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Polymer modified asphalt binders, part 1

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Abstract

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Mixtures of the styrene-butadiene-styrene (SBS) and styrene-ethylene-butene-styrene (SEBS) respectivly with different types of bituminous materials or oils have been invesigated. We can here, with the aid of size exclusion chromo-tography (SEC), show that pronounced molecular weight changes occur both in the bitumen and the polymer phase due to processing and ageing. The processing temperature was chosen to 200 °C and the ageing temperature to 70 °C. The changes in molecular weight are correlated to changes in mechanical properties. Compatibility conditions also seem to influence the degradation course. Prolonged exposure of the materials to 200°C in inert, nitrogen, atmosphere has also been performed. No detectable difference in molecular weight could be found.The results give important implications for both processing handling and long term properties of modified bitumen.

Keywords: SBS- , SEBS-bitumen mixtures, processing, ageing, SEC, mechanical properties.

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Preface

This report is the result of a research work sponsored by The Board of Civil Aviation, The Royal Fortification, the Swedish National Road Administration, Nynäs Petroleum AB and the Road Department in Stockholm. It deals with stability and degradation of polymer modified bitumen at elevated temperatures and continues the work published in SP-Report 1987:29, "Degradation of styrene - butadiene - styrene elastomers (SBS) in bitumen blends at elevated temperatures, part one" by Sune Linde.

Lots of people have been involved in this work but I would like to mention Ulf Antonsson and Torbjörn Klaesson at the Swedish National Testing and Research Institute. They have performed most of the tensile tests and SEC-analyses.

Borås, Januari 1991

Ulrika Johansson

1 Introduction

The use of polymer modified binders has increased considerably in recent years. The need of research is obvious and different investigations have been performed. Some of the latest developments in this field were presented at the 4th Eurobitume Symposium in Madrid 1989. Many of the papers submitted to this symposium dealt with polymer modified bitumen, for instance [1],[2],[3]. To our knowledge no one has yet performed a thorough investigation of elastomer - bitumen blends, correlating the chemical and mechanical properties as follows.

2 Experimental

Mixtures of different elastomers in bituminous materials have been investigated in order to study stability and degradation at elevated temperatures. Two different temperatures were used. 200 °C was chosen as processing temperature. 70 °C was chosen for accelerated ageing, a typical temperature for ageing of rubbery materials. The elastomers used are of SBS type (styrene - butadiene - styrene) and one of SEBS type (styrene - ethylene - butylene - styrene), all of them from Shell. The SBS elastomers are: Cariflex TR-1101, a linear block copolymer and Cariflex TR-1186(M) a branched block copolymer. Both of them have a styrene content of 30% by mass . The SEBS-elastomer is Kraton G 1652. The bitumen used are B 180 and B 85 from Nynäs Petroleum AB. The oil, 2HL, used in one of the experiments is a naphtenic oil fraction from Nynäs Petroleum which gives a similar chemical environment as bitumen. The percentage of aromat, naphtenic and paraffin content are C_A=23%, C_N=30% and C_P=47%. In this experiment Finaprene 416, a SBS radial block copolymer was used. See also appendix 1 - 3 for specifications of the materials.

All blends of elastomer - bitumen / oil were carried out in the following way; Bitumen / oil was heated in an electrically heated pot to 160 °C while stirring at 600 rpm. Then 8 weight % of elastomer was added and the temperature raised to 200 °C. The mixture was stirred at this temperature for up to 27 hours. During the experiment samples were taken for analyses with size exclusion chromotography, SEC (also called gel permeation chromotography, GPC) and tensile tests, to correlate chemical and mechanical properties.

A Waters SEC equipment, operating at room temperature with a M 6000 A pump and a refractive index (RI) detector was used with THF at a flow rate of 1 ml/min. The column set consisted of three μ-styragel columns with nominal exclusion limits of 1000, 500 and 100 Å respectively. The sample was dissolved in THF to a known concentration of 10 mg/ml and centrifugalized for 5 minutes before 500 μl was inserted to the SEC.

Mechanical properties were determined with tensile tests. A tensile test rig, Instron 1195 equipped with a climate chamber was utilized for the tensile measurements which were carried out at -10 °C with a crosshead speed of 50 mm/min. The test specimens of the polymer / bitumen mixture were produced by casting in a silicone mould. The dumb-bell shaped test specimens were fitted into an aluminium holder with epoxy, see figure 1.

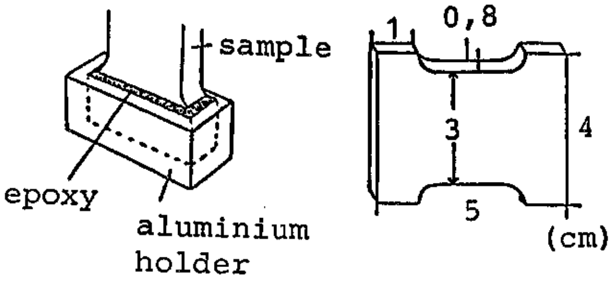


Figure 1; Tensile test specimen

3 Results at 200 °C

3.1 Mixtures produced with access to air

B 180 + 8% Cariflex TR-1101 / Cariflex TR-1186(M)

The SEC analyses show changes in the molecular weight distribution both in the polymer and bitumen phase. Already after a few hours there is a pronounced change in the polymer phase and after 24 hours almost all of the original SBS has degraded to lower molecular weight fractions. The bitumen phase shows the opposite behaviour, higher molecular weight fractions are formed, see figures 2 , 3.

