Characterisation of polymeric network structures

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3 Integrated approach to characterise the styrene/di-methacrylate network structures. Influence of styrene and radical-transfer agent.

Abstract

An integrated approach, involving the use of different analytical techniques, was used to study the chemical network structure of cross-linked styrene/di-methacrylate polymers. The mean cross-link density was varied in these networks by changing the concentration of styrene, while the gel time was increased by adding low concentrations of the radical-transfer agent 4-*t*-butylcatechol (TBC) to the styrene/di-methacrylate mixtures before cross-linking. The composition of the starting materials was analysed by chromatographic and mass spectrometric techniques, while the cross-linking reaction of styrene and di-methacrylate was studied using real-time infrared spectroscopy. The resulting cross-linked materials were hydrolysed and – without additional sample preparation – subsequently analysed by both size-exclusion chromatography and nuclear-magnetic resonance spectroscopy. The analyses revealed that the mean molecular weight of the polymeric backbone chains and the mean styrene sequence length increased linearly with increasing styrene concentration. The addition of TBC did not show any significant effect on the mean styrene sequence length, nor on the overall chemical composition of the polymeric backbone chains, while a strong influence on the molecular weight of the polymeric backbone chains was observed. Detailed insight into the chemical network structure was obtained by combining the results of all the different analyses. The mean molecular weight of chains between network junctions (M_c) was calculated and correlated with the glass-transition temperature (T_g) and the degradation temperature (T_{deg}). The compositional heterogeneity of the polymeric backbone seemed to be increased by addition of TBC, which resulted in a strong change of the T_g and the T_{deg} of these networks.

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3.1. Introduction

Styrene cross-linked with a so-called vinyl-ester polymer has found widespread application in fibre-reinforced composites [1]. Due to their superior mechanical properties, their chemical resistance and the ability to withstand water absorption, these materials are mainly used for applications in corrosive environments (*e.g.* storage containers) and, increasingly, for dental applications. These polymeric networks are commonly prepared by mixing a bi-functional vinyl-ester (*e.g.* di-methacrylate oligomers) with 20 to 50% (*w/w*) of styrene. Dilution with styrene lowers the viscosity of the mixture and facilitates impregnation and fibre wetting during fabrication of fibre-reinforced composites [1]. Styrene and bi-functional vinyl-esters are cross-linked to form a void-free network by a free-radical copolymerisation between the styrene monomers and the reactive vinyl-groups, as outlined in *Fig.* 3.1. The curing reaction is exothermic, which provides sufficient heat for archieving a high curing level. The final physical and mechanical properties of these highly cross-linked styrene/vinyl-ester polymers depend on the chemical network structure formed. Structure parameters include the mean molecular weight of visco-elastic chains between network junctions, the type of network junctions, and the network imperfections. Thus, probing the chemistry of the resulting network structure is important for understanding the physical and mechanical properties of these networks, as well as for designing networks with specific physical and mechanical properties.

A number of approaches have been described to study both the network formation and the network structure of cross-linked styrene/vinyl-esters copolymers.

(1) Curing of vinyl-esters with styrene and network-formation kinetics were extensively studied using differential scanning calorimetry (DSC) and Fourier-transform infrared (FT-IR) spectroscopy [2-5]. DSC provides the heat of polymerisation, but yields limited insight into copolymerisation reactions, since it does not provide information on the reaction-rate, nor on the degree of conversion for the individual monomers. FT-IR provides a means for measuring the depletion of reactive sites of both the styrene and the vinyl-ester during the cross-linking [6]. Newman and Patterson [7] showed that during the copolymerisation of styrene with unsaturated polyester the reactivity of styrene increased with increasing conversion, while the reactivity of multi-functional unsaturated polyester decreased with increasing conversion. The combined use of DSC and FT-IR leads to various

(often strongly simplified) curing models [4]. These models were used to describe the free-radical curing kinetics and reactivity ratios during the curing step in order to understand the network formation of styrene/vinyl-ester copolymers. Also the average sequence length of the monomers in the copolymer backbone was modelled using DSC and FT-IR data [4]. The resulting models, which are only valid for the investigated systems [4], provide valuable insight in the network formation for different curing conditions, such as different monomer compositions and different curing temperatures. However, the curing models have been evaluated predominantly for networks that were only characterised by their mechanical properties, such as the glass-transition temperature, rubber-modulus, fracture toughness, and tensile strength [2,9-10]. The cross-linking reaction of unsaturated polyester with styrene was also studied using real-time nuclear-magnetic resonance (NMR) relaxation experiments [11,12].

(2) Another approach is the characterisation of the final chemical structure of the styrene/vinyl-ester networks. Chemical degradation of the structure is necessary to perform detailed analysis, since the formed network is insoluble in any solvent. Conclusions about the network structure can be drawn from the nature and concentration of the hydrolysis products. Funke *et al.* [13] carried out extensive studies of the chemical degradation of styrene/vinyl-ester networks. The network was hydrolysed and the hydrolysis products were made soluble by esterification/methylation with diazomethane. The derivatised degradation products were analysed by several techniques, including osmometry, viscometry [14,15] and IR [15] and NMR [16-18] spectroscopy. ^{13}C-NMR analysis of the derivatised hydrolysis products revealed a pattern of resonance due to the quaternary carbon atoms of the styrene group, which originated from the different types of sequences in the styrene/vinyl-ester enchainment. Configurational differences caused small chemical shifts, while the structural differences caused a significant chemical shift [19]. This resulted in distinct broad peaks for different structural units, which could be used for the determining the comonomer distribution and, thus, the mean styrene sequence length in the copolymer. This was shown by several l-NMR [20-22] and s-NMR spectroscopy studies [11,23-25] on copolymers of styrene with different unsaturated and/or vinyl-ester oligomers.

The approaches described above have provided many valuable insights into styrene/vinyl-esters networks. However, they did not yield any detailed

information on the final network structure in terms of concentration and molecular weight distribution of the polymeric-network backbone chains. The length of these chains is also referred to as the kinetic chain length, *kcl*. Descriptive parameters of the chemical network structure and the network density, such as the *kcl*, are necessary to understand the mechanical/physical properties [26,27]. The network properties are often tailored in commercial styrene/vinyl-ester networks by changing the concentration of styrene or the chemical nature of the vinyl-ester, and also by the use of an inhibitor, such as the radical-transfer agent 4-*t*-butylcatechol (TBC). The latter reagent is used for stabilisation during storage of the uncured formulation and to tune the gel time.

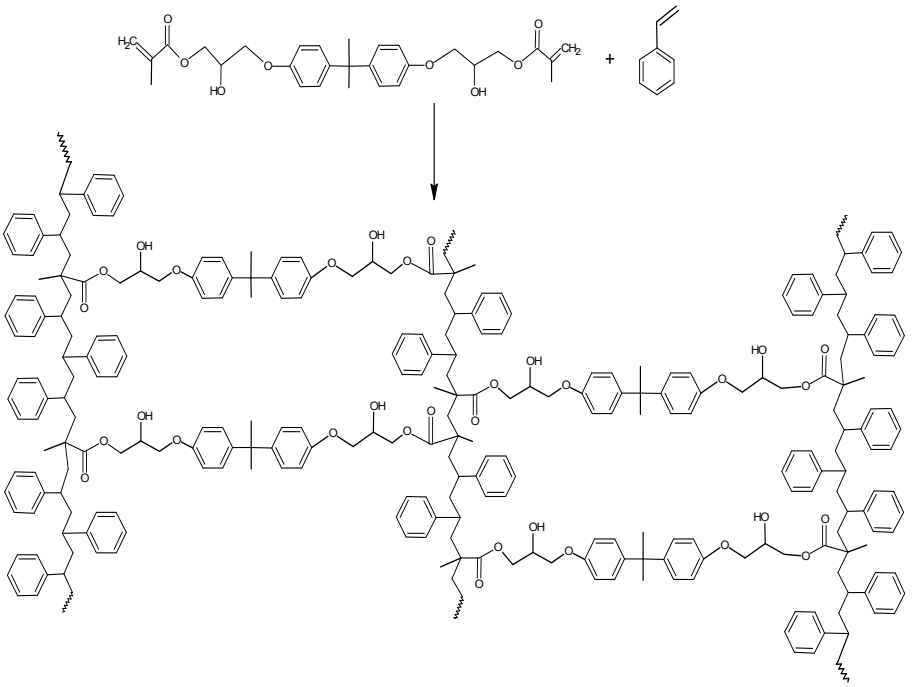


Fig. 3.1. Schematic representation of the resulting ideal network structure of cross-linked styrene and bi-functional vinyl-esters.

