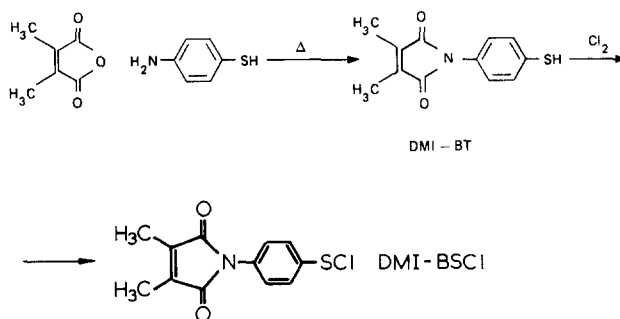
Polybutadiene (PBU), Solprene^(R) 250 (Phillips Petroleum), containing 36% *cis*-1,4, 54% *trans*-1,4 and 10% 1,2-vinyl, $\bar{M}_w = 2.3 \times 10^5$, $\bar{M}_w/\bar{M}_n = 1.9$.

cis-*Polyisoprene* (*cis*-PIP), Carifles^(R) IR-305 (Shell), contains 92% *cis*-1,4, $\bar{M}_w = 1.2 \times 10^6$, $\bar{M}_w/\bar{M}_n = 1.56$.

trans-*Polyisoprene* (*trans*-PIP), (a product of EGA Chemie (Aldrich Co.)), $\bar{M}_w \approx 0.5 \times 10^6$.

Polyoctenamer (PONAM), Vestenamer^(R) 8012 (Chemische Werke Hüls), containing $\approx 20\%$ *cis*- and $\approx 80\%$ *trans*-structures.

4-(*N*-dimethylmaleimido)-benzenesulphenyl chloride (DMI-BSCI). The light-sensitive BSCI-DMI was prepared in the following manner:

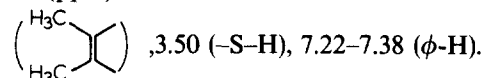


Preparation of 4-(*N*-dimethylmaleimido)-benzenethiol (DMI-BT)

Equimolar amounts of dimethylmaleic anhydride and 4-aminothiophenol were dissolved in toluene. Water was distilled off continuously by azeotropic distillation for 130 h. The product was then purified by distillation, b.p. 155–160°C/0.1 Torr. Yield 52%, m.p. 124–126°C, elemental analysis:

	C	H	N	S	(%)
calc.:	61.80	4.72	6.01	13.73	
found:	61.75	4.81	5.95	13.65	

N.m.r. spectrum δ (ppm): 2.07

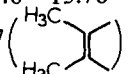


Preparation of DMI-BSCI

500 ml CCl_4 was cooled to 0–+5°C and saturated with chlorine for about 15 min. A solution of 28.0 g DMI-BT in 300 ml CCl_4 was slowly added to this solution. The addition of chlorine was prolonged for a further 2 h. Then the solution was warmed up to 20°C and the solvent was distilled off. The product was dried in vacuum and used without further purification.

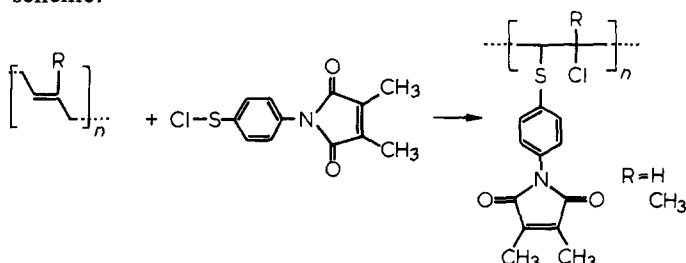
Elemental analysis:

	C	H	N	Cl	S	(%)
calc.:	53.83	3.76	5.23	13.24	11.97	
found:	53.70	3.83	5.46	13.76	11.47	

N.m.r. spectrum δ (ppm): 2.07 (), 7.44–7.76 (ϕ -H).

