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1 Introduction to polymeric networks and their analysis

A macromolecule [1] is a molecule of high relative molecular mass, where the structure essentially comprises the multiple repetition of units derived, actually or conceptually, from molecules of low relative molecular mass.
A polymeric network [1] is a highly ramified macromolecule, in which essentially each constitutional unit (comprising a part of the essential structure of a macromolecule, an oligomer molecule, a block, or a chain) is connected to each other constitutional unit and to the macroscopic phase boundary by many permanent paths through the macromolecule. The number of such paths increases with the average number of intervening bonds; the paths must *on the average* be co-extensive with the macromolecule.

[1] *IUPAC GLOSSARY OF BASIC TERMS IN POLYMER SCIENCE, Pure Appl. Chem., Vol. No. 68, 8 (1996) 1591–1595.*

1.1. Introduction to polymers

A polymer is a very large molecule which consists of many identical or different units joined together. The unit forming the repetitive pattern is called a monomer. In the case of one type of repeating units, the polymer is called a homopolymer, while a copolymer consists of more than one type of repeating units. Polymers are a very important class of materials. They occur naturally in the form of proteins, DNA, cellulose, starch, natural rubber, *etc.*. Since the 18th century synthetic polymers have been developed [1,2]. Nowadays, synthetic polymers have a broad range of properties and resulting applications that far exceed any other class of materials available to man. The field of synthetic polymers is one of the fastest growing material fields; the polymer industry has grown to be larger than the aluminium, copper and steel industries combined [1]. Current applications are adhesives (*e.g.* glues, tapes), coatings (*e.g.* paints), foams, gels (*e.g.* absorbent in diapers, controlled drug delivery systems, cosmetics, foods), packaging materials, industrial fibres (*e.g.* textiles, ropes, cables), as additives to other materials (*e.g.* thickeners in cosmetic industry, foods), and structural plastics (*e.g.* containers, boat hulls, vehicles).
In general polymers can be divided into two groups called thermoplastics and thermosets [1–3].
Thermoplastics, which are the polymers used most, have a long molecular chain, with one or more molecular architectures (see *Fig*. 1.1): linear, branched (short, long, star) or ladder [4]. In the case of copolymers, even more complex architectures may be obtained, *i.e.* alternating, random, graft, block copolymer, and combinations of these. Thermoplastic polymers have intramolecular covalent bonds and interact with other polymer molecules through weak intermolecular van der Waal's interactions. As a result, thermoplastics can be repeatedly melted and shaped by increasing or decreasing the temperature. The microstructure can be either amorphous (random molecular orientation) or crystalline (densely packed crystallites), which affects the properties of the thermoplastics to a large extent. Most thermoplastics (> 90%) are common plastics, *e.g.* polyethylene, polypropylene, polystyrene and polyvinyl chloride [1]. A small part of the thermoplastics are engineering plastics which exhibit superior properties, in comparison with commodity plastics. The latter include better mechanical properties, better heat resistance and higher impact strength. Examples of engineering plastics are acrylonitrile-butadiene-styrene, nylon and polycarbonate [1].
Thermosets differ from thermoplastics by their behaviour. Thermosets cannot be softened or recycled at any time by reheating [1]. Thermosets can be either

liquids or solids at room temperature and need to be heated to cure (harden), giving the desired shape and solid properties. This deviating behaviour arises from a basic difference between thermoplastics and thermosets. In addition to normal (intramolecular) covalent bonds, the thermosets feature also strong intermolecular covalent bonds (so-called cross-links) that connect separate polymer chains together. This results in one large three-dimensional molecular network (see *Fig.* 1.1). Unsaturated polyesters, polyurethanes and melamine-formaldehyde [1] are examples of polymers that can be cross-linked.