Knowledge of the influence of the concentration of both styrene and TBC on the chemical network structure is important for designing materials suitable for specific applications. Therefore, the characterisation of the chemical network structure of a series of styrene/vinyl-ester networks with systematically varied concentrations of styrene and TBC was the subject of the present study. The vinyl-ester used was prepared by endcapping the reaction products of bisphenol-

A bis-glycidyl ether products with methacrylic acid. This resulted in a bi-functional methacrylate, which was cross-linked with styrene. The cross-linking was initiated and accelerated by suitable reagents added to the styrene/di-methacrylate mixture, *viz.* methyl-ethyl-ketone peroxide and cobalt-octoate. Since the resulting polymer had an insoluble three-dimensional network structure, hydrolysis [28] of the formed network was necessary as a sample preparation method prior to chromatographic and spectrometric analysis. In the case of highly cross-linked styrene/di-methacrylate, selective scission of the ester-bonds by hydrolysis releases bisphenol-A containing fragments, which represent the chains between cross-links junctions, and styrene/methacrylic acid copolymer, which represents the polymeric backbone chains. The monomer distribution of the backbone chains is usually determined after hydrolysis of the network followed by esterification/methylation of the formed hydrolysis products with diazomethane ($R—COOH + CH_2N_2 \rightarrow R—COO–CH_3 + N_2$) [17,18]. Diazomethane is carcinogenic and has explosive properties, while the derivatisation reaction is laborious and possible side reactions could take place, *viz.* no full derivatisation reaction and/or the formation of unwanted-products [29]. Therefore, the hydrolysis products, without derivatisation reaction, were dissolved in a mixture of tetrahydrofuran/formic acid (THF/FA), which turned out to be a good solvent for the copolymeric backbone chains. The dissolved backbone chains were subsequently analysed with ^{13}C-NMR. A monad, a diad and a triad sequence were defined in order to assign the NMR peaks to specific styrene units along the copolymeric backbone chain. With this method, the chemical composition and the average styrene and methacrylic acid sequence length of the polymeric backbone chains were determined. The same hydrolysis products were analysed by size-exclusion chromatography (SEC), which gives detailed information on the network structure in terms of molecular weight distribution of the polymeric backbone chains (*kcl*). To ensure unambiguous interpretation of the network structure, the composition of the used di-methacrylate was analysed by liquid chromatography – mass spectrometry (LC-MS) and direct MS (MALDI-TOF-MS). Secondly, the relative change in double bond consumption during cross-linking was studied using real-time FT-IR. The results obtained from the different analysis techniques were used to calculate the following network parameters: the mean number of styrene and methacrylic acid units, the average degree of cross-linking as the mean number of cross-linked monomeric units of the polymeric backbone chains, and the network density as the mean molecular weight of networks chains between chemical network junctions (M_C). The latter was related to the glass-transition temperature (T_g) and the degradation temperature (T_{deg}) of the series of cross-linked styrene/di-

methacrylate polymers. The chemical network structure in relation to the styrene and the TBC concentration will be discussed.

3.2. Experimental

The formulations of the styrene/di-methacrylate polymers were prepared from mixtures of styrene (S) and di-methacrylate bis-glycidyl bisphenol-A (MA). The latter one is an experimental batch of methacrylic acid endcapped EPON 828, prepared in the laboratory of DSM Research. The styrene and methacrylic acid were purchased from Merck (Darmstadt, Germany), while the EPON 828 was purchased from Shell Chemicals Company (The Netherlands). The weight fraction styrene was varied from 32.5 to 59.5% (*w/w*) styrene, while the concentration TBC was varied from 0 to 5 mmol/kg (see Table 3.1). The formulations contained 0.295% (*w/w*) Cobalt NL-51P (contains 6% Co) and 3.0% (*w/w*) peroxide Butanox M50 (consists of 33% (*w/w*) methyl-ethyl-ketone peroxide (with a half life-time of 16 hours at 100°C), 65% (*w/w*) dimethyl-phthalate and 1% (*w/w*) diethyl-ethyl-ketone). Both the Cobalt NL-51P and the Butanox M50 were purchased from Akzo Nobel Chemicals (Amersfoort, The Netherlands). The mixtures were cured in bulk according to DIN 16945. The exotherm of the reaction was followed using a so-called gel-timer, while the final conversion of the samples was measured using ATR-FT-IR. None of the cross-linked polymers showed residual C=C IR signals of the methacrylate and/or the styrene, which suggests a conversion of more than 98% (limit of detection), considering that the depth of the IR signals is approximately 1.5 μm.
All the chromatographic experiments were performed on an Agilent 1100, equipped with a quaternary pump, degasser, autosampler, column oven, diode-array detector (DAD) with 10-mm cell and a single-quadrupole MS (Agilent, Waldbronn, Germany). The atmospheric pressure chemical ionisation (APCI-MS) ran in the positive mode with the following conditions: *m/z* 100-1500, 70 V fragmentor, 0.1 *m/z* step size, 350°C drying gas temperature, 10 L N_2/min drying gas, 45 psig nebuliser pressure, 4 kV capillary voltage and 4 μA corrona current. The LC analysis was performed with a 250×3 mm ODS-3 column at 40°C (Inertsil, Varian Inc, Palo Alto, CA, USA). Mobile phase A consisted of 0.1% (*v/v*) formic acid (Merck) in ultra-pure water and mobile phase B was acetonitrile (Merck). The gradient was started at t=0 min with 100% (*v/v*) A, stayed there for 5 minutes and changed in 40 minutes to 100% (*v/v*) B (t=45 min). The flow rate was 0.5 mL/min and injection volume was 5 μL. The molar ratio C=C of styrene and methacrylate was determined using ^{1}H-NMR

measurements with a Varian Inova 600 MHz NMR Spectrometer (Varian, Palo Alto, US). The mixture (Table 3.1, sample 1-0) was dissolved in $CDCl_3$ (Merck) while the spectrum was recorded using 32 scans and 30 s relaxation-time. The MALDI-TOF-MS experiments were conducted on a Kratos-Axima-CFR 4.2.1 (Shimadzu, Duisburg, Germany). The sample was dissolved in tetrahydrofuran (THF, Merck) and mixed with the matrix 2,5-hydroxybenzoic acid (2,5-DHB, Merck) in the ratio sample:2,5-DHB:THF=3:6:1000. The conditions used are; positive polarity, reflection mode, laser power 128 and 100 shots per sample spot.

The glass-transition temperatures (T_g) were measured using a Mettler DSC 82 (Mettler-Toledo International, Inc., Tiel, The Netherlands). About 5 mg sample was placed in an open aluminium cup and purged with 50 mL N_2/min during the experiment. All samples were heated from 0°C to 220°C, at a rate of 3°C/min. Results were reported from the first heating scans. Data analysis was performed with Mettler Toledo Star System (Mettler-Toledo Int.). The degradation temperature (T_{deg}) was determined with direct probe-EI-MS (thermal desorption inside the MS-source). These experiments were performed with the use of an E/B/E sector instrument (AutoSpecE, Micromass, Manchester, UK) under standard EI conditions (70 eV). A few µg of sample in a borate-silica cup (solid-probe) in high vacuum (10^{-7} mbar) was heated from 20°C (6 min isothermal) to 500°C (6 min isothermal) with a heating rate of 10°C/min.

Table 3.1. Starting compositions (%, w/w) of the different networks

Sample	Styrene (%, *w/w*)	di-MA (%, *w/w*)	TBC (mmol/kg)
1-0	32.5	67.5	0
2-0	39.3	60.8	0
3-0	46.0	54.0	0
4-0	59.5	40.5	0
1-1	32.5	67.5	1
1-2	32.5	67.5	2
1-3	32.5	67.5	5

The real-time FT-IR measurements were performed on a Perkin Elmer Spectrum One, equipped with a Golden Gate ATR accessory (single bounce diamond)(Perkin Elmer**,** Monza, Italy). The spectra were recorded between 4000 and 650 cm^{-1}, averaging 32 scans with a spectral resolution of 4 cm^{-1}. The functional group conversions were determined using the peak height for methacrylate and styrene at 1637 and 1631 cm^{-1} respectively, applying a single sided baseline at 1650 cm^{-1}.

The hydrolysis of the cross-linked polymers (0.5 gr) was performed in 40 mL methanol (Merck) and 2.5 gr potassiumhydroxide (Merck) using an autoclave (Roth, Karlsruhe, Germany) for 72 h at 140°C and 5 bar. After hydrolysis the liquid phase was removed with water, while the sticky residue was dissolved in a mixture of THF and formic acid (4:1%, *v/v*) (both from Merck).
The SEC separations were performed with 4× (300 mm × 7.5 mm) PLgel MIXED-C (5 µm particle size) and 1× (50 mm × 7.5) mm, PLgel guard column (5 µm particle size) columns at 30°C, with a separation range of 0.2-2000 *kDa* (Polymer Laboratories, Varian BV, Middelburg, The Netherlands). The mobile phase, which consists of THF (HiPerSolv CHROMANORM for HPLC) with 5% (*w/w*) acetic acid (Merck), was pumped at a flow rate of 1.0 mL/min. The injection volume was 150 µL. The SEC experiments were performed on an Hewlet Packard 1090 M1 with UV-DAD (Agilent) coupled to a Viscotek Triple Detector Array 302 at 30°C (DRI, viscometry and RALS)(Viscotek, Berkshire, UK). The software used was TRISEC 3.0. Narrow polystyrene standards (Polymer Laboratories, Shropshire, UK) were used to calibrate the SEC system.
^{13}C-NMR measurements were performed on a Varian Inova 600 MHz NMR Spectrometer, equipped with a 10 mm Broadband probe. To ensure quantitative data, inverse gated proton decoupling was used. Depending on the concentrations between 10000–70000 scans were accumulated with a relaxation delay of 5 s and an acquisition time of 1.3 s. The sum was estimated to be enough to ensure nearly complete relaxation of the quaternary carbon of the styrene ring [17]. The effect of relaxation delay was verified by repeating the measurement of a sample (Table 3.1, sample 1-0) with different delay values (1, 2, 5, 10 s). Samples were dissolved in a mixture of THF/FA (4:1%, *v/v*). THF-D_8 was used to allow shimming and locking; chemical shifts were referenced to FA-D_2 at 164.5 ppm. ACD software (ACD/CNMR Predictor, v9.02, ACD/Labs, Toronto, Canada) was used to verify the identification by NMR.