The modification of unsaturated polymers with DMI-BSCI

The polymers were modified according to the following scheme:



The modification (to different degrees, as shown in Figure 1) was carried out as follows: DMI-BSCI dissolved in dry toluene was slowly added at 20°C under nitrogen and intensive stirring to a 1% polymer solution in toluene. The product was worked up after 24 h of stirring at 20°C. The solubilities of the products in toluene decrease with increasing content of DMI-BSCI in the polymer. Polymers with less than about 50% saturation are soluble in toluene and those with more than about 80% precipitate quantitatively. Polymers with about 50–80% saturation are partially soluble: they are opaque or gelled.

Polymers soluble in toluene were isolated by direct precipitation in ether. Dimethyl formamide was added to the partially soluble polymers and the product was then precipitated in ether from the clear solution. Polymers insoluble in toluene were filtered off, dissolved in dimethyl formamide and precipitated in ether. All three sorts of polymers were dried under vacuum at 20°C. The degree of saturation was determined from elemental analysis.

The melting temperature T_m , the glass transition temperature T_g and the crystallinity of the polymers was measured by the thermoanalyser TA 3000-System of Mettler, Switzerland.

RESULTS AND DISCUSSION

Efficiency of the modification and the influence of the saturation on T_g

The efficiency of the modification, i.e. the ratio between DMI-BSCI which is bound (b), and reacts with the polymer (a), is 0.9 for PBU, and 0.7 for *cis*- and *trans*-PIP and PONAM (Figure 1). These differences show that the efficiency of the sulphenyl chloride (SCI) addition might be dependent on the nature of the double bond along the chain, according the following mechanism²:

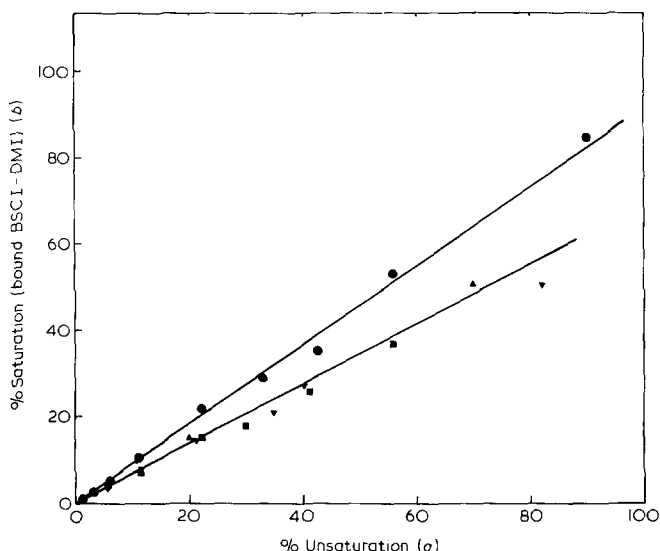
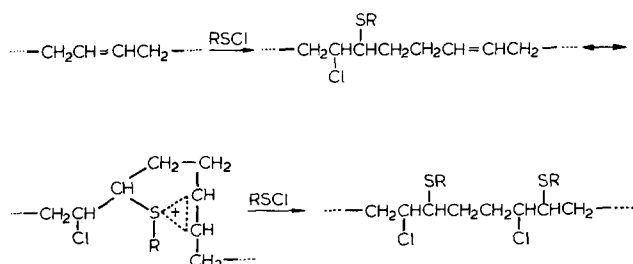


Figure 1 Obtained saturation (b) vs. saturation that would result from quantitative addition of DMI-BSCI (a): ● PBU, ■ *cis*-PIP, ▲ *trans*-PIP, ◆ PONAM