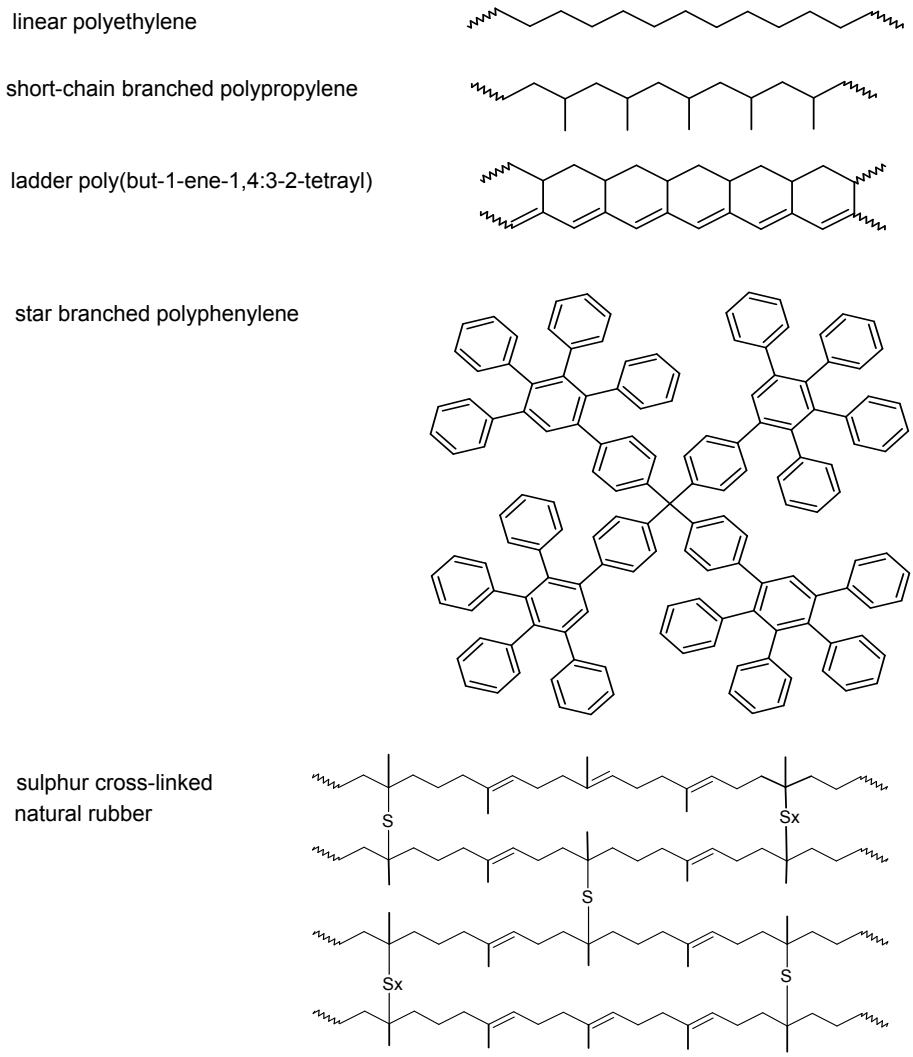

Fig. 1.1. Examples of different molecular architectures.

1.2. Polymeric networks

1.2.1. Chemically vs. physically cross-linked networks

In general, a cross-linked structure in a polymeric network is defined as a small region in the polymer chain structure from which *at least three* chains emanate [5,6]. Although this thesis focuses on chemically cross-linked polymers, it should be mentioned that the cross-link structures (also called network junctions) need not to be formed exclusively by chemical cross-links, since physical interactions between polymers can also result in network structures. In the case of physically cross-linked networks, the cross-links are not permanent and are often (thermally) reversible [7]. A typical example are physically cross-linked linear polymers of lactide and/or glycolide prepared by solvent or salt casting, which are used for controlled release of bioactive agents and for encapsulation of cells or biomolecules [8].
Chemical cross-linking is often performed to increase the strength of polymers through the formation of *one* big molecule. Cross-linking gives polymers some outstanding macroscopic properties that make them ideal for many applications. These properties include: excellent dimensional stability, high resistance to many solvents and high heat stability.