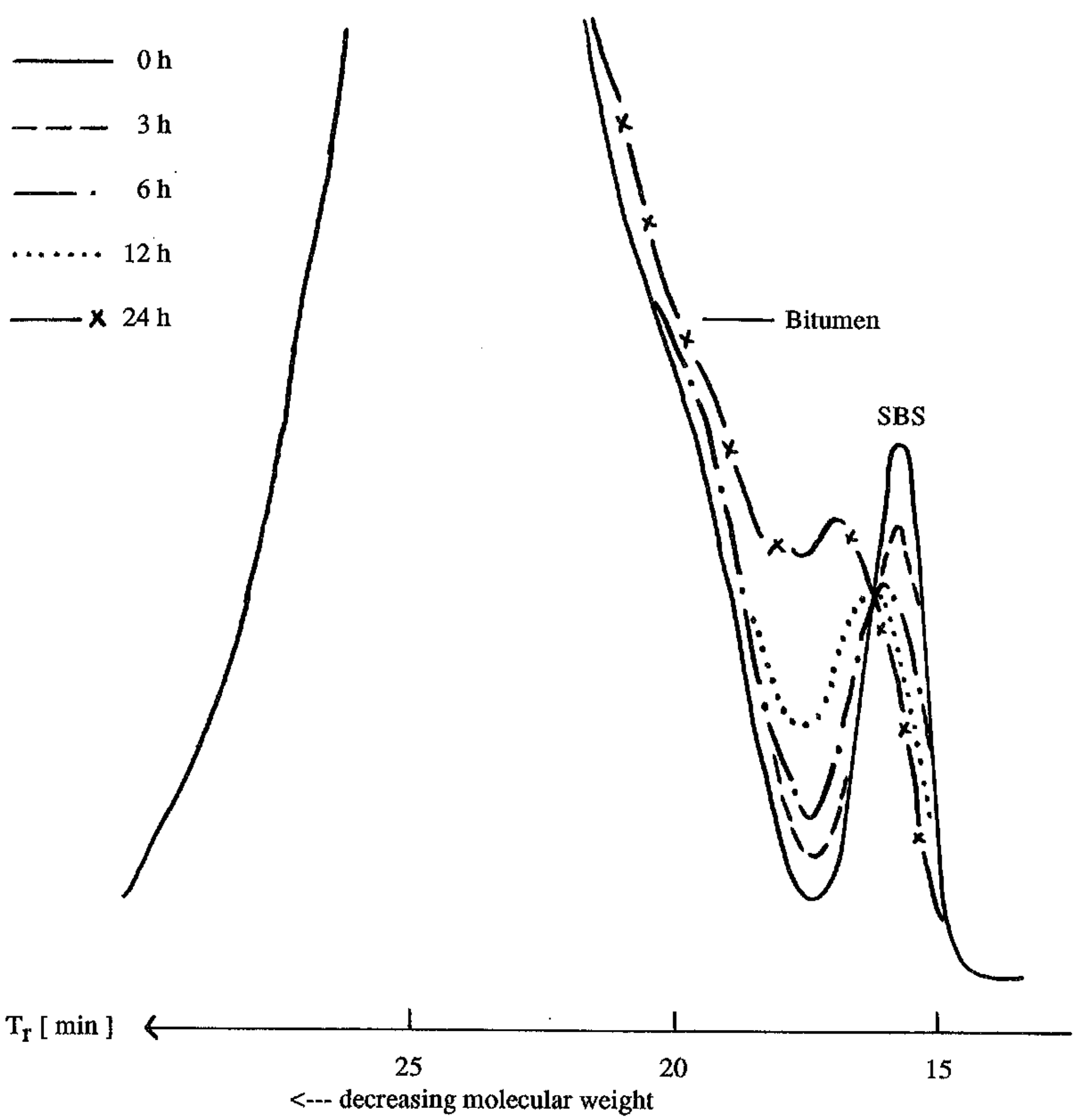


Figure 2; SEC analyses of B 180 + 8% Cariflex TR-1101

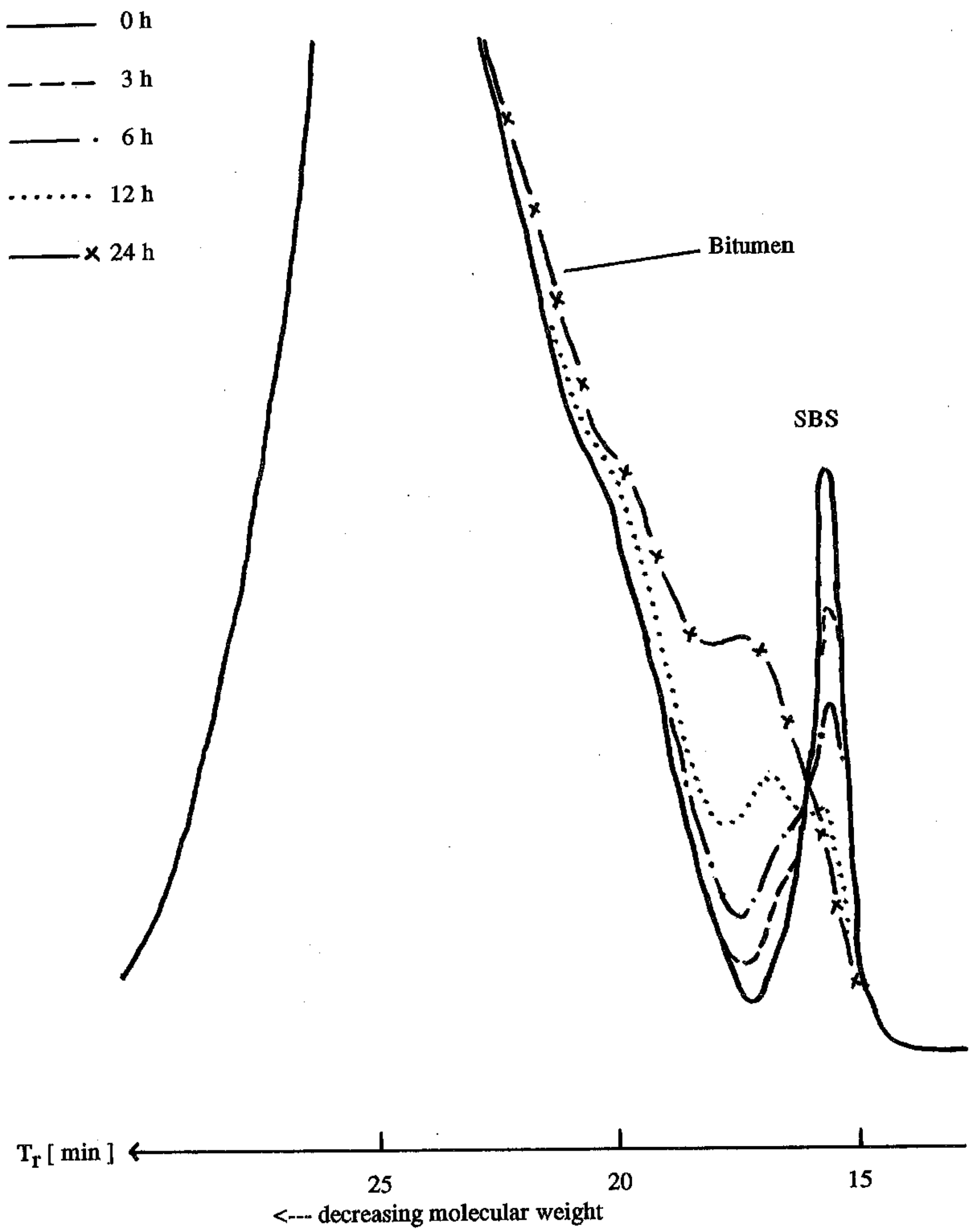
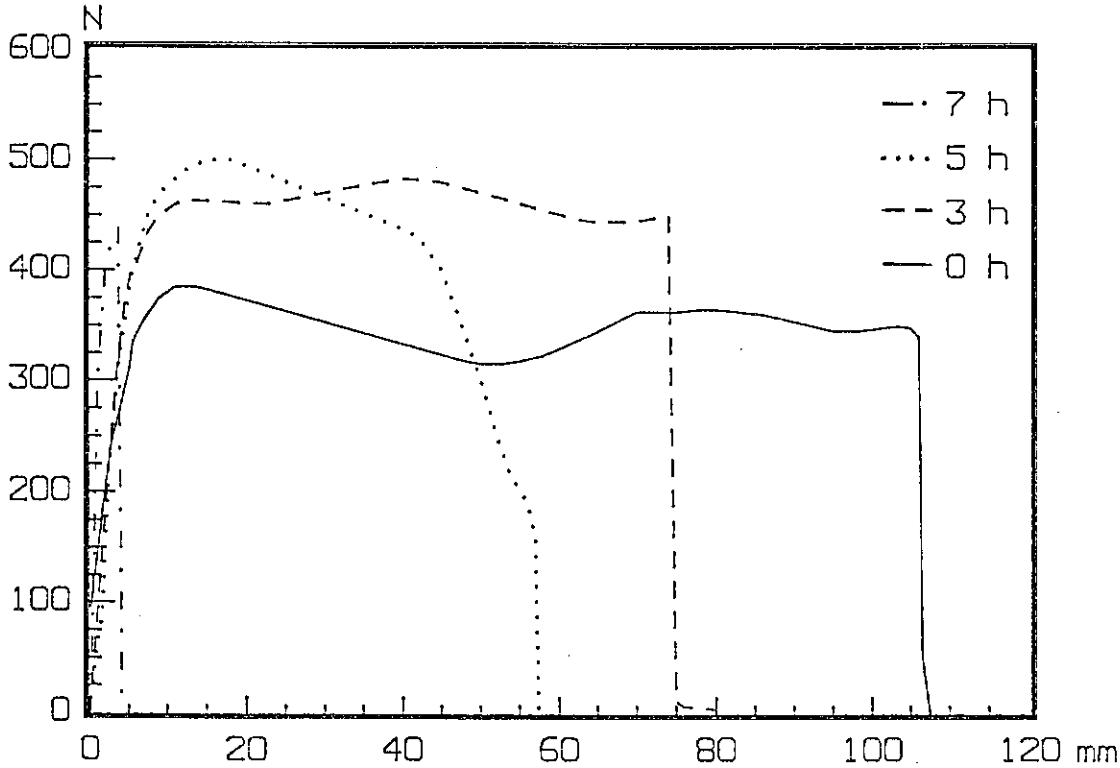


Figure 3; SEC analyses of B 180 + 8% Cariflex TR-1186(M)

Typical results from the tensile tests are shown in figures 4 - 6.
A drastic decrease in tensile strength occurs after 6 - 8 hours at 200 °C.