3.3. Results and discussion

3.3.1. Characterisation of the starting materials by LC-UV-MS and MALDI-TOF-MS

The used vinyl-ester is prepared by end-capping the reaction products of bisphenol-A and epichlorohydrine with methacrylic acid. It is well known, that the reaction between bisphenol-A and epichlorohydrine gives oligomers with

different endgroups, and even branched molecules could be formed [30-34]. The resulting molar, functional and topological heterogeneity affects the di-methacrylate properties and, thus, the final network structure. Therefore, the composition of the di-methacrylate was determined by LC-UV-APCI(+)-MS measurements of an uncured mixture of styrene and di-methacrylate. A typical UV-chromatogram (λ=275 nm) of sample 1-0 (see also Table 3.1) is shown in *Fig.* 3.2. The APCI-MS spectra of the different chromatographic peaks were investigated. Three different oligomeric series could be distinguished. All these series have a repeating unit of 284 *Da*, which is the product of bisphenol-A and epichlorohydrine. The major peak has a molecular weight of 512 *Da* and is part of a series, with the typical ion peak-to-peak mass increments of 284 *Da*. This series could be assigned to oligomers of di-methacrylate bis-glycidyl ether of bisphenol-A, up to n=4 (Table 3.2, series 1). In addition to this series, at least two series of lower intensity were observed. One of them is assigned to mono-methacrylate bis-glycidyl ether of bisphenol-A oligomers, up to n=2 (Table 3.2, series 2), while the third series is assigned to branched tri-methacrylate bis-glycidyl ether of bisphenol-A oligomers, up to n=3 (Table 3.2, series 3).

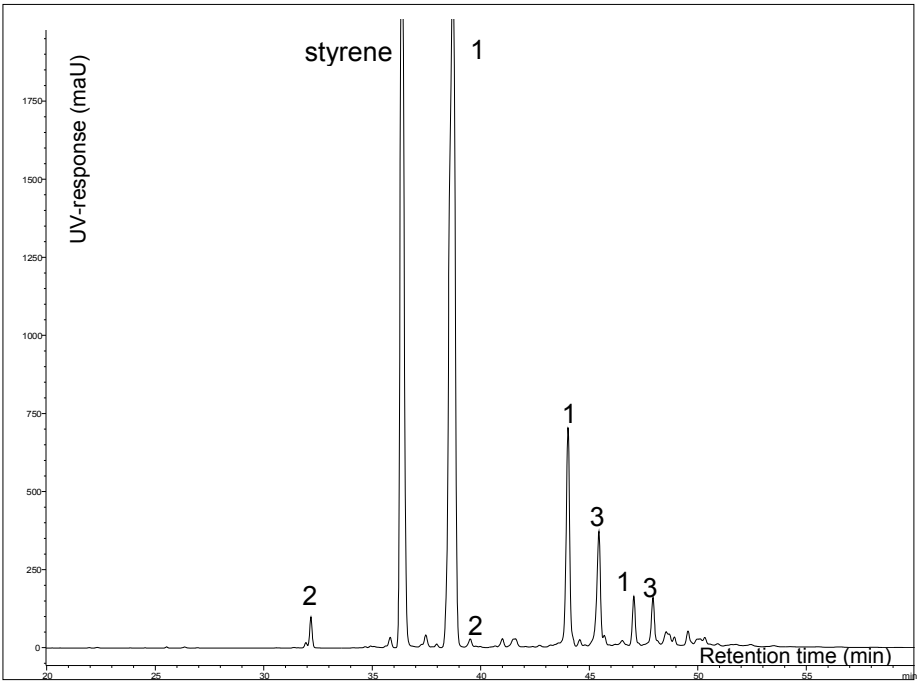
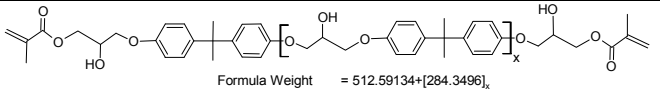
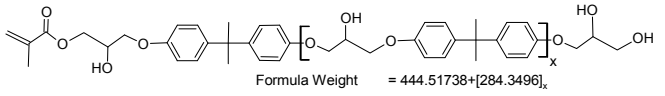
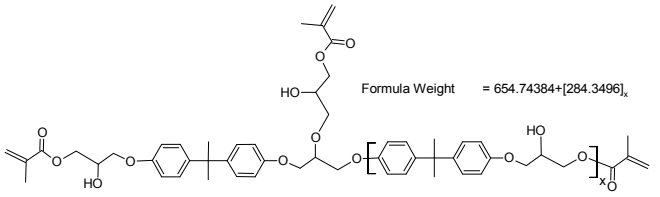


Fig. 3.2. UV-chromatogram (λ = 275 nm) of the reaction mixture before curing (sample 1-0). The oligomeric methacrylate series are designated as outlined in Table 3.2. The used conditions are given in the experimental section.

MALDI-TOF-MS measurements were performed to verify the qualitative result obtained by the LC-UV-MS analysis. Three main ions series were observed, which were identified as mono-, di-, and tri-methacrylate bis-glycidyl ether of bisphenol-A, as outlined in Table 3.2. Besides these three ion series, two other ion series at lower intensity were observed. These ion series are elucidated as reaction products of the matrix 2,5-DBH with either the mono- (*m/z* = 621.2, 905.2) and the bi-functional methacrylate oligomers (*m/z* = 689.2, 973.4, 1257.5). These series are probably the result of a reaction during or immediately after the high energetic ionisation by the MALDI-TOF-MS [35]. These side reactions, as result of the ionisation, show that the MALDI-TOF-MS result has to be used with care. Secondly, quantification of these compounds using MALDI-TOF-MS is very difficult in contradiction to suggestions in the literature [31]. Nevertheless, the MALDI-TOF-MS analysis confirms qualitatively the result of the LC-UV-MS analysis.

Table 3.2. Identified oligomeric series of methacrylate

Series	*m/z* ($M+Na^+$)	Structure
1	535.2, 819.4, 1103.5	 Formula Weight = 512.59134+[284.3496]$_x$
2	467.2, 751.3	 Formula Weight = 444.51738+[284.3496]$_x$
3	961.4, 1245.5, 1529.5	 Formula Weight = 654.74384+[284.3496]$_x$

The concentrations of the monomer and the different oligomeric series in an uncured mixture of styrene and di-methacrylate were determined using the UV-signal. The monomer styrene is quantified with external calibration of the pure standard, while the different methacrylate oligomers are quantified using a molar correction of the UV-contribution of the bisphenol-A part [36]. The

determined concentrations are given in Table 3.3. No unreacted bisphenol-A was observed (<0.01%, *w/w*). The concentration of methacrylic acid (0.05%, *w/w*) was determined using a pre-column derivatisation with 2-nitro-phenylhydrazine followed by LC-UV analysis [37]. To verify the concentrations of styrene and methacrylate oligomeric series determined, the molar ratio of styrene and methacrylate was determined by NMR. The molar ratio of styrene versus methacrylate is 2.52, which is in good agreement with the LC-UV result, *viz.* 2.48. This indicates that the used molar correction of the UV-contribution of the bisphenol-A part used during LC-UV analysis is correct.

Table 3.3. Composition (%, w/w) of the different oligomeric series of methacrylate bis-glycidyl compounds as determined by LC-UV

t_R (min)	M_w (*Da*)	Compound	% (*w/w*)
30.10		bis-phenol A	<0.01
36.20	104	styrene	32.5
38.67	512	series 1 (di-methacrylate), n=1	58.3
43.91	796	n=2	4.28
47.01	1080	n=3	0.32
48.44	1364	n=4	0.12
32.10	444	series 2 (mono-methacrylate)	1.00
39.40	728	n=2	0.33
45.34	938	series 3(tri-methacrylate)	2.46
47.95	1222	n=2	0.53
49.45	1506	n=3	0.12

In summary, the results show that the fraction of methacrylate groups from branched tri-functional methacrylate oligomers is 3.7% (*n/n*), while a small fraction of methacrylate groups from mono-functional methacrylate oligomers (1.1%, *n/n*) is formed. The mean M_n is 538 *Da*, with an overall methacrylate functionality of 2.03.

3.3.2. Curing of the network

The various mixtures of styrene, di-methacrylate and TBC are cured in bulk. The gel time (t_{gel}), the exothermic peak time (t_{peak}) and the maximum

temperature of the curing reaction (T_{max}) are shown in Table 3.4. The gel time and exothermic peak time increase with increasing concentration styrene, while the highest curing temperature is observed for the cross-linking of 63% (*n/n*) styrene with 27% (*n/n*) di-methacrylate (sample 2-0, Table 3.1).