1.2.2. Types of chemically cross-linked networks

The aim of this section is to give an overview of chemically cross-linked networks. However, it should be recognised that the list of cross-linked polymers is enormous. A classification of polymer networks can be made based on different criteria: physical/chemical, natural/synthetic, applications (*e.g.* coatings, biomaterials), kind of reactive groups, network density, kind of polymer chains (*e.g.* interpenetrating polymer network), *etc.* Since this thesis describes the analysis of chemical network structures, our classification is based on the way in which networks can be chemically formed:

(1) The skeletal chains or the side chains of the polymer are chemically cross-linked using peroxides, high-energy radiation and/or sulphur compounds (vulcanisation). A typical example is the peroxide cross-linking of ethylene-propylene-diene terpolymer (EPDM) (see *Fig.* 1.2). The cross-linking results from the combination of macro-radicals generated by the thermal decomposition of the peroxide and from the addition of macro-radicals to unsaturated moieties of other macromolecules [9]. The cross-

links are introduced in a highly random manner (statistical process), resulting in an ill-defined network topology. Dangling ends will always be present in the final network, due to its infinite molecular weight [10]. These polymeric networks are used where toughness or resistance to impact is desired, since they can be stretched to many times their original length, and bounce back without permanent deformation. Typical applications are tires, window/door sealings, but also latex gloves.

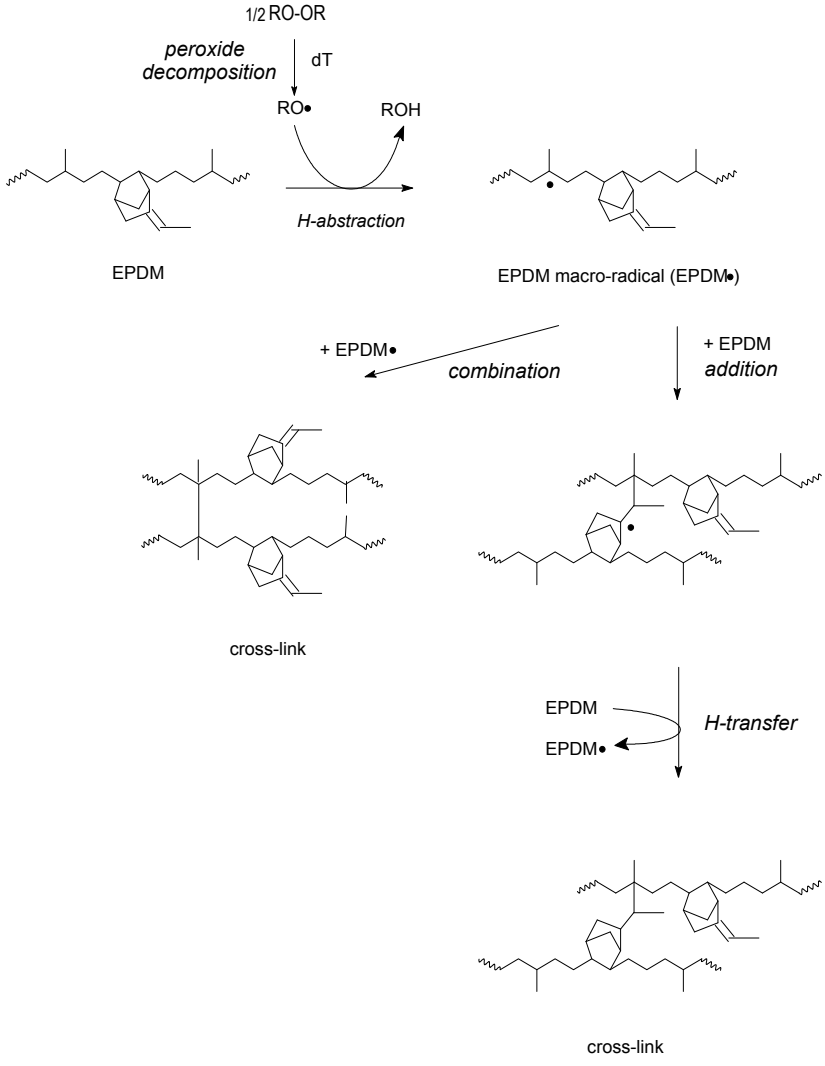

Fig. 1.2. General scheme for peroxide cross-linking of EPDM with 5-ethylidene-2-norbornene (ENB) as a diene.