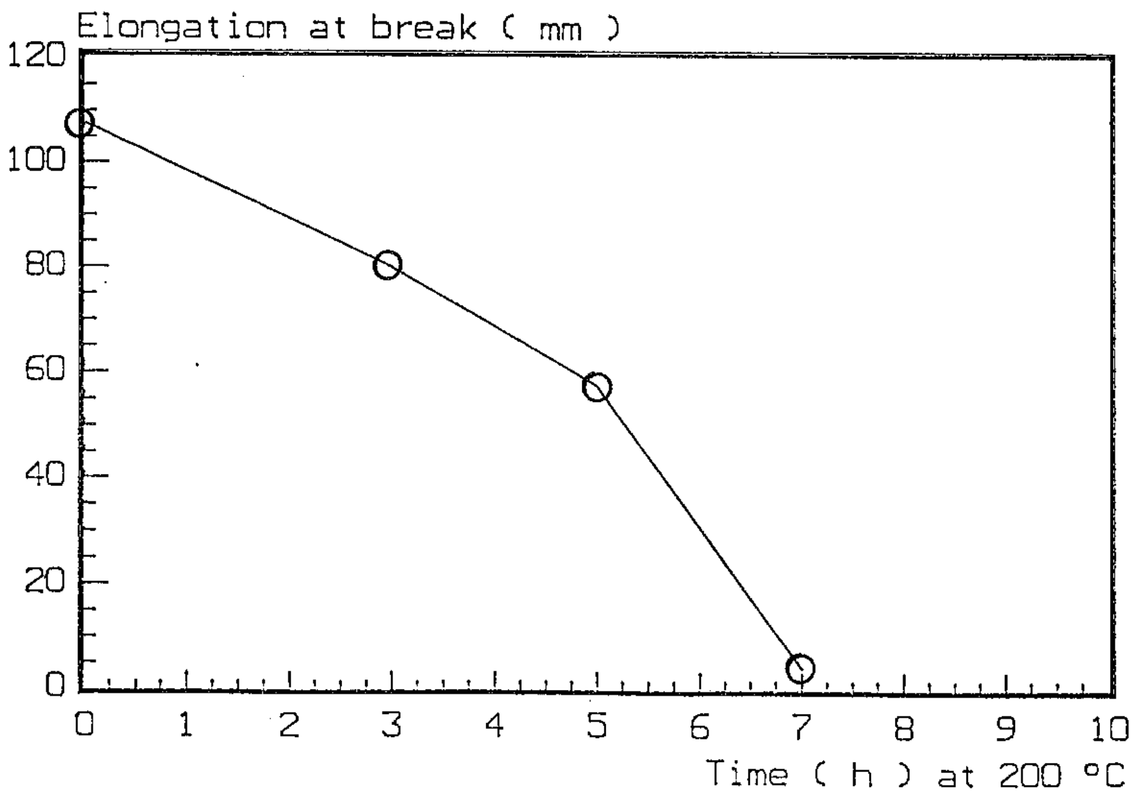
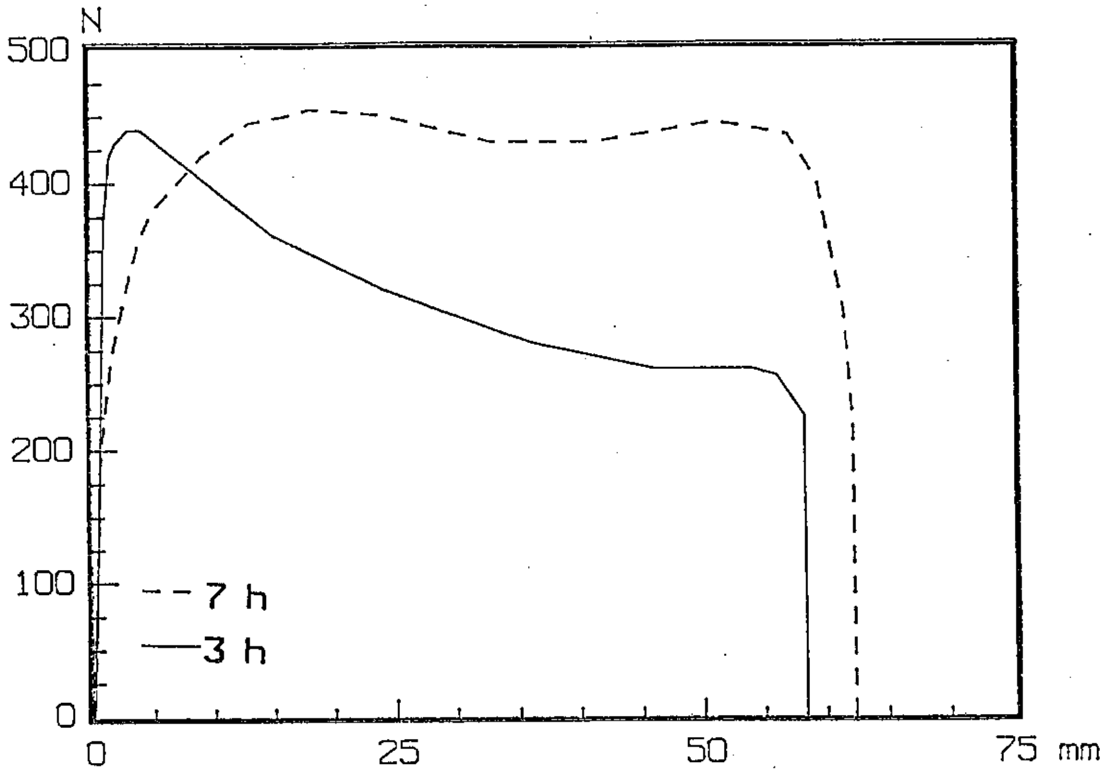


Figure 4; tensile tests of B 180 + 8% Cariflex TR-1101, 50 mm/min, -10 °C



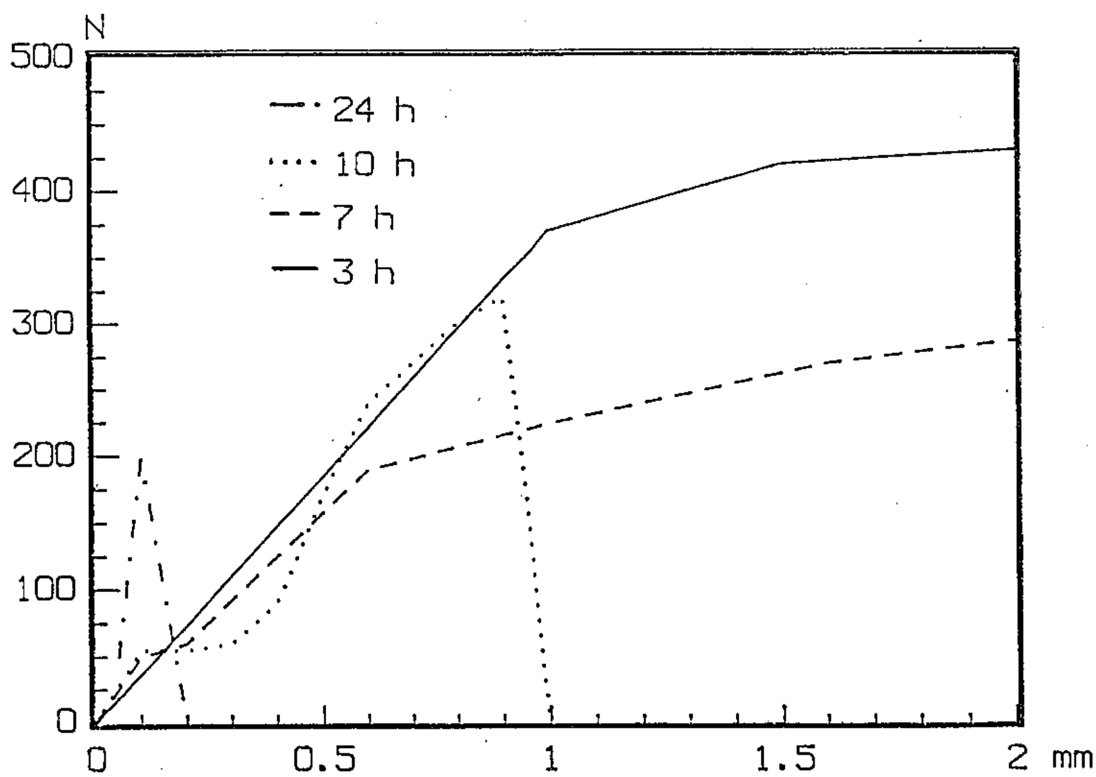


Figure 5; tensile tests of B 180 + 8% Cariflex TR-1186(M) , 50 mm/min, -10 °C
the lower figure is an enlargement of the initial part of the upper figure