Table 3.4. Curing properties and final network properties of the different networks

C=C styrene (%, *n/n*)	TBC (mmol)	t_{gel} (min.)	t_{peak} (min.)	T_{max} (°C)	T_g (°C)	T_{deg} (°C)
55.4	0	8.4	19.7	172	127.8	438
62.7	0	9.5	20.9	178	127.3	443
68.7	0	10.5	25.2	175	126.4	453
79.7	0	20.1	67.4	141	125.2	464
55.4	1	20.7	29.1	167	138.2	426
55.4	2	39.0	46.5	161	145.0	436
55.4	5	169.3	181.2	144	145.4	464

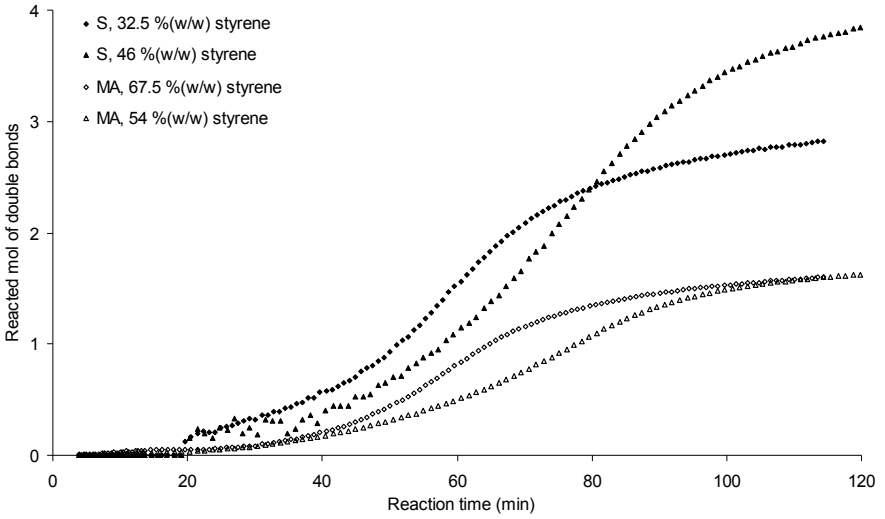


Fig. 3.3. Concentration of reacted double bonds (mol/kg sample) of methacrylate (MA) and styrene (S).

The formation of the styrene/di-methacrylate network was studied using real-time FT-IR, measuring the relative changes in double bond consumption during cross-linking. From an experimental viewpoint, the cross-linking is studied with a thin film of styrene/di-methacrylate, which may cure differently compared to

bulk samples due to the temperature variations by the transfer of heat evolved during cross-linking [6]. Therefore, the concentration of reacted double bonds (mol/kg sample) for both styrene (S) and methacrylate monomer (MA) as function of time was used only in a qualitative way. A typical curve of reacted double bonds is shown in *Fig.* 3.3. An increase in the styrene concentration results in a lower reaction rate for both the styrene and methacrylate. It is also apparent that the reaction of styrene starts before the reaction of methacrylate, which indicates that the initiation mainly occurs at styrene.

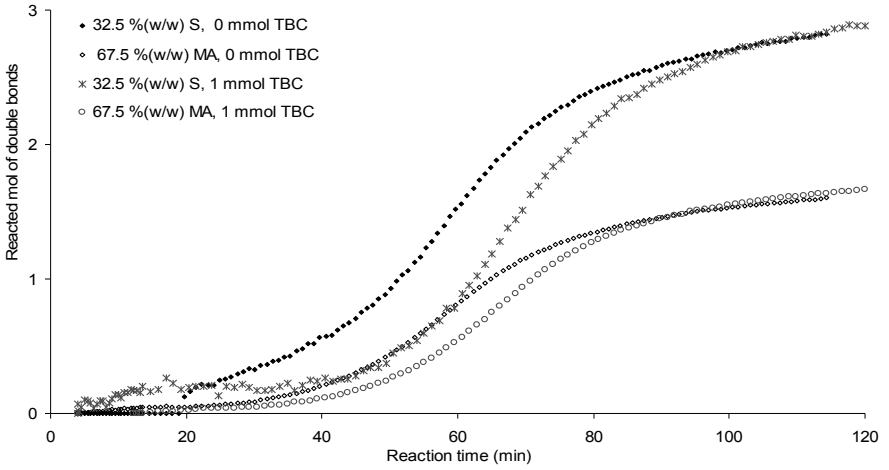


Fig. 3.4. Concentration of reacted double bonds (mol/kg sample) of methacrylate (MA) and styrene (S) with and without additional TBC.

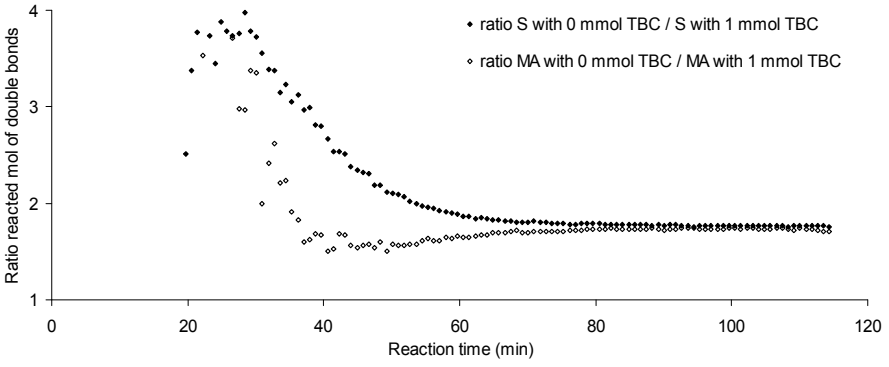


Fig. 3.5. Ratio of reacted double bonds (mol/kg sample) of methacrylate (MA), with and without addition of TBC, and styrene (S), with and without additional TBC.

A typical curve of reacted double bonds, with and without addition of TBC is given in *Fig.* 3.4. Addition of TBC shows a delay in the reaction of styrene and methacrylate. Nevertheless, similar conversions of styrene and methacrylate are observed for the reaction with and without TBC. The reaction rate of methacrylate decreases to a lesser extent than the reaction rate of styrene (see *Fig.* 3.5). This indicates that the effect of TBC is only a temporary reduction in the propagating radical concentration of both the styrene and the methacrylate.

3.3.3. Glass-transition and degradation temperature of network

The glass-transition temperature (T_g) of the formed networks without additional TBC increases upon a decrease in the styrene concentration [38], as shown in *Fig.* 3.6. All the samples show only one T_g, which indicates a good miscibility of styrene and di-methacrylate at a molecular level. In general, the T_g of networks were expected to be relatively insensitive to changes in chemical composition, but sensitive to cross-link density [2]. However, the additions of 1 up to 5 mmol TBC/kg sample, which act as radical-transfer agent, show a non-linear increase of the T_g (*Fig.* 3.6). An increase of more than 17°C was observed for addition of 2 to 5 mmol TBC.

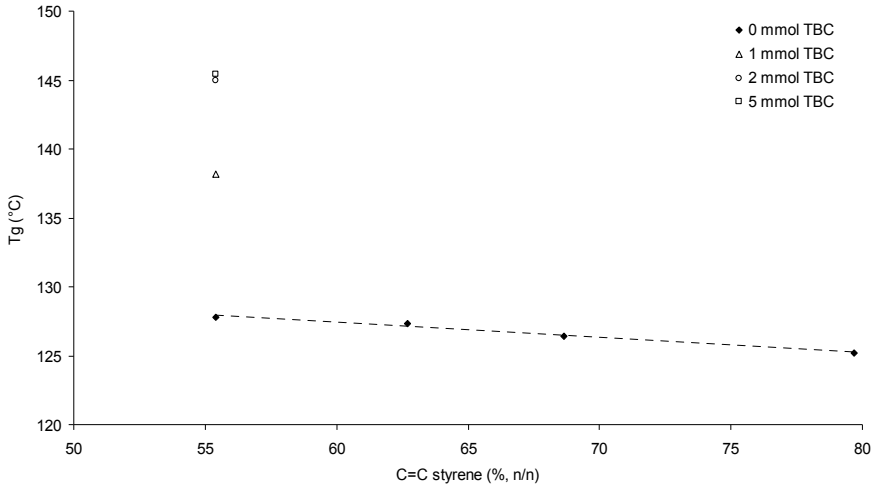


Fig. 3.6. Influence of the concentration styrene and the TBC on the glass-transition temperature (T_g).

The degradation temperature (T_{deg}), determined using direct probe-MS, increases linearly upon an increase in the concentration of styrene (see Table 3.4). The

presence of TBC during curing has a strong influence on the degradation temperature; a low concentration of TBC decrease the degradation temperature, while a high concentration of TBC increases the degradation temperature.

3.3.4. Analysis of the polymeric backbone

Since the network has an insoluble three-dimensional network structure, hydrolysis is necessary as a sample preparation for both SEC and ^{13}C-NMR analysis. Hydrolysis of the cross-linked samples at enhanced temperature and pressure in the presence of an organic alkali resulted in a liquid and a solid phase. To determine the completion of the hydrolysis, both phases were isolated and subsequently analysed using different techniques; IR, probe-MS, SEC and LC-UV-MS. The liquid phase was analysed as such, while the solid residue was totally dissolved in a mixture of THF and FA (4:1%, *v/v*) to perform SEC and LC-UV-MS analysis.