(2) Cross-linking occurs via free-radical chain (co)polymerisation of bi-functional vinyl monomers. Typical examples are the copolymerisation of acrylamide and N,N'-methylene bisacrylamide in aqueous solutions leading to highly swollen polyacrylamide gels [11] and the photo-polymerisation of di-acrylates into glassy, dense networks [12] (see *Fig.* 1.3). In the case of acrylates, the functionality is incorporated into the monomer/polymer through an ester-bond. Therefore the individual resin types differ only in the chemistry of the bi-functional vinyl oligomer and not in the polymerisable group. The first step in this kind of cross-linking polymerisation reaction is initiation, which involves the formation of a free radical. The middle step is chain polymerisation where successive monomers are attached to the growing polymer chain. The last step is the (bi-molecular) termination reaction.

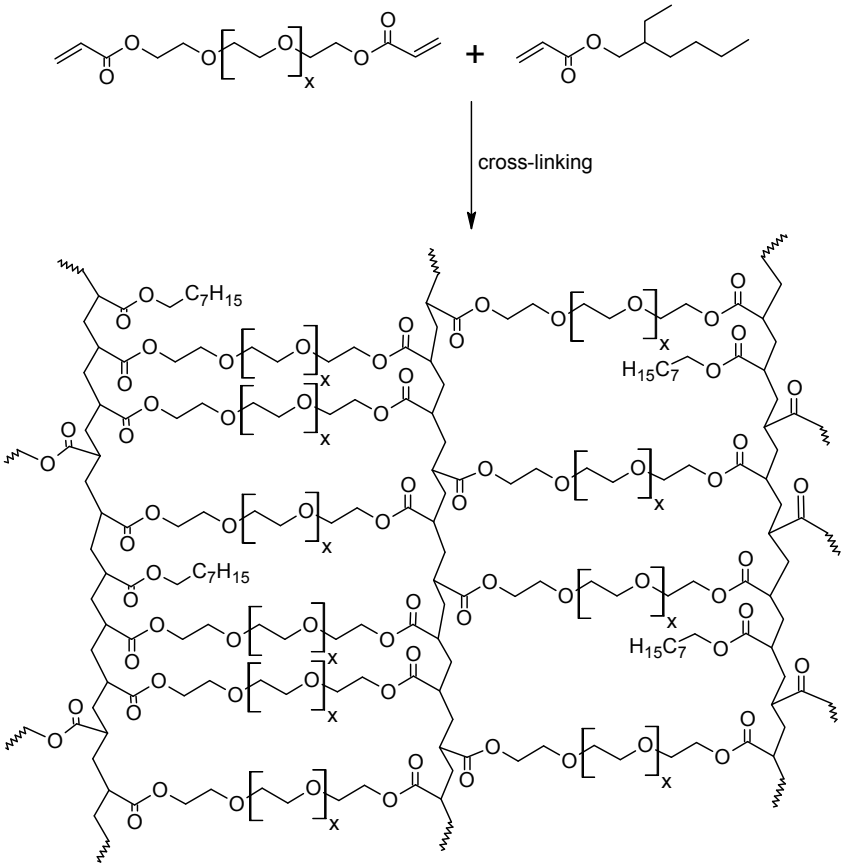

Fig. 1.3. General scheme for UV-curing to a highly cross-linked polyethylene glycol di-acrylate/2-ethylhexyl acrylate network.