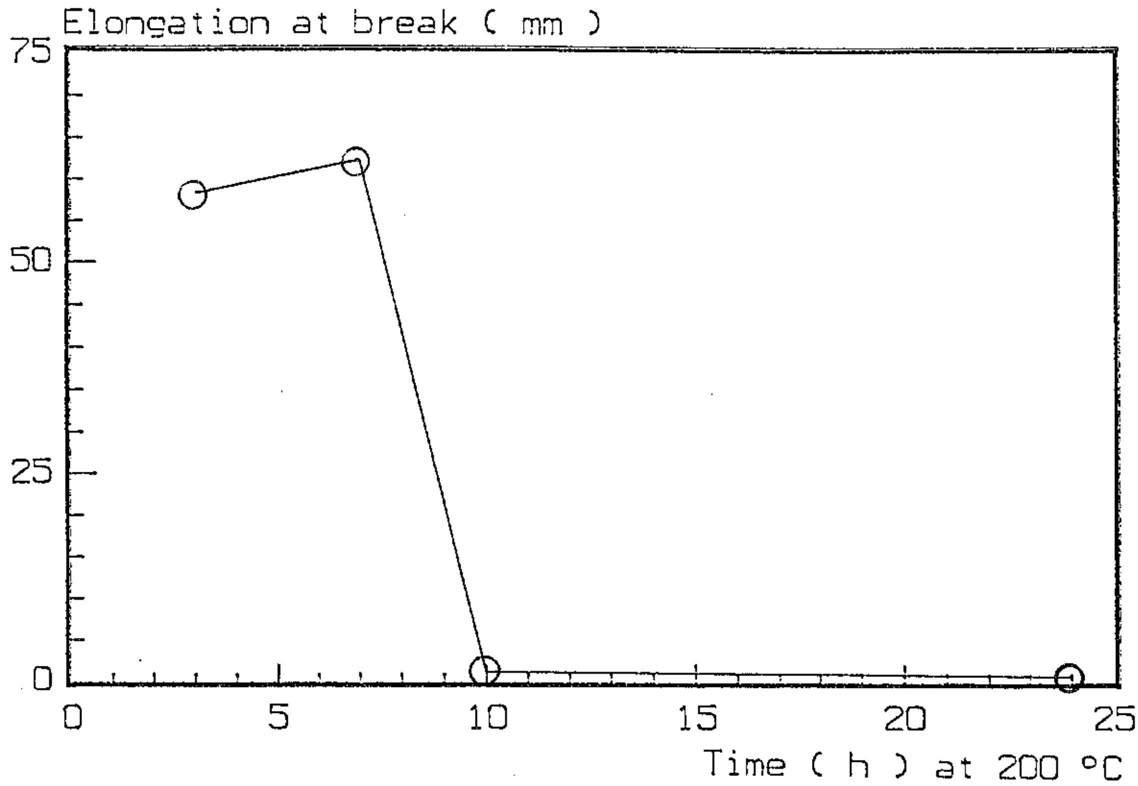


Figure 6; tensile tests of B 180 + 8% Cariflex TR-1186(M), 50 mm/min, -10 °C

The tensile tests show that the blends become more brittle after prolonged exposure to high temperature. The tensile strength and the elongation at break decrease drastically after 6 - 8 hours at 200 °C. Even longer exposure leaves almost no tensile strength or elasticity at all.

<u>B 180 + 8% Kraton G 1652</u>

Figures 7 and 8 show the result of SEC - analyses and tensile test of the mixture with SEBS

The SEC - curves show that the bitumen phase undergoes changes which result in increasing molecular weight - as previous - but the polymer is almost unaffected even after 27 hours at 200 °C ! Successfull tensile tests could unfortunately only be performed at the beginning and in the end of the experiment, at 0 and 27 hours. Thus there is some uncertainty about the behaviour in between these values, questionmark and dashed line in the lower part of figure 8. The result is however very interesting. Since the polymer fraction did not change much during the experiment, the pronounced changes in tensile strength must be due to the changes in the bitumen phase!