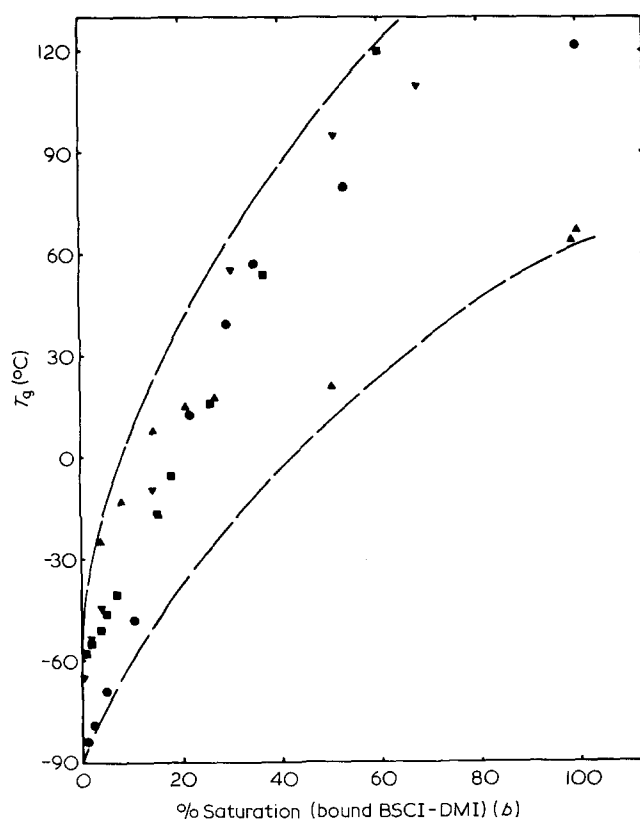


Figure 2 The dependence of glass transition temperature T_g on the concentration of bound BSCI-DMI (b) ● PBU, ■ *cis*-PIP, ◆ *trans*-PIP, ▲ PONAM

In this way polydienes can form blocks with respect to the segments with pendant groups. The necessary condition for the block formation is the proximity of the neighbouring double bond so that it can be activated by the thioether sulphur for the addition of the next sulphenyl chloride. This requirement is fulfilled in polydienes. The large distance between double bonds in PONAM probably does not allow the activation of the neighbouring group.

T_g of the modified polymers are very strongly dependent on the concentration of the bound DMI-BSCI (Figure 2). The differences of the T_g values between the

non-modified (T_g^0) and maximal saturated polymer (T_g^m) are clearly higher in polydienes (PBU and both PIPs) than in PONAM (Table 1). Even if the T_g of 100% saturated *cis*- and *trans*-PIP cannot be determined, these values certainly lie nearer to the T_g^m of PBU than of PONAM. This estimate can be obtained by extrapolation of values in Figure 2 to higher degrees of saturation.

The concept of forming blocks by the modification of polydienes with sulphenyl chlorides seems to be confirmed by the finding of two distinctive T_g in *trans*-PIP modified by DMI-BSCI. A second T_g in *cis*-PIP and PBU cannot be confirmed (Table 3).

Reaction rates of *cis*- and *trans*-structures of PONAM with the sulphenyl chloride derivative

PONAM was modified by different concentrations of DMI-BSCI and the *trans*- and *cis*-content of the remaining double bonds was determined by ^{13}C -n.m.r. spectroscopy. The dependence of the *trans/cis* ratio on the DMI-BSCI bound in PONAM is linear (Figure 3). The *trans*- (curve A) and *cis*-configurations (curve B) are calculated from the *trans/cis* ratio at different degrees of modification (Figure 4). The ratio in which *trans*- and *cis*-positions are occupied is 1.33:1, and considering the original ratio of

Table 1 ΔT_g in elastomers modified by DMI-BSCI

Polymer backbone	T_g^0 (°C)	T_g^m (°C)	Saturation (%)
PBU	-86	122	100
<i>cis</i> -PIP	-58	120	60*
<i>trans</i> -PIP	-65	110	68*
PONAM	-65	67	100

* *cis*- and *trans*-PIP have a T_g^m of 120°C, and of 110°C, respectively. The T_g at higher saturations cannot be determined because of the dehydrochlorination of the polymer at temperatures higher than 120°C.

Table 2 Polymers with two T_g

Polymer backbone	DMI-BSCI bound (mole%)	T_g^1 (°C)	T_g^2 (°C)	Remark
<i>trans</i> -PIP	28.3	56	-20	
	50.8	95	18	
	67.4	110	19	
<i>cis</i> -PIP	16.1	-5	-20	T_g^2 uncertain
	36.8	55	-17	
PBU	53.2	80	-29	"

Table 3 T_m and crystallinity of PONAM modified by DMI-BSCI

Content of DMI-BSCI in polymer (mole %)	T_m (°C)	Crystallinity, (%) (approx.)
0	56	30
3.74	54	24
8.11	50	23
14.30	41	16
27.15	38	1
50.69	-	-