(3) Polymeric networks can also be formed by the reaction of a multi-functional (pre)polymer with a low-molecular weight cross-linking agent. The latter has a functionality of two or higher. A classic example is the polycondensation of dicarboxylic acids with glycerol leading to cross-linked polyester [5]. A more actual example is the cross-linking of the ethyl ester of lysine-di-isocyanate with glucose to generate a polyurethane network that upon degradation only yields metabolisable products [13] (see *Fig*. 1.4). In general, this kind of cross-linking results in well defined network topology, since the networks have "known" values of cross-linking functionality and number-average molecular weights (and its molecular weight distribution) of the (pre)polymer used prior to cross-linking. One of the imperfections known to be present in network structures are the dangling chain ends, the concentration of which may be very small when this kind of cross-linking reaction is carried out stoichiometrically and to high conversion of the functional groups [10].

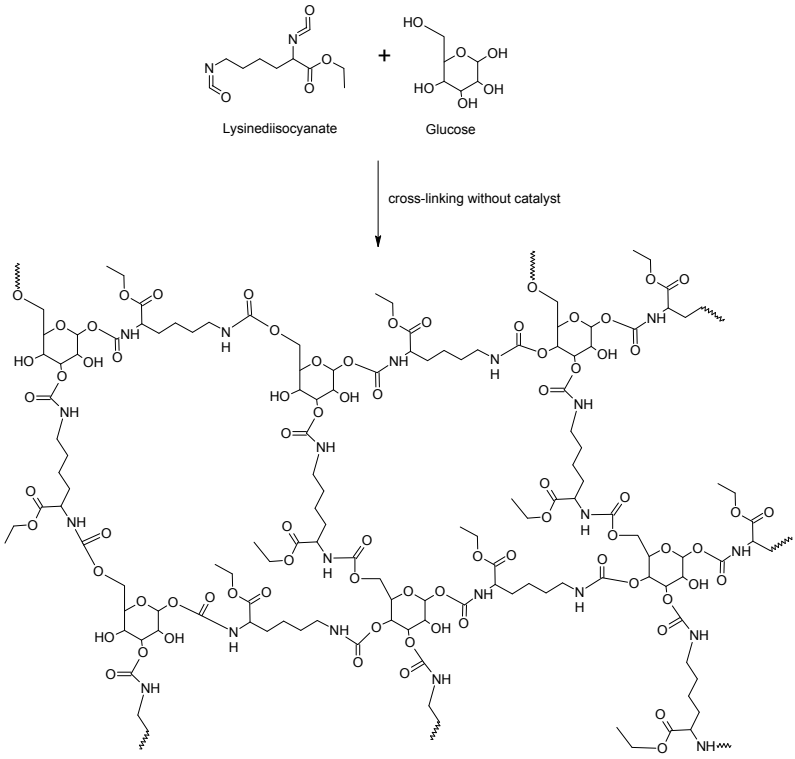

Fig. 1.4. Schematic representation of cross-linking of the ethyl ester of lysine-di-isocyanate with glucose to generate a bioerodable polyurethane network.

1.2.3. Network imperfections

Cross-linked polymers always deviate from perfect networks. These are defined as random, homogenous collections of chains with a Gaussian chain-length distribution between network junctions under the conditions that all the functionalities of the junction points have reacted [14]. Real cross-linked polymers contain network imperfections (see *Fig.* 1.5) which may be introduced upon network formation.