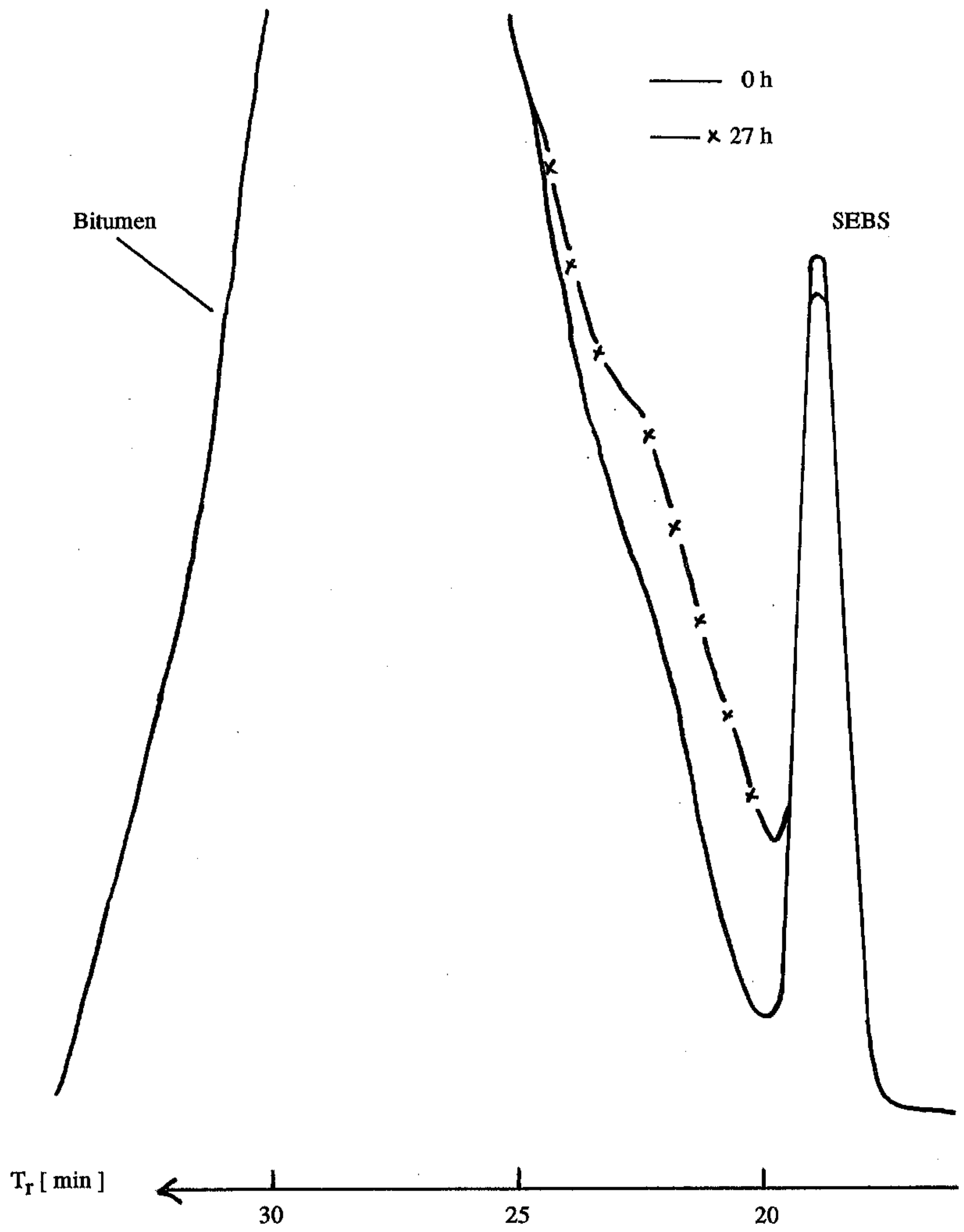


Figure 7; SEC analyses of B 180 + 8% Kraton G 1652

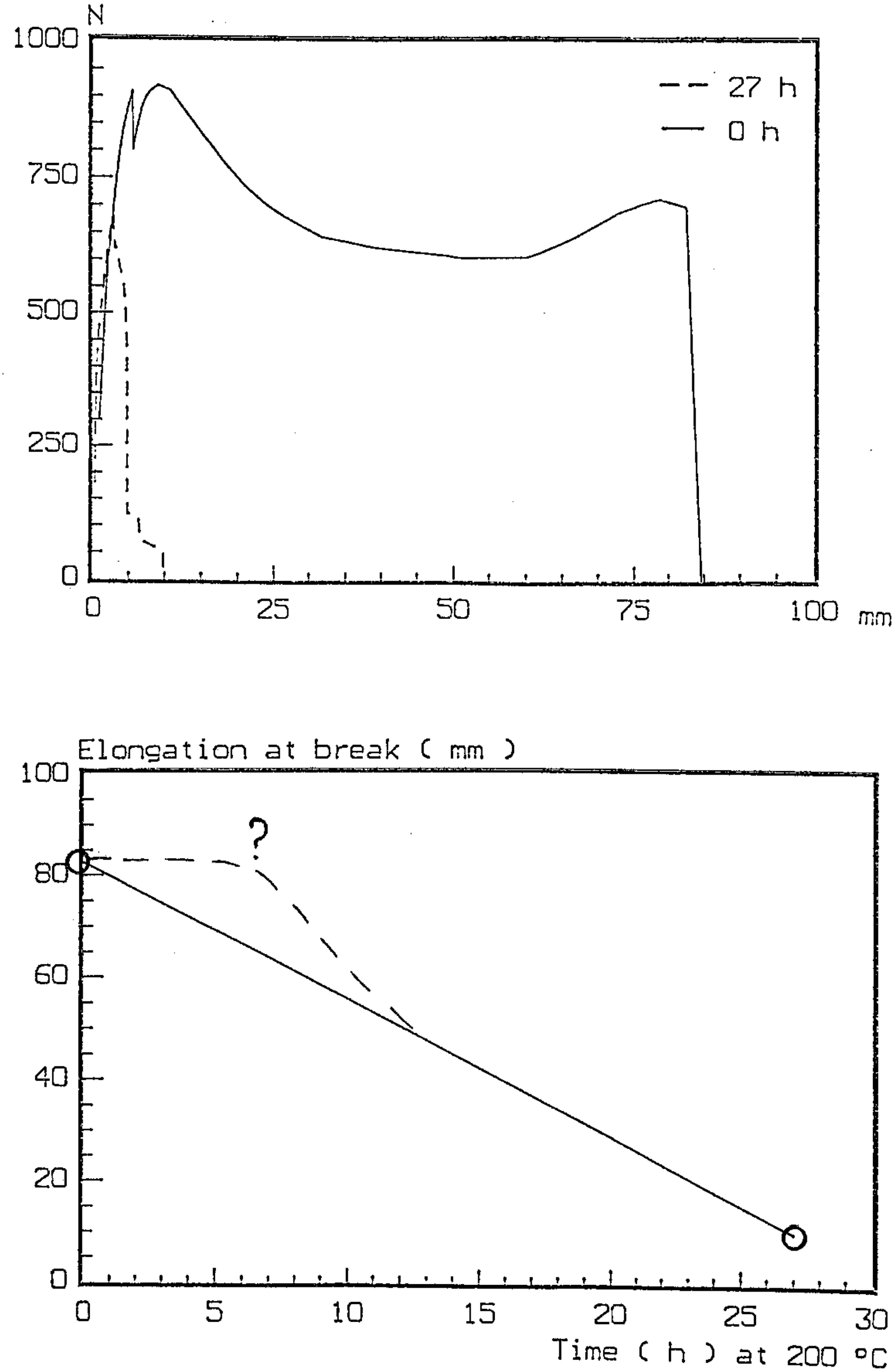


Figure 8; tensile tests of B 180 + 8% Kraton G 1652, 50 mm/min, -10 °C

3.2 Mixtures produced under an inert atmosphere

Tests were done with the two SBS - elatomers mixed with bitumen B 180 in an inert atmosphere, nitrogen, to exclude the influence of oxygen, figures 9, 10.