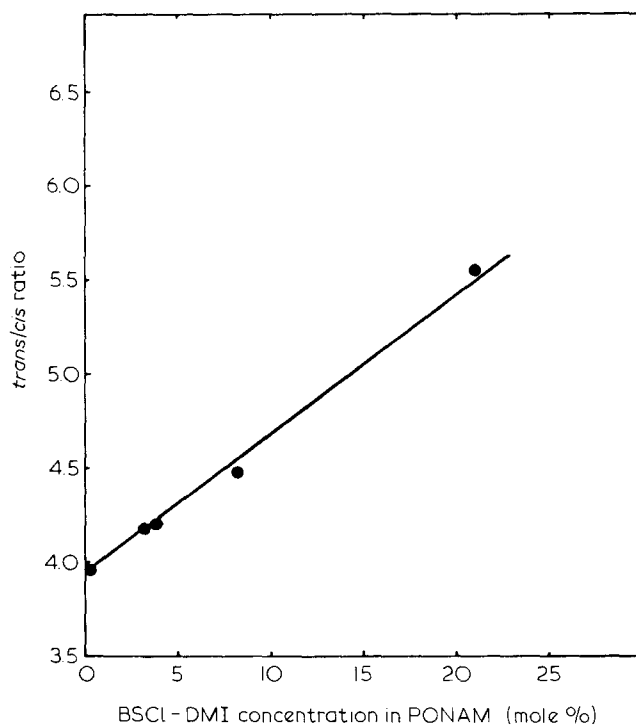


Figure 3 The dependence of the *trans/cis* ratio on the bound DMI-BSCI in PONAM ^{13}C n.m.r. 62.9 MHz: *trans* 130.7 ppm, *cis* 130.2 ppm

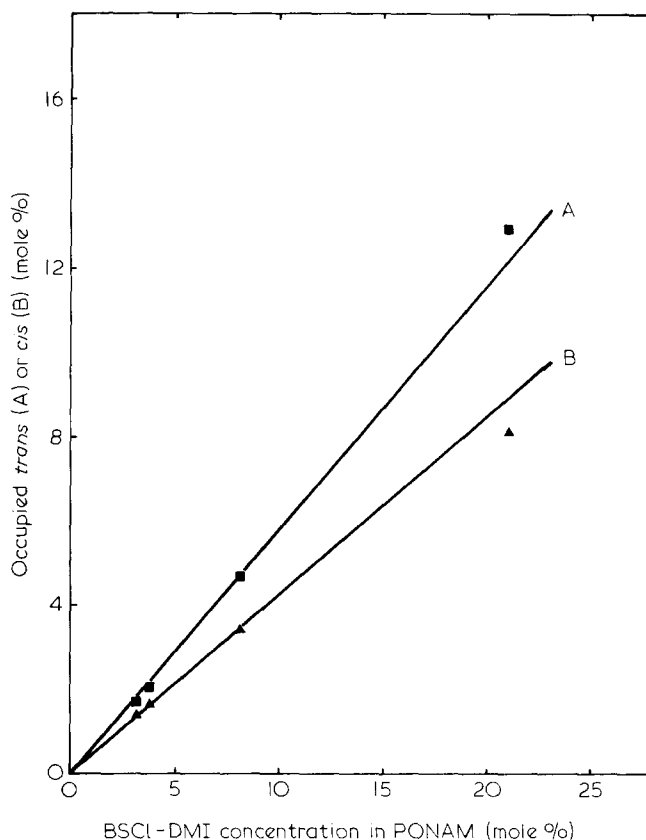


Figure 4 The dependence of the concentrations of occupied *trans*- (curve A) and *cis*-configurations (curve B) on the DMI-BSCI bound in PONAM

concentrations $\text{trans/cis} = 3.95/1$, the ratio of the corresponding rate constants can be determined as $k_{\text{trans}}/k_{\text{cis}} = 1.33/3.95:1$, i.e.

$$k_{\text{trans}}/k_{\text{cis}} = 0.34$$

For the kinetic measurements for *cis*- and *trans*-PBU modified by toluenesulphenyl chloride Cameron¹ found:

$$k_{trans}/k_{cis} = 0.25$$

T_m-crystallinity-configuration relationship

Bound DMI-BSCI influences directly the crystallinity and the melting temperature *T_m* of PONAM. It is known that in PONAM, which consists of *cis* and *trans* structures, only the *trans* is responsible for the crystallinity¹⁰. On the other hand, as shown above, sulphenyl chloride prefers the *cis* structures (Table 3).