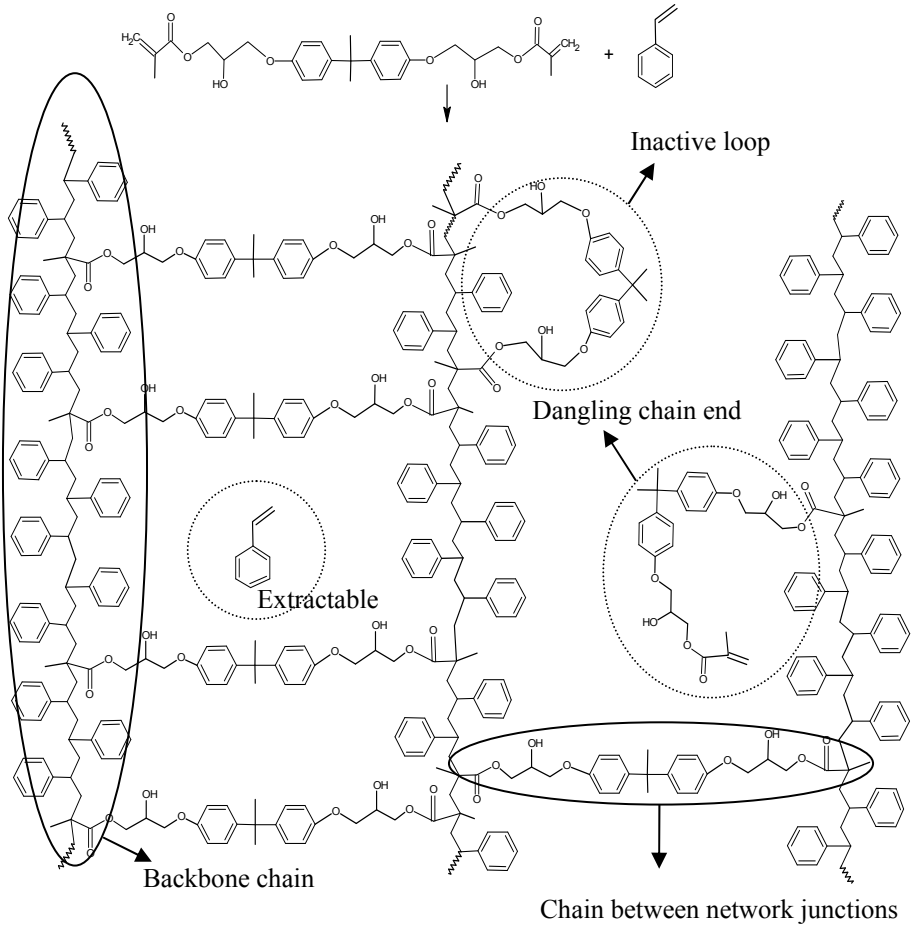

Fig. 1.5. Schematic representation of the resulting ideal network structure (solid lines) and some network imperfections (dashed lines) of styrene cross-linked bi-functional vinyl-esters.

These network imperfections include network defects, such as dangling chain ends, which are chains attached to the network at only one of their ends, elastically inactive loops resulting from intramolecular reactions, monomeric/polymeric material not attached to the network, physical chain entanglements and spatial heterogeneity. The number of network defects depends on the way in which the network has been formed (conditions, chemistry, *etc.*).

The final physical and mechanical properties such as stress to break, strain hardening, tear strength, creep (deformation), and glass-rubber transition temperature are influenced by the chemical composition (chain mobility) and by the cross-link density of the network. The latter is defined as the number-average molecular weight of visco-elastic chains between chemical and physical network junctions. Polymers can have different degrees of cross-linking: networks with similar chemical compositions show an increase in the glass-transition temperature and in the modulus with increasing network densities. Thus depending on the chemical composition and the cross-link density, the polymeric network can have a rubbery (posses memory) or a rigid (brittle) behaviour. Although, the cross-link density and the chemical composition have a large influence, conversion of functional groups, type of network junctions, network imperfections and heterogeneity also influence the physical and mechanical properties of the polymeric network [1]. As may be expected, the properties of the final polymeric network affect the application of these materials. The relation between formulation, network structure, properties and applications is schematically represented in *Fig*. 1.6.