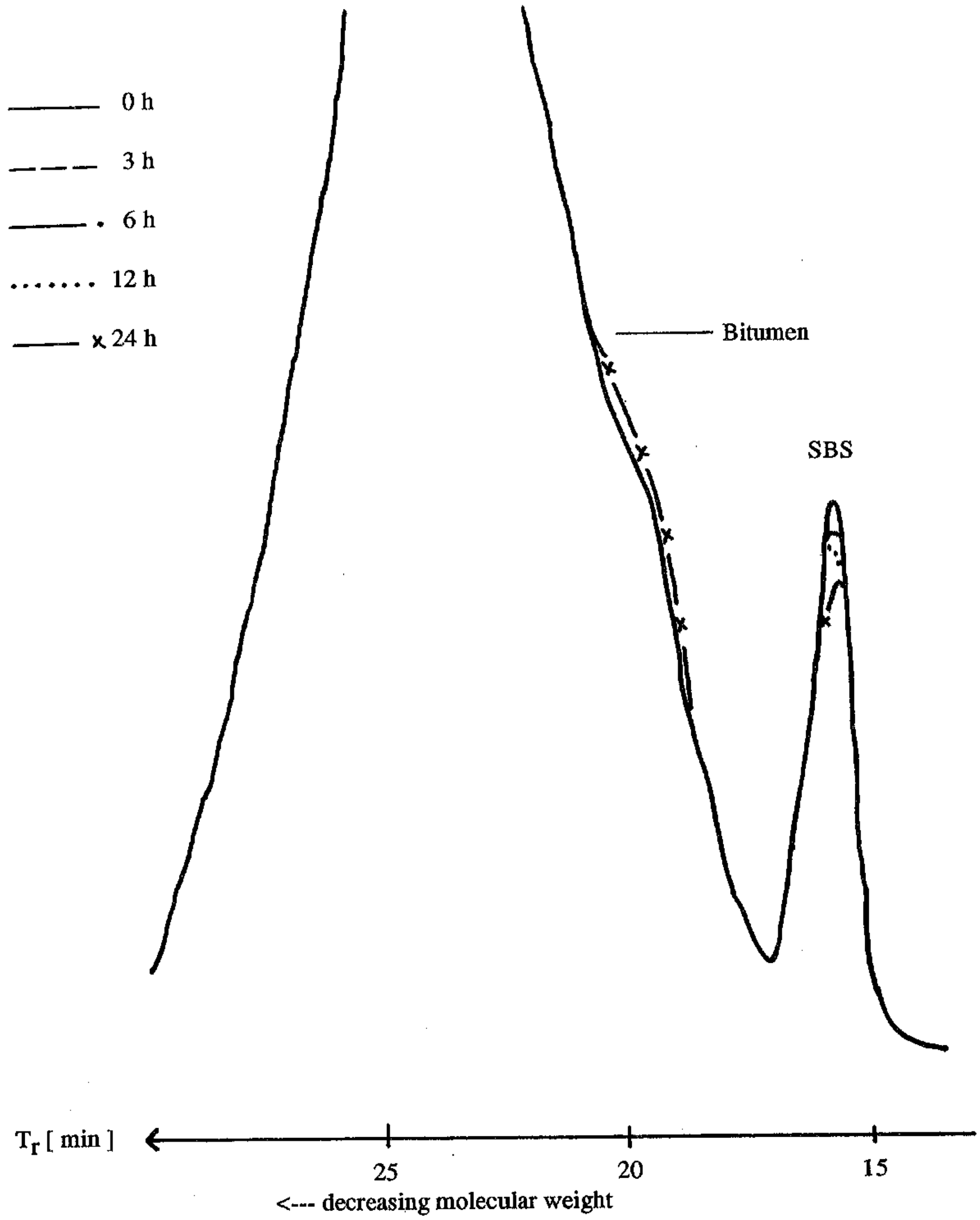


Figure 9; SEC analyses of B 180 + 8% Cariflex TR-1101 , inert atmoshere

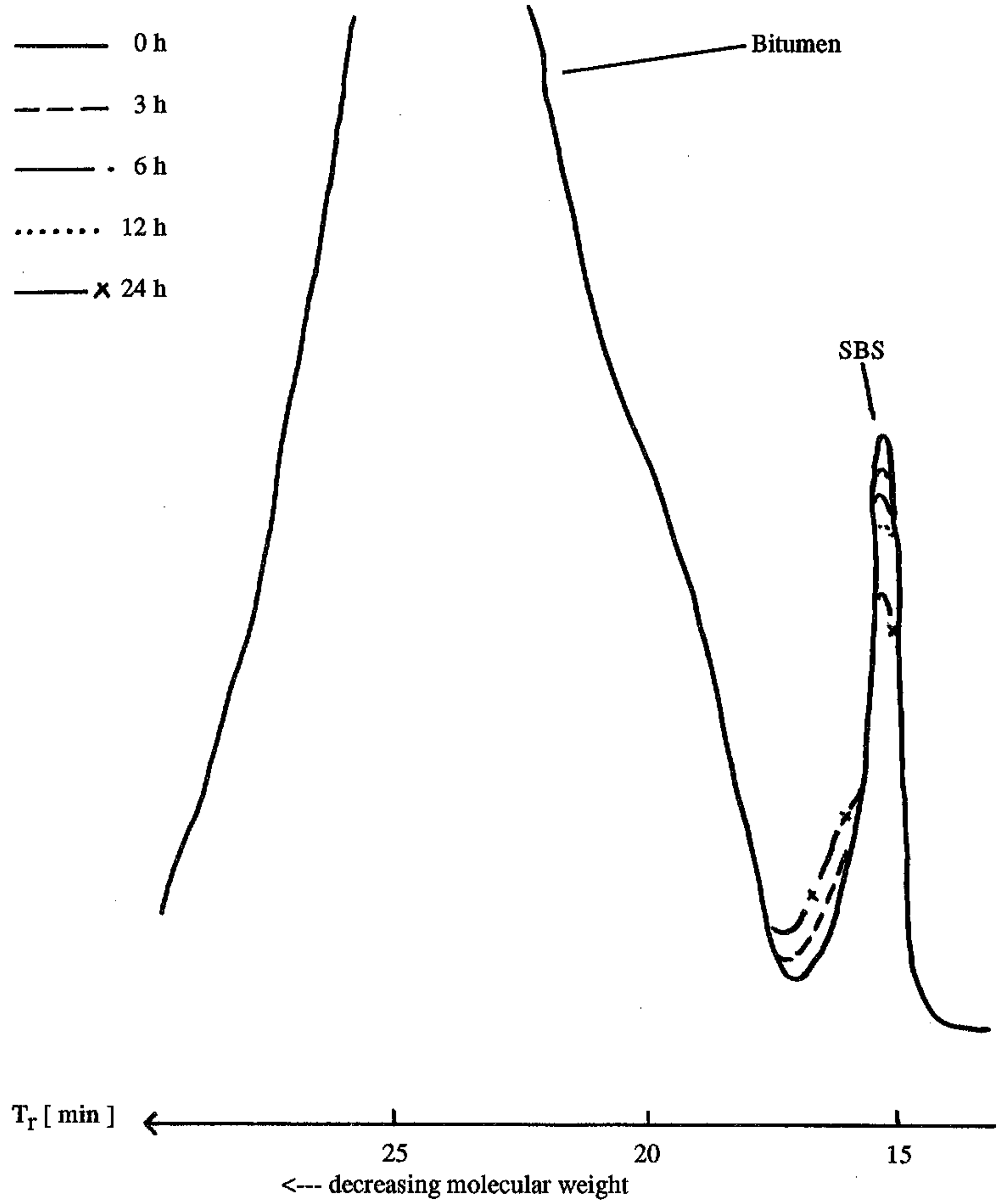


Figure 10; SEC analyses of B 180 + 8%Cariflex TR-1186(M), inert atmoshere

The SEC analyses show that there is almost no difference in the molecular weight distribution even after 24 hours neither in the polymer nor in the bitumen phase. Thus we conclude that influence of oxygen is very hazardous during processing. The enlargement reactions occurring in the bitumen phase, with its undesired effects on the mechanical properties, is probably due to oxidation and various polymerisation reactions. The enlargeing effect of oxygen upon bitumen is not unknown but used in the production of bitumen, in the blowing operation.

B 85 + 8% Cariflex TR-1101 / Cariflex TR-1186(M) , 2HL + 8% Finaprene 416

Softer bitumens like B 180 tend to give compatible blends more readily than harder ones. The two types of SBS were mixed with a harder bitumen, B 85 in order to study the effect of the compatibility condition. The opposite compatibility condition is obtained when SBS is mixed with a naphtenic oil, 2HL [4]. A homogenous solution is formed almost immediately. The mixtures were analysed with SEC throughout the 24 hours at 200 °C see figures 11 - 13