Table 3.5. Analysis result of probe-MS, LC, SEC and IR of the solid and liquid fraction after hydrolysis of the cured styrene/di-methacrylate network

Analysis	Liquid fraction	Solid fraction
Probe-MS	not analysed	Polystyrene fragments
LC-MS	Bisphenol-A fragments, no free styrene	No bisphenol-A fragments (<1%), no free styrene
SEC	No polymer (<1%)	Polymer
IR	-OH, -OK, -OCH_3 groups	Polystyrene, like segments, -COOH and –COOK groups

The different analytical results indicate (Table 3.5) that the liquid phase contains different compounds related to bisphenol-A with -OH and –OCH_3 endgroups. The different compounds indicate that a significant part of the ether-bonds were cleaved using the extreme hydrolysis conditions. No styrene compounds and/or free styrene (<1%, *w/w*) are observed in the liquid phase. The solid phase contains a copolymer of styrene and methacrylic acid and no bisphenol-A related compounds (<1%, *w/w*). Since no ester-groups were observed in either phases, only –OCH_3 groups, the result indicates complete hydrolysis of the cross-linked styrene with di-methacrylate (>98%). Secondly, after hydrolysis, the polymeric backbone chain is present in the solid phase, as it does not

dissolve in the organic alkalic solution, in contrast with the bis-phenol-A chains between cross-links junctions, which are dissolved in organic alkalic solution. The complete hydrolysis and isolation of the polymeric backbone chains and the hydrolysis matrix/products makes the sample preparation for the analysis of the polymeric backbone very straightforward; the solid phase is isolated from the liquid phase and completely dissolved in THF/FA (4:1%, *v/v*).

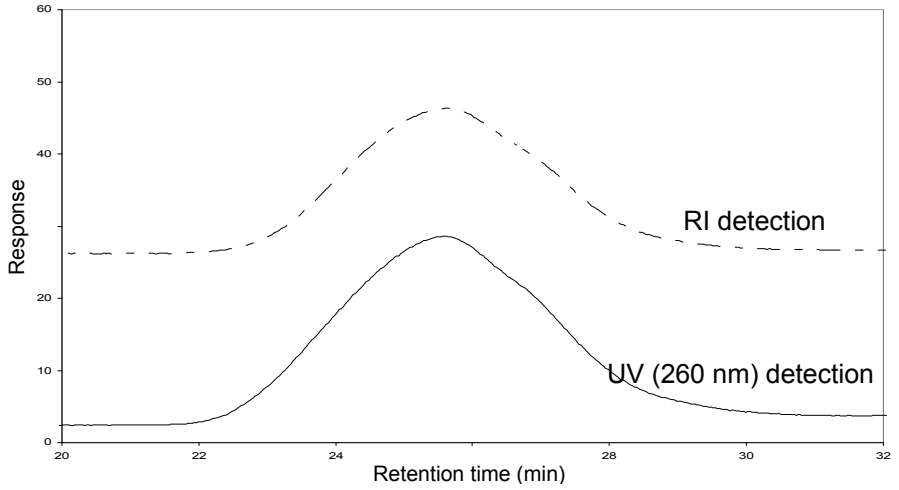


Fig. 3.7a. Typical SEC-RI and SEC-UV chromatogram of sample 1-2. The conditions used are given in the experimental section.

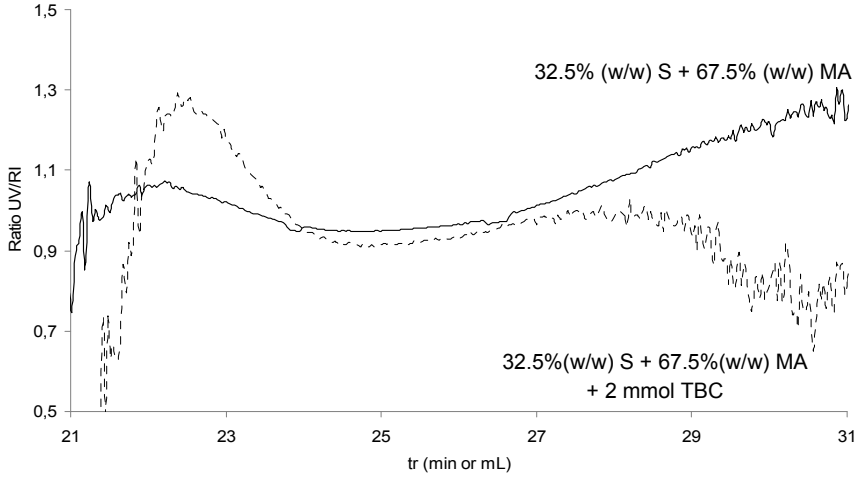


Fig. 3.7b. Compositional heterogeneity by ratio UV/RI versus the SEC elution time (sample 1-0 and 1-2).

The weight-average molecular weight (M_w) of the polymeric backbone chains (*kcl*), which is an important network parameter, is determined by SEC. The M_w is calculated with conventional calibration, since the *dn/dc* of the copolymer is not known. A typical SEC chromatogram is given in *Fig.* 3.7a. In general, the SEC-RI and SEC-UV chromatogram are similar. Both the RI and UV curve shows a minor distribution at retention time (t_R) ± 26.6 minutes. This indicates two different molecular weight distributions. The tri-functional methacrylate, which was present at low concentrations in the used unsaturated polyester, could cause this. The ratio between the UV- and the RI-peak area increases with the styrene content in the samples. This indicates that the UV-signal mainly originates from the styrene unit and the RI signal by both the styrene and methacrylic acid unit. The ratio UV versus RI at each elution time can give information about the compositional heterogeneity that is related to the molecular weight of the copolymeric backbone. The ratio UV/RI at each elution time is calculated, after correction of the time differences between both detectors (Δt_R = 0.376 min). As demonstrated in *Fig.* 3.7b, the polymeric backbone chains from the network with TBC opposite to the polymeric backbone chains from the network without TBC, seem to contain lower concentration styrene at low M_w and more styrene at higher M_w. This result regarding to the compositional heterogeneity has to be used with care, as the deviating ratio UV/RI is at the extremes of the curves. Secondly, the RI-signal depends on the M_w [38] and the UV-signal can be influenced by the average styrene sequence length in the copolymeric backbone.

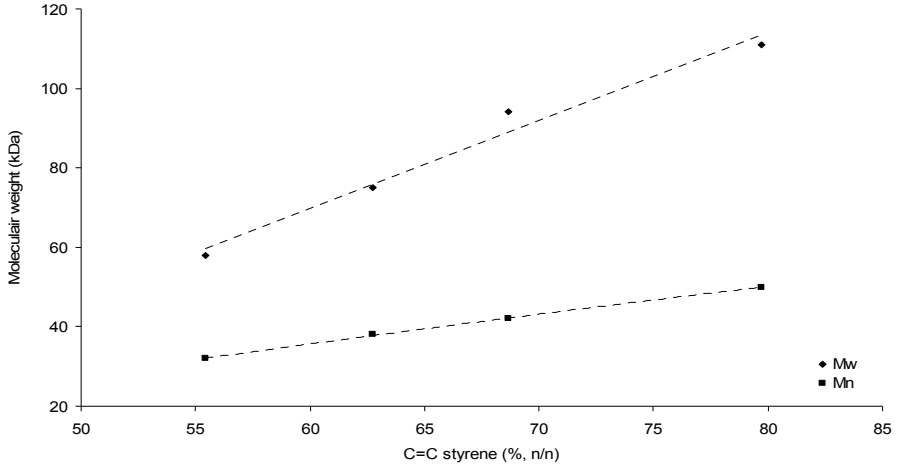


Fig. 3.8a. Correlation of concentration styrene and the mean molecular weight of the copolymer backbone chains.

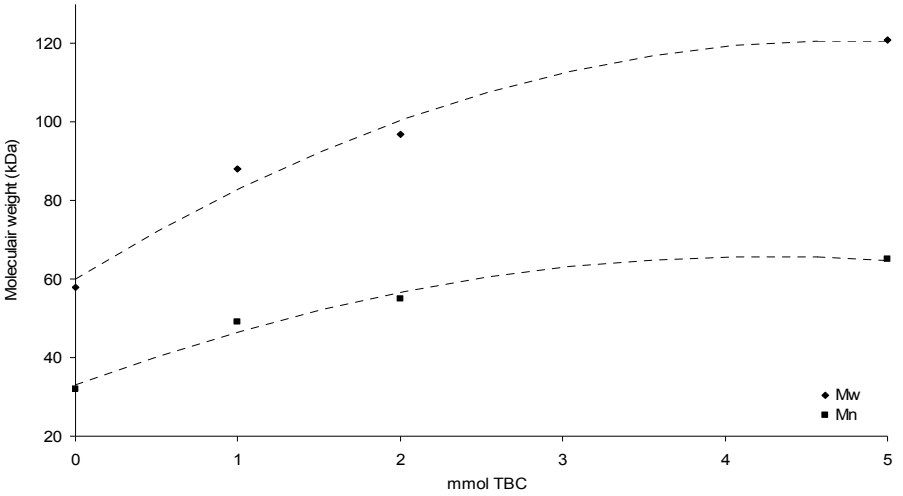


Fig. 3.8b. Influence of additional TBC on the mean molecular weight of the copolymer backbone chains.