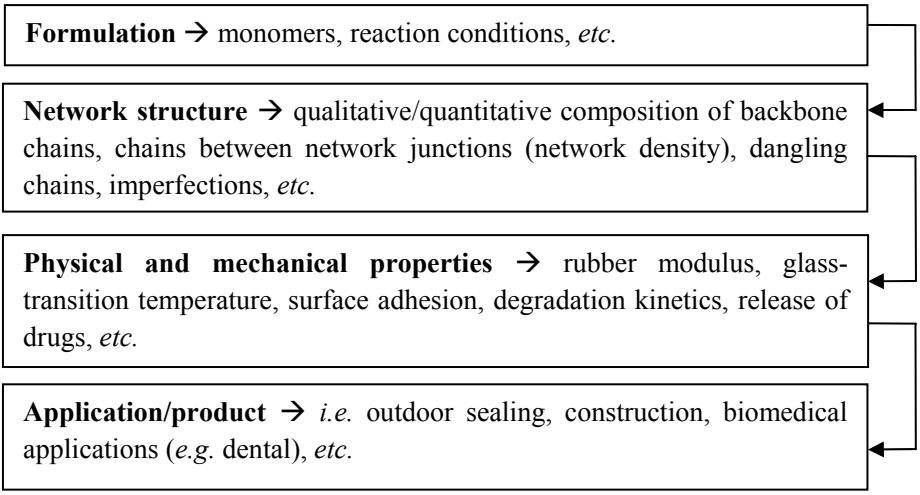

Fig. 1.6. The relation between formulation, network structure, properties and application.

1.3. Analysis of polymeric networks

The analysis of cross-linked industrial- and biopolymers, especially the relation between chemistry (cross-linking) and (mechanical and physical) properties, have been the objective of a large number of academic and industrial studies during the past two decades. The motivation is to find guidelines to tailor cross-linked materials for various applications without the need of extensive trial-and-error experimentations. To be able to relate the final properties of cross-linked polymers to their chemistry, it is essential to understand the network topology, which significantly affects the functional properties.

Since cross-linked networks can have a large variety of structures, it is important to have techniques to characterise the structural parameters, such as the mean molecular weight of the chains between cross-links (cross-link density), the molecular-weight distribution of the polymeric backbone chains, and the (im)perfections of the network. The characterisation of the network structure is complicated further, since the network may or may not be "regular" and may feature various imperfections, such as intramolecular loops, dangling ends, molecules trapped in the network, cross-link junctions with a higher functionality and combinations of these. The fact that the networks are resistant to chemicals (insoluble in any solvent) makes the analysis and characterisation of the network structure even more difficult.

In principle there are two kinds of network-analysis methods: direct and indirect analysis of the cross-linked networks (see *Fig.* 1.7).

The direct approach is preferred. However, the poor analytical accessibility of cross-linked polymers (solubility) in combination with the relatively low concentrations of cross-linking structures, make the analysis of the chemical structure of the formed networks by spectroscopic and/or chromatographic techniques often rather difficult.

The indirect approach includes the degradation of the network structure in such a way that essential information on the identity of the cross-links is maintained, followed by analysis of the degradation products. The degradation is typically performed thermally (*i.e.* pyrolysis) or chemically (*i.e.* enzymatic or chemical hydrolysis). Another indirect analysis method is the use of low-molecular-weight model compounds in "cross-linking" reactions, followed by analysis of the "cross-linked" model compounds.

Both the direct and indirect approach provide valuable insight in the different aspects of cross-linking chemistry and network structures, as will be explained below.