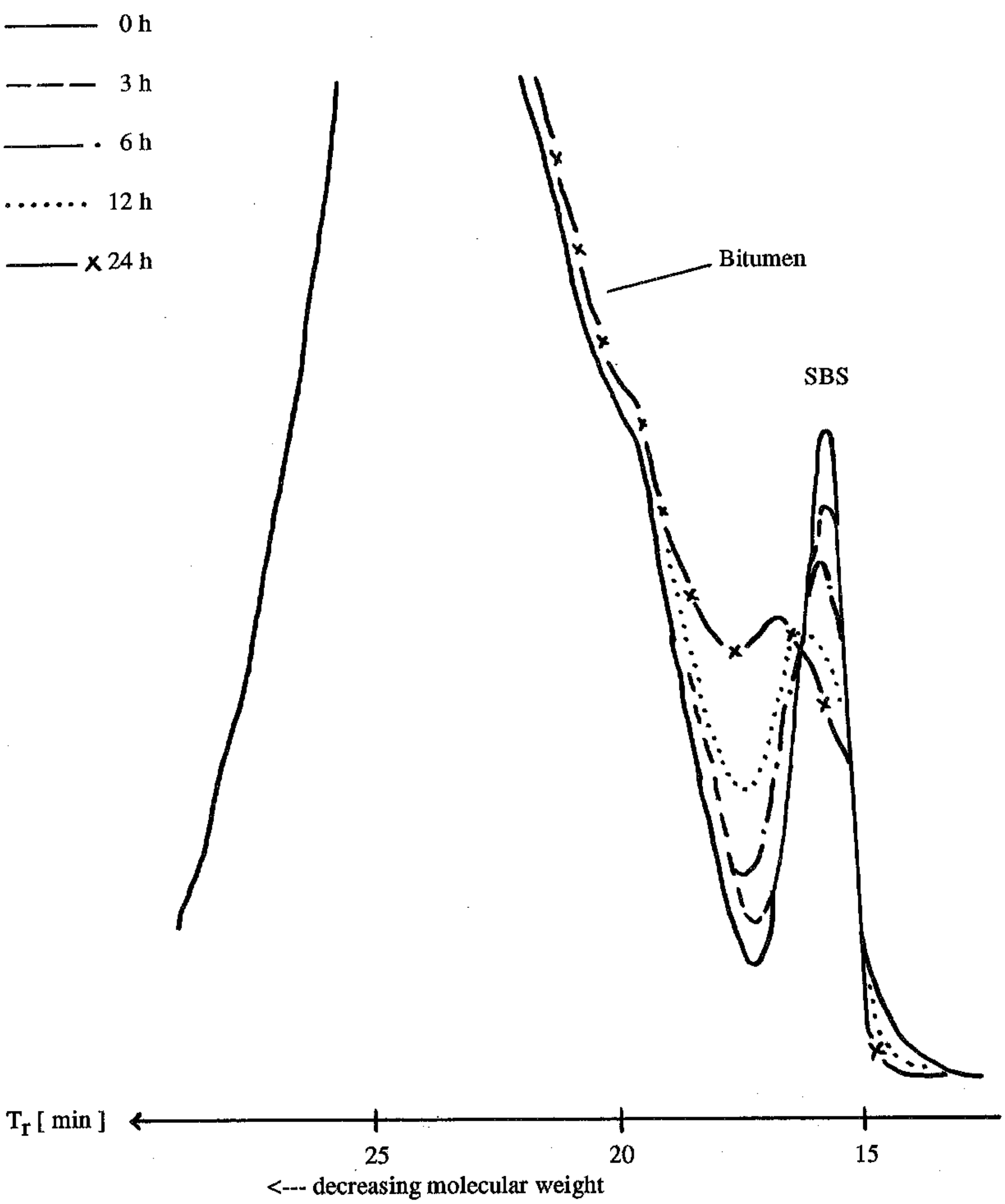


Figure 11; SEC analyses of B 85 + 8% Cariflex TR-1101

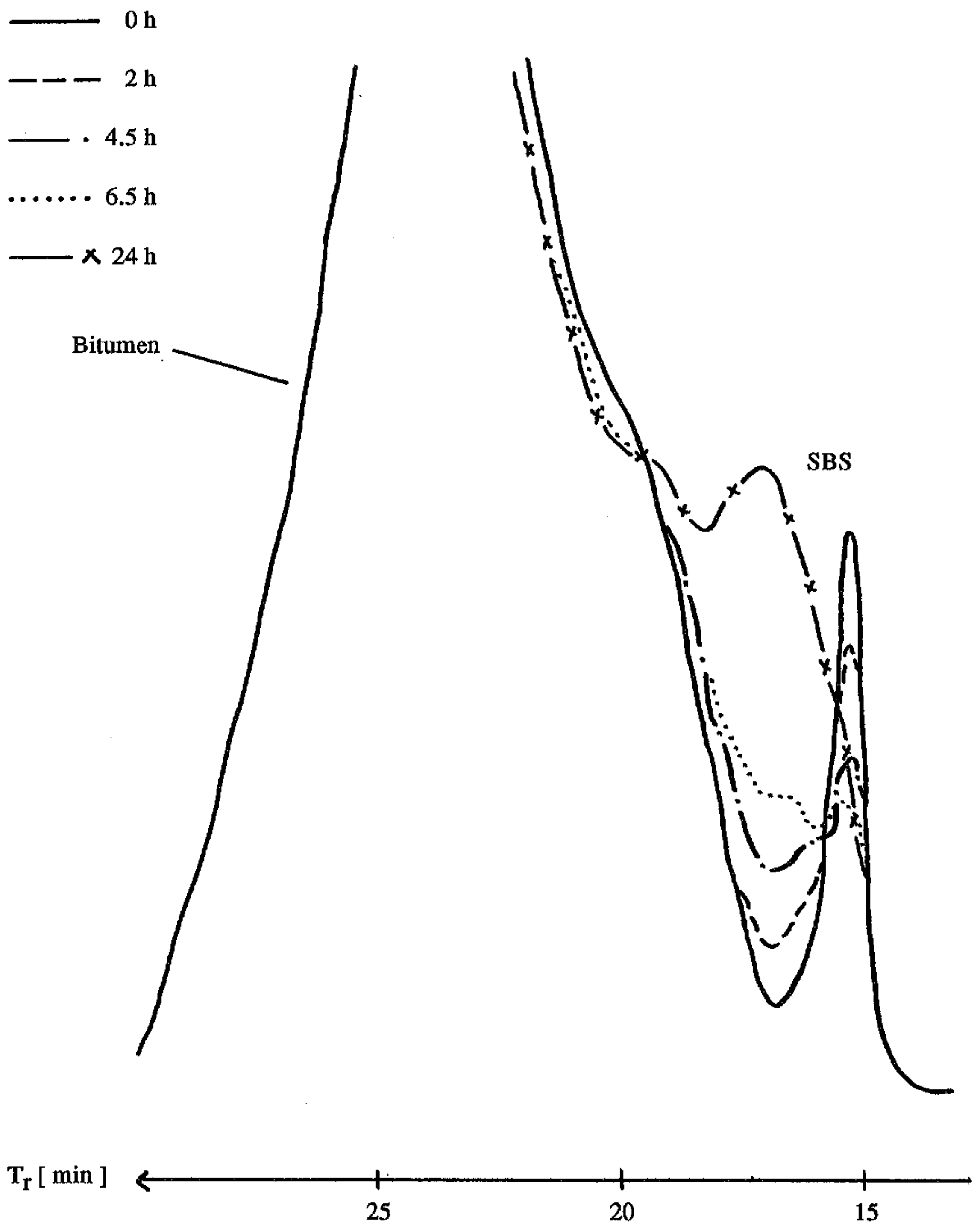


Figure 12; SEC analyses of B 85 + 8% Cariflex TR-1186(M)