In PONAM modified with DMI-BSCI, a linear dependence between *T_m* and the *trans*-content was found (Figure 5, curve A), similarly to the results of Calderon¹⁰ for poly(octenamer) with different *trans*-contents (Figure 5, curve B). Extrapolation of both straight-lines to 100% *trans* gives a common value for *T_m*⁰ of 85°C.

For copolymers with the two units occurring in random sequence along the chain and with only one component which can crystallize, the relationship between *T_m* and composition is¹¹

$$(1/T_m) - (1/T_m^0) = -(R/\Delta H_n) \ln N_A$$

(*N_A* is mole fraction of *A* units which crystallize, ΔH_n is the heat of fusion per repeating unit and *R* is the gas constant.)

The linearity of $1/T_m$ versus $(-\log N_A)$ for PONAM modified with DMI-BSCI (Figure 6) is another evidence

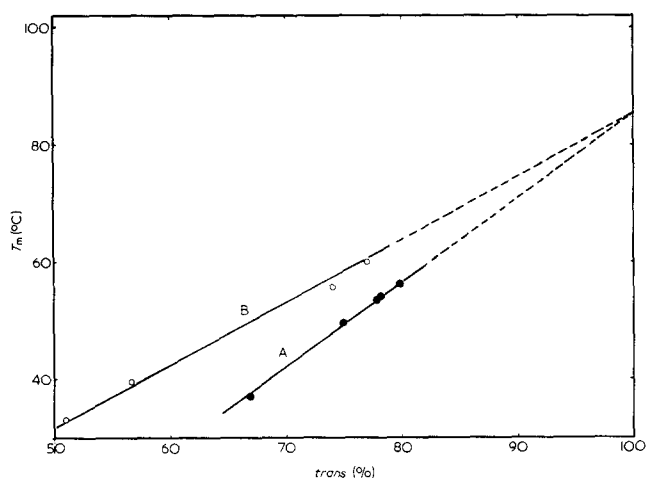


Figure 5 *T_m* versus *trans*-content in PONAM. Curve A: PONAM modified with DMI-BSCI. Curve B: Poly(octenamers) with different *trans*-contents (ref. 10)

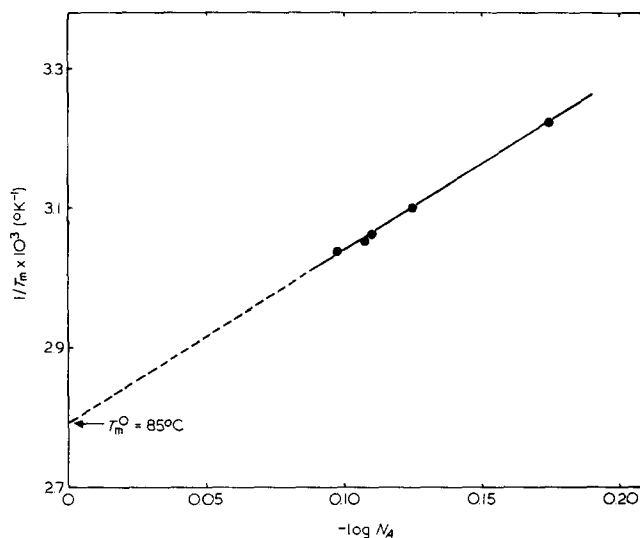


Figure 6 $1/T_m$ versus $(-\log N_A)$. PONAM modified with DMI-BSCI

for statistical addition of the sulphenyl chloride to this polymers. On the other hand, for isoprenes the above dependence is not linear. The extrapolation of the straight-line on Figure 6 to $(-\log N_A) \rightarrow 0$ (i.e. *n_A* = 1 or 100% *trans*) gives the identical value of *T_m*⁰ = 85°C as the *T_m*⁰ value determined from *T_m* versus *trans* dependence.

The elastomers modified by DMI-BSCI are high light-sensitive. Their photochemical properties will be discussed in a later paper.

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