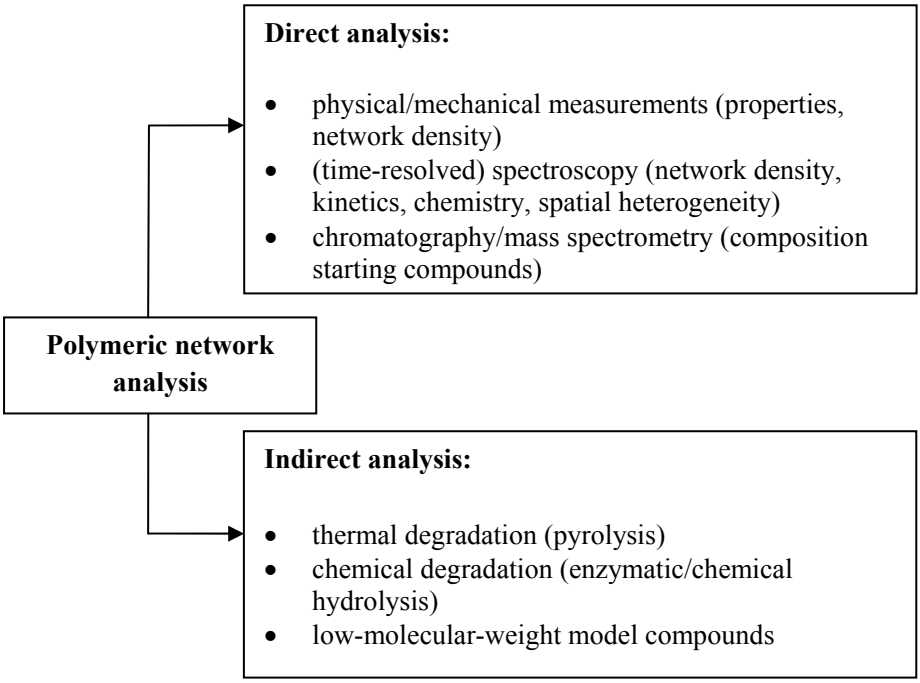

Fig. 1.7. Direct and indirect approaches for the analysis of cross-linked networks.

1.3.1. Direct approach

There are several main methodologies based on the direct approach to obtain insight in the network structure. These will be explained below.

1.3.1.1. Physical/mechanical measurements

Establishing the mechanical properties of cross-linked materials, such as the modulus, stress-strain behaviour, hardness, volume shrinkage, and glass-transition temperature (transition of solid to rubber phase, T_g), can be done by mechanical measurements. These provide information that is desirable for practical applications.
An important parameter to characterise the polymeric network is the network density, which is defined as the number-average molecular weight of polymers between cross-links (M_c) or as the mole fraction of monomeric units which are cross-links points [6]. The network density (M_c) can be determined using different approaches.

The first approach involves physical measurements, such as equilibrium swelling [12]. The swelling-behaviour theory describes the relation between the swelling and the number-average molecular weight between the cross-links (M_c). This theory is fairly complete for moderately cross-linked polymers in liquids [15]. However, the swelling of densely cross-linked polymers (M_c much less than 5000 *Da*) is very low. To apply this theory, the solubility parameters of the polymers must be known. These can be estimated by the group-contribution method of Hoftyzer and van Krevelen [16]. The low degree of swelling and the need to estimate the polymer-solubility parameter make the relation between the swelling and the M_c of densely cross-linked materials quite inaccurate.

An analogous approach to obtain insight in the network density is the determination of the gel content (insoluble fraction) in cross-linked polymers, which is a measure for the degree of cross-linking [17]. Since densely cross-linked polymers contain very low concentrations of soluble fractions, this approach is most often performed on low-density cross-linked polymers, such as cross-linked polyethylene [18].

The kinetic theory of rubber [19] relates the equilibrium elastic modulus at temperatures above T_g, which can be measured by dynamic mechanical analysis, to the density of cross-links, expressed as the number-average molecular weight of chains between chemical cross-links and chain entanglements (M_{c+e}) [20]. Although the kinetic theory of rubber is no longer valid in the case of very high degrees of cross-linking, the elastic moduli still appear to be nearly independent of the chemical structure of the network. Thus, even at a very high degree of cross-linking, the elastic moduli at high temperatures are still good empirical parameters for the characterisation of cross-linked polymers [21–25].

As stated before, cross-linking increases the glass-transition temperature (T_g) of a polymer [26]. A highly cross-linked polymer gives a very large shift in T_g and is sensitive to relatively small changes in M_c [27]. The shift of T_g depends also on the chemical composition of the polymer. This renders the relationship highly complex and only a rough estimation of M_c can be made. The M_c can be estimated more accurately with the use of empirical equations [28,29].

With the use of these traditional methods, the effect of cross-linking on the mechanical properties has been investigated for a broad range of cross-linked polymers (EPDM, acrylates, *etc*.). However, these methods are based on “ideal” networks in which no defects are present. Nowadays, a great deal of work is done to bring these relationships up to date, but it is accepted that these traditional methods