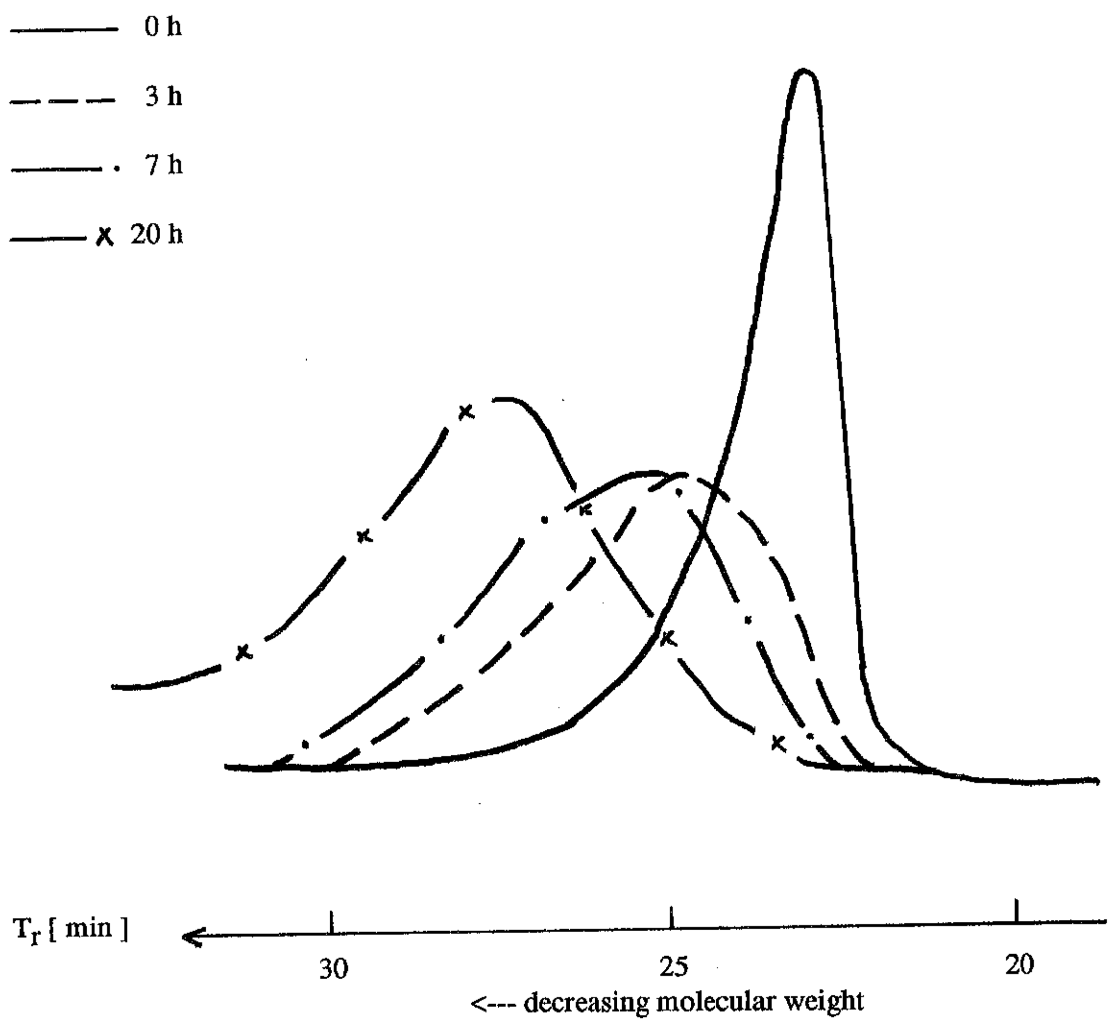


Figure 13; SEC analyses of 2HL + 8% Finaprene 416, peaks showing polymer only

There is a tendency that the polymer does not degrade as quickly in B 85 as in B 180, which is especially appearent for the linear type of SBS, figure 11. The tests in B 85 and oil taken together may give possible explanations. Since the oil dissolves the SBS almost completely the sensitive double bonds in the butadiene part is exposed to all the oxygen that is dissolved in the oil. Furthermore, any present stabilizer will be diluted and thus consumed both by the oil and the butadiene. This may also explain why the polymer remains undegraded longer in B 85 than in B 180. Since SBS is less compatible with B 85 than B 180 there is more of a two-phase system in B 85. If the stabilizers stay in the polymer phase this may contribute to the increased stability.

4 Accelerated ageing

Ylva Colldin at VTI, Swedish Road an Traffic Reseach Institute has exposed SBS modified bitumen to accelerated ageing. The material was kept at 70 °C for 6 months which corresponds to approximately 25 years of exposure at 15 °C. SEC - analyses were performed at SP after 0, 3 and 6 months and show similar results as before, i.e. degradation of the polymer and an increased molecular weight of the bitumen, see figure 14.

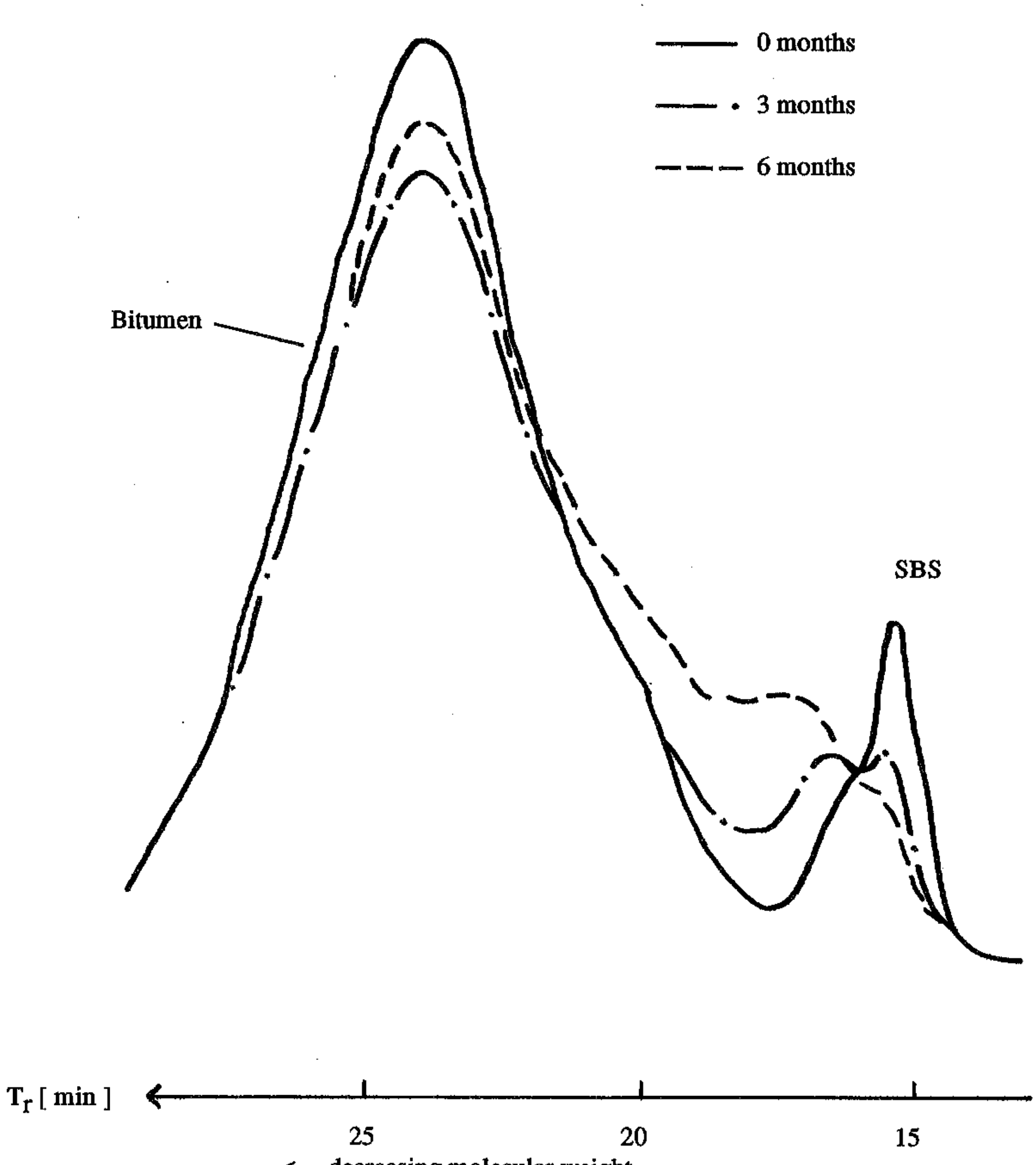


Figure 14; SEC analyses of SBS modified bitumen after accelerated ageing

5 References

[1] Diani, E., Gargani, L., "Bitumen modification with SBS thermoplastic elastomers," 4th Eurobitume Symposium 1989 Volume 1 summaries and papers

[2] Vonk, W. C., Van Gooswillingen, G., "Improvement of paving grade bitumens with SBS polymers," 4th Eurobitume Symposium 1989 Volume 1 summaries and papers

[3] Öster, R., Silén, B., "The durability of modified bitumen in the asphalt making process and during one year on the road," 4th Eurobitume Symposium 1989 Volume 1 summaries and papers

[4] Linde, S., "Degradation of styrene - butadiene - styrene elastomers (SBS) in bitumen blends at elevated temperatures, part 1" SP-Report 1987:29, Swedish National Testing and Research Institute.

Appendix 1

Specifications for distilled bitumen , B 180 and B 85

Property	Unit		B 180 value	B 85 value
Penetration at 25 °C	1/10mm	min	145	70
	1/10mm	max	210	100
Dynamic viscosity at 60 °C	Ns/m^2	min	45	120
Kinematic viscosity at 135 °C	mm^2/s	min	180	260
Solubility in toluene	weight-%	min	99.5	99.5
Flash point acc. to Pensky - Marten	°C	min	185	215
After heating:				
Weight loss	weight-%	max	1.5	1.0
Break point	°C	max	- 15	- 10
Dynamic viscosity at 60 °C	Ns/m^2	max	350	800
Ductility at 25 °C	cm	min	100	50

Appendix 2

Specifications for the polymers

Property	Unit	Cariflex TR-1101 value	Cariflex TR-1186(M) value
Styrene content	% mass	30	30
Melt flow rate 200 °C/5 kg	g/10 min	< 1	< 1
Tensile strength	MPa	33	24
Modulus 300%	MPa	2.9	3.0
Elongation at break	%	880	800

Property	Unit	Finaprene 416 value	Kraton G 1652 value
Styrene content	% mass	30	
Tensile strength	MPa	18	31
Modulus 300%	MPa		4.8
Elongation at break	%	800	500

Appendix 3

Specifications for oil fraction 2HL

Property	Unit	typical value
Density	g/m^3	0.942
Viscosity 40 °C	mm^2/s	130
100 °C	mm^2/s	8.9
Flash point, PM	°C	212
Pour point	°C	- 18
Total acid number	mg KOH/g	0.01
C_A	%	23
C_N	%	30
C_P	%	47