The determined M_w and M_n of the different samples are shown in *Fig.* 3.8. The M_w and M_n increase linearly upon increasing styrene concentration. Since styrene acts as a diluent, the styrene enables the styrene/di-methacrylate molecules to find available reactive sites due its high mobility. The M_w and M_n increase also with increasing the concentration of TBC, which is probably caused by a decreasing concentration of available free radicals.

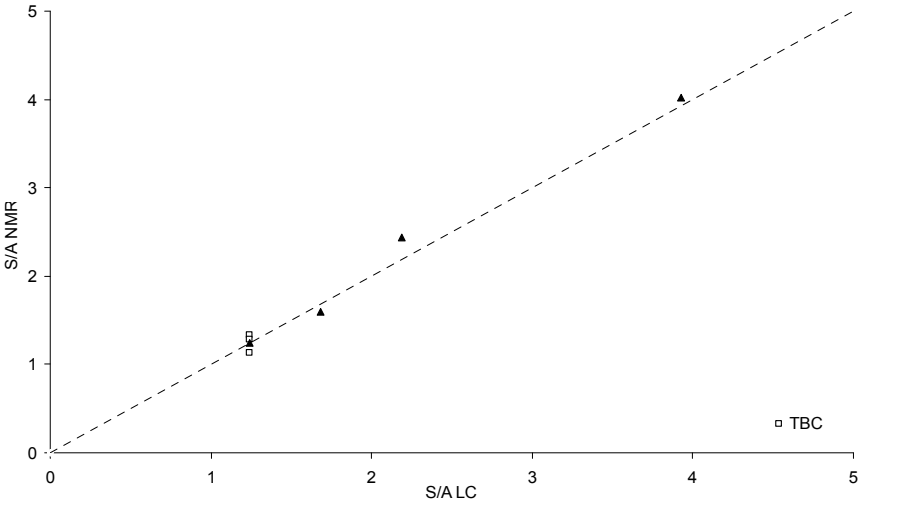


Fig. 3.9. Molar ratio of styrene/methacrylic acid (S/A) determined by NMR and calculated of the LC-UV result are in good agreement (line is guide to the eye).

The overall ratio of styrene (S) to methacrylic acid (A) copolymeric backbone chains, obtained after hydrolysis, is determined by ^{13}C-NMR. The mol ratio of styrene versus methacrylic acid is determined from the quaternary carbons of the styrene triads (147-150 ppm) and the carbonyl carbon of the methacrylic acid (180 ppm). Variation of the relaxation delay between 2 and 10 s shows that the value of molar ratio determined is rather constant, which indicates that the determination is quantitative. Triplicate experiments of sample 1-0 show a relative standard deviation (*RSD*) of ~5% of the determined NMR signals. The experimentally determined molar ratio S/A by ^{13}C-NMR versus the calculated S/A ratio using the purity of the uncured formulation determined by LC-UV-MS is shown in *Fig.* 3.9. A good correlation between the molar ratio found with NMR of the hydrolysed products and the calculations from the LC-UV results is found ($S/A_{(LC)} = 1.031 \times S/A_{(NMR)}$, $R^2 = 0.988$). This indicates that the used hydrolysis and sample preparation method is representative for styrene/methacrylic acid copolymers backbone chains of the network formed.
Summarised, the different analyses performed on the hydrolysates of the different samples show that the hydrolysis and dissolution procedures used are representative for the polymeric backbone chains of the formed network.

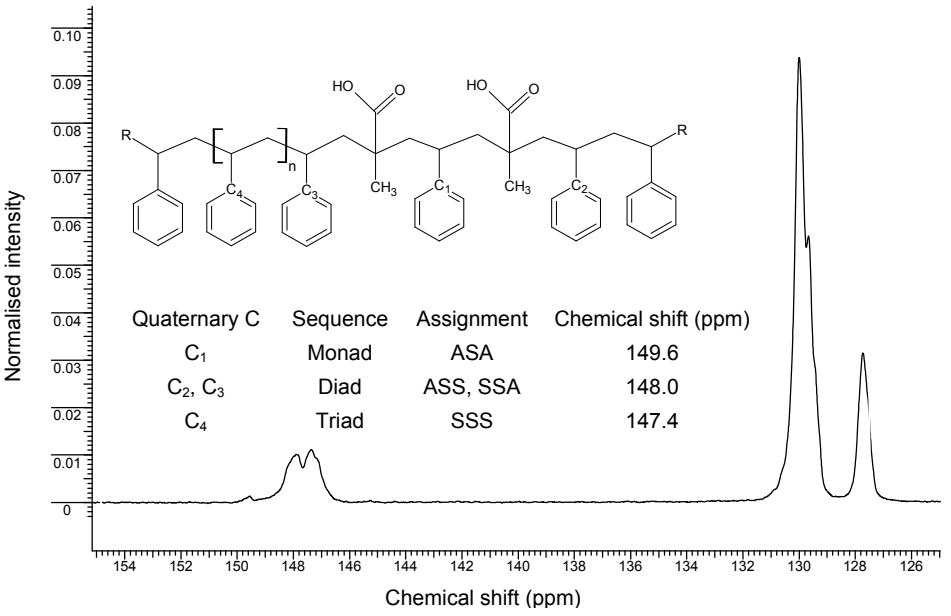


Fig. 3.10. ^{13}C-NMR spectrum of sample 4-0 in THF-D_8/ FA-D_2 (4:1%, v/v) with the assigned chemical shifts of the different styrene sequences.

The chemical shift assignment for the styrene/methacrylate sequences are only known for styrene/acrylonitrile [40] and styrene/maleic anhydride, after esterification with diazomethane [17,22] and dissolution in typical NMR solvents (*i.e.* $CDCl_3$). The copolymeric backbone chains of the hydrolysed networks, which consist of styrene and uncapped methacrylic acid units, are not soluble in typical NMR solvents ($CDCl_3$, *etc.*), but THF-D_8/ FA-D_2 (4:1%, *v/v*) turns out to be a good solvent. It is well known that the chemical shift can be solvent dependent and the chemical shifts for the present copolymer are not described before. For these reasons, the chemical shift for the monad, diad and triad sequences of the specific styrene units along the copolymer backbone (see *Fig.* 3.10) must be assigned.

The isomeric forms (isotactic, syndiotatic and heterotactic configurations) have been ignored, since they result in small chemical shifts (< 1 ppm). The quaternary phenyl carbon C_1 (see *Fig.* 3.10) constitutes a structural unit on its own, as it is flanked by two methacrylic acid units (monad, A**S**A). The C_2 and C_3 carbons (see *Fig.* 3.10) are structurally similar, since they have a styrene unit on one side and a methacrylic acid unit on the other side (diad, S**S**A = A**S**S). The C_4 carbon (see *Fig.* 3.10) contributes to a structural unit on its own, as it is flanked by two styrene units (triad, S**S**S). A typical ^{13}C-NMR spectrum of a sample is shown in *Fig.* 3.10. The chemical shift is downfield to the values reported in the literature for the esterified maleic acid/styrene systems in $CDCl_3$ (139-145 ppm) [17]. In order to assign the chemical shifts, ^{13}C-NMR spectra of the samples are recorded, but also a styrene/maleic anhydride polymer and the samples with additional polystyrene. The NMR signal at 147.5 ppm increases with increasing concentration of styrene in the copolymer and/or with addition of polystyrene. This indicates that this chemical shift can be assigned to the quaternary carbon of the styrene surrounded by styrene units (S**S**S). As a consequence, the chemical shift increases with increasing surrounding of methacrylic acids units (see *Fig.* 3.10). The diads S**S**A and A**S**S give similar chemical shifts since the phenyl quaternary carbon atom of S**S**A and A**S**S has the same distance to the methacrylic acid. Obviously, this is only true in the case of head-to-tail polymerization. Experimental chemical shifts of a CH_2-group next to a quaternary carbon in small organic molecules (*e.g.* 27 ppm for 2,2-dimethyl hexanoic acid) were near 30 ppm [41]. This fits with predicted values of the chemical shift for the CH_2-carbon in a head-to-head arrangement, which is 33±4 ppm. For the head-to-tail structures, the chemical shifts were 44±6 ppm and 39±5 ppm for the CH_2- and CH-carbons respectively. Experimentally, broad signals were observed at 47 and 41 ppm, which is indicative of head-to-tail polymerization.

The molar fraction of triades ($n_{(ASA)}$, $n_{(ASS)}$ and $n_{(SSS)}$) versus the mol fraction of styrene is shown in *Fig.* 3.11. The mean styrene length (N_S) of a random styrene/methacrylic acid distributed copolymer, such as the polymeric backbone chain, can be described by [42]:

$$N_S = \left(\frac{n_{(ASA)} + n_{(ASS)} + n_{(SSS)}}{n_{(ASA)} + 0.5 \times n_{(ASS)}} \right) \tag{1}$$

Since the mean number of styrene/methacrylic acid units is known from the triades, the mean methacrylic acid length (N_A) of a random styrene/methacrylic acid distributed copolymer can be calculated from:

$$N_A = \frac{N_S}{ratio\left(\frac{S}{A}\right)} \tag{2}$$

The calculated N_A and N_S versus the mol fraction styrene are given in *Fig.* 3.12.

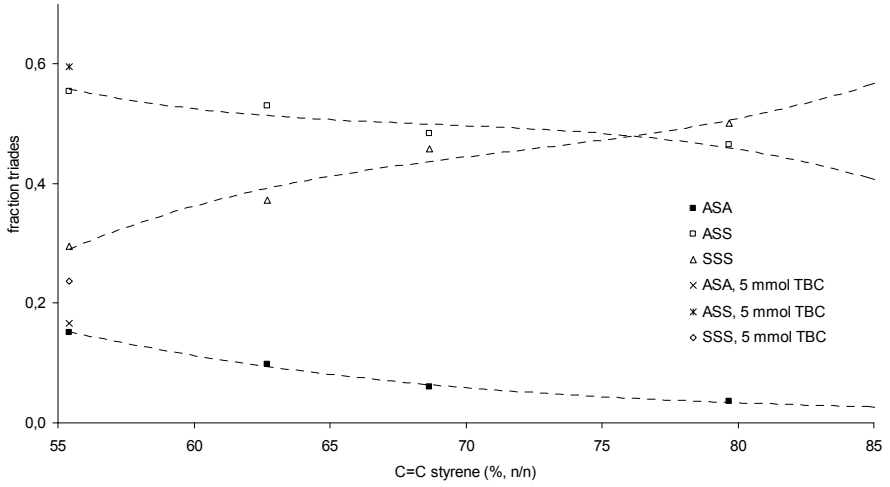


Fig. 3.11. Influence of the concentration styrene and a high concentration TBC (5 mmol) on the molar fraction of the assigned triades.

An increasing concentration of styrene in the formulation results in a linearly increasing mean length of styrene in the polymeric backbone chains. Both the mean styrene length and the methacrylic acid length of the polymeric backbone

chains for the copolymers with low styrene concentration are much higher than expected from a randomly distributed copolymer in which both monomer radical centres show no substantial preference for either one.
A clear trend is observed; higher concentrations of TBC during the cross-linking reaction increase the molar fraction of A**S**A and A**S**S-sequences while the molar fraction of S**S**S-sequences decreases. However, the observed differences in sequences are smaller than the relative standard deviation of the analysis (*RSD* of ~5%). Thus the mean length of styrene and methacrylic acid sequence do not seem to be significantly influenced (less than 5%) by the addition of TBC.

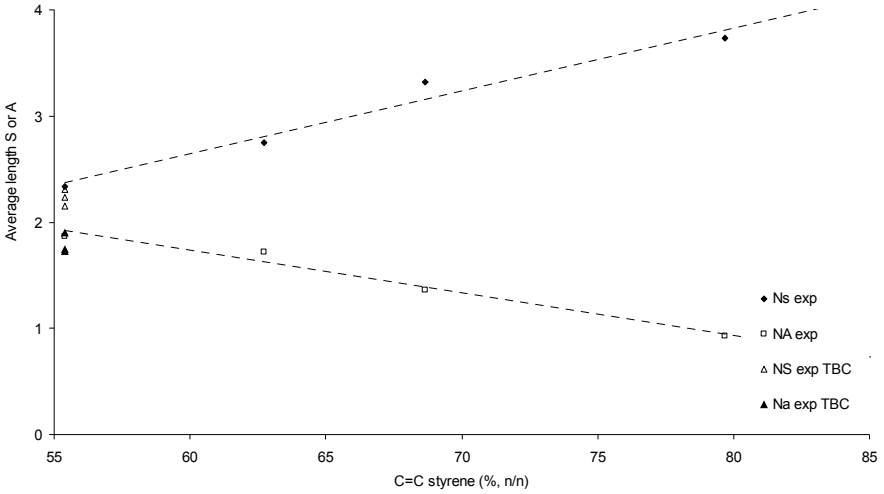


Fig. 3.12. Linearly increasing mean styrene (N_S) and decreasing methacrylic acids length (N_A) in the polymeric backbone chains with increasing concentration styrene.

3.4. Chemical network structure

The analysis of the starting materials and the copolymeric backbone chains of the formed network lead to a network structure of styrene/di-methacrylate, as proposed in *Fig.* 3.13. The presence of mono-functional methacrylate results in dangling chain ends, while both the di- and tri-methacrylate contribute to the network.
The influence of the styrene concentration on the network structure is determined. The gel time and peak time increase with increasing concentration of styrene, which is in agreement with the observations of Hietalahti *et al.* [24]. The increasing gel time shows that the initiation period depends on the styrene

content. This was confirmed by real-time FT-IR measurement on networks with different concentrations of styrene. Secondly, real-time FT-IR indicates that the initiation reaction occurs mainly at styrene, while the propagation decreases with increasing concentrations of styrene. The use of SEC and ^{13}C-NMR, directly after dissolving the hydrolysis products of the network, gives insight in the molecular weight distribution and the mean styrene and methacrylate sequence length of the polymeric backbone chains of the network.

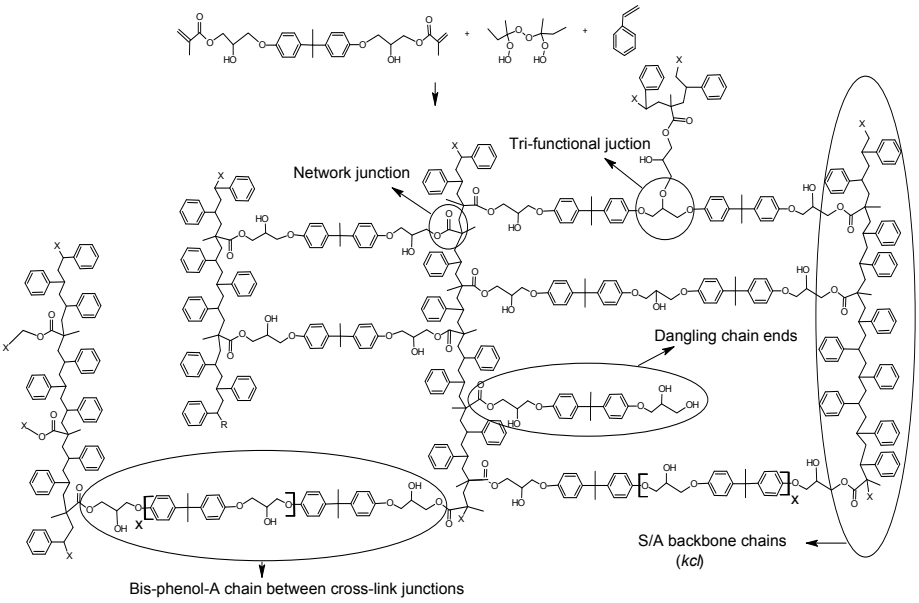


Fig. 3.13. Styrene/di-methacrylate network structure as determined by different analysis techniques.

In general, the M_n and the mean styrene sequence length of the polymeric backbone chains increase linearly upon an increase in the concentration of styrene. However, the mean styrene sequence length of the copolymeric backbone with low styrene concentration is higher compared to a random copolymer. SEC indicates that the polymeric backbone chains from the network seem to contain more styrene at low M_w. Both observations are the result of the initiation reaction which occurs mainly at styrene. This causes a higher styrene sequence length in the copolymeric backbone at the beginning of the cross-linking reaction and a higher sequence length of the methacrylate units at the end of the cross-linking reaction.

The starting concentration styrene influences the average degree of cross-linking, which is defined as the percentage of the mean number of cross-linked

monomeric units from the total mean number of monomeric units of the polymeric backbone. The average degree of cross-linking, which can be calculated from the composition of styrene and methacrylic acid units in the backbone chain as determined by NMR combined with the SEC results, is given in Table 3.6. The average degree of cross-linking shows a decrease as a result of increasing number of non-cross-linking styrene units in the copolymeric backbone chains.

Table 3.6. Mean number of methacrylic acid (n_{acid}) and styrene ($n_{styrene}$) units in the polymeric backbone as determined by SEC and NMR and the average degree of cross-linking (XL)(when correcting for mono-methacyate in the starting material)

Sample	C=C Styrene (%, *n/n*)	TBC (mmol)	n_{acid} (XL_{non})	n_{acid} (XL)	$n_{styrene}$	n_{total}	XL (%)
1-0	55.4	0	1.6	148	185	333	44
2-0	62.7	0	1.6	151	240	391	38
3-0	68.7	0	1.3	124	301	425	29
4-0	79.7	0	1.1	99	399	498	20
1-1	55.4	1	2.3	218	291	509	43
1-2	55.4	2	2.7	251	321	572	44
1-5	55.4	5	3.4	319	361	680	47

The network density can be expressed as the mean molecular weight between chemical network junctions (M_c), and was calculated from the qualitative and quantitative NMR data of the copolymeric backbone and the composition of the starting material:

$$\begin{aligned} Mc = {} & (n/n)_{di-MA} * ((2*(S/A)*M_S + M_{di-MA})/3) + \\ & (n/n)_{m-MA} * ((3*(S/A)*M_S + M_{di-MA} + M_{m-MA})/3) + \\ & (n/n)_{tri-MA} * (((S/A)*M_S + 0.33*M_{tri-MA})/2) \end{aligned} \quad (3)$$

where (S/A) is the mol ratio of styrene *vs.* methacrylic acid, M_S is the molecular weight of the styrene, $M_{m\text{-}MA}$ is the average molecular weight of mono-methacrylate (514.9 *Da*), $M_{di\text{-}MA}$ is the average molecular weight of di-methacrylate (535.8 *Da*) and $M_{tri\text{-}MA}$ is the average molecular weight of tri-methacrylate (1008.6 *Da*). The mol-fraction of the various methacrylates ($(n/n)_{m\text{-}MA}$, $(n/n)_{di\text{-}MA}$ and $(n/n)_{tri\text{-}MA}$) is respectively 0.011, 0.952 and 0.037.

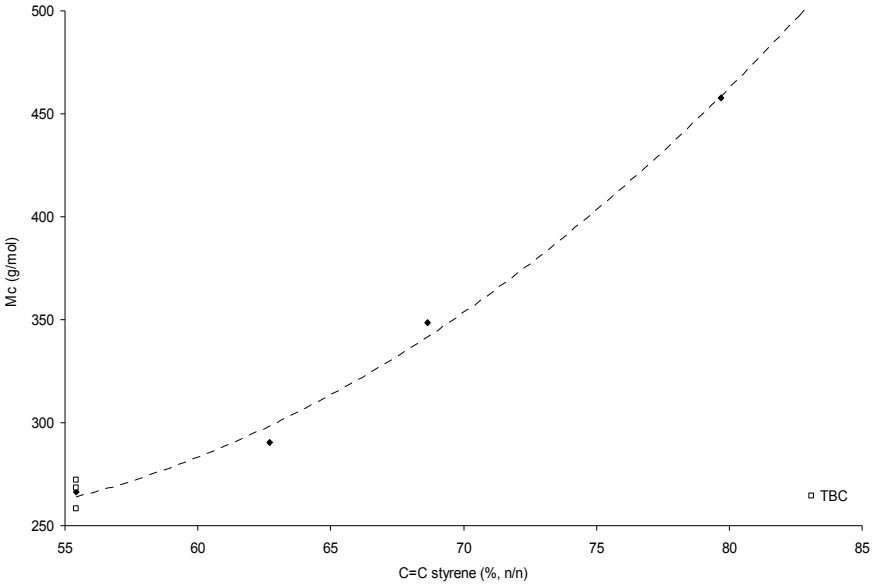


Fig. 3.14. Mean molecular weight between chemical cross-links (M_c) in cured styrene/di-methacrylate networks against the mol fraction styrene.

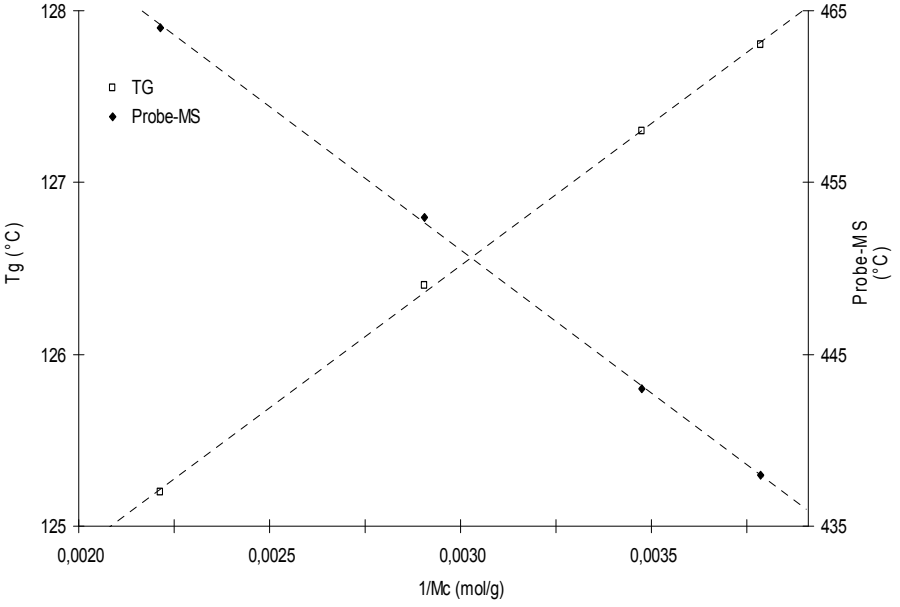


Fig. 3.15. Experimental relation between $1/M_c$ to T_g and T_{deg}.

The influence of the concentration of styrene on the M_c is shown in *Fig.* 3.14. The network density, defined as M_c, shows a non-linear dependence on the styrene concentration. The M_c values are related to the T_g and T_{deg}, as shown in *Fig.* 3.15. This result in linear relationships between T_g and $1/M_c$; the T_g increases with increasing values of $1/M_c$ [43]. This suggests that the cross-link density is a strong determinant for the glass-transition temperature [44]. The same is true for the degradation temperature, which linearly decreases upon the increase of $1/M_c$. This is probably related to the concentration styrene, which depolymerises (ceiling) at higher temperature.

The influence of the TBC concentration on the network structure has been determined. The inhibitor TBC is normally used for stabilisation during storage and to tune the gel time. As expected, TBC has a strong influence on the gel time and peak time. It is generally accepted that TBC has no influence on the chemical network structure. SEC analysis shows that the mean molecular weight of the polymeric backbone increases strongly with increasing concentration of TBC. This is probably directly related to the initiation reaction; the concentration of radicals decrease, and as a consequence the *kcl* increases. Since the overall styrene/methacrylate composition is not significantly influenced by TBC concentration, the degree of cross-linking and the network density, as M_c, are similar for the networks without or with various concentrations of TBC. However a strong influence on T_g and T_{deg} (Table 3.4) as a consequence of the TBC concentration was observed. This will be explained below in terms of another compositional heterogeneity of the copolymeric backbone chains when TBC is added before curing. First, ^{13}C-NMR showed small differences in the overall sequence length for the different concentration of TBC added; NMR indicates that the molar fraction of A**S**A and A**S**S-sequences seems to be higher and that the molar fraction of S**S**S-sequences seems to be lower, compared to a styrene/di-methacrylate network without additional TBC (see also *Fig.* 3.11). However, this trend is within the uncertainty of the determined NMR signal (*RSD* ~5%). Secondly, real-time FT-IR measurements show that TBC reduces the reaction rate of styrene more than the reaction rate of methacrylate, which results from a lower concentration of styrene-radicals at the start of the curing reaction in contrast to networks without additional TBC. This leads to another compositional heterogeneity of the polymeric backbone chains when TBC is added before curing. Finally, SEC analysis indicates that the heterogeneity is dependent of the molecular weight of the polymeric backbone chains; *viz.* the low M_w polymeric backbone chains seem to contain a higher concentration of methacrylic acid units, while the concentration of styrene units seems to be higher for high M_w polymeric backbone chains. In conclusion, low

concentrations of TBC influence the *kcl*, but likely also the chemical heterogeneity of the polymeric backbone chains, compared to the network without additional TBC. This causes the deviating T_g and T_{deg}. Today, no analysis method is available to determine quantitatively the chemical heterogeneity of these polymeric backbone chains. Therefore, this consistent set of results forms the starting point for the study of the chemical heterogeneity of the polymeric backbone chains of the formed network using LC×NMR and/or LC×SEC techniques.

3.5. Conclusion

This study shows the development and the use of a straightforward sample preparation method subsequently followed by ^{13}C-NMR and SEC analysis to study the copolymeric backbone chains of styrene/di-methacrylate networks. The combination of these results with the composition of the starting materials, the depletion of the reactive groups during curing to the resulting network, and final network properties give valuable insight into these styrene/di-methacrylate networks.

Different analysis techniques are used to study the influence of the concentration styrene and TBC on the final network structure. The initiation reaction occurs mainly at styrene, while the propagation decreases with increasing styrene concentrations. This results in linearly increasing M_n, and mean styrene sequence length of the copolymeric backbone chains upon an increase in the concentration of styrene in the starting composition. Secondly, the copolymeric backbone has a relatively higher number of styrene units in the copolymeric backbone at the beginning of the cross-linking reaction, while the number of the methacrylate units is relatively higher at the end of the cross-linking reaction. An interesting observation is that increasing the concentration of TBC during the cross-linking has a strong influence on the *kcl*, which is probably directly related to the initiation reaction; *viz.* the concentration of styrene-radicals decrease, and as a consequence the mean molecular weight of the polymeric backbone increases.

SEC and ^{13}C-NMR analysis after hydrolysis and real-time FT-IR during curing indicates that low M_w polymeric backbone chains seem to contain a higher concentration of methacrylic acid units, while the concentration of styrene units seems to be higher for high M_w polymeric backbone. These analyses give strong indications, although their significance can be disputed. In conclusion, TBC seems to influence the heterogeneity of the polymeric backbone chains and has a

strong impact on the network structure, which in turns determinates the T_g and T_{deg}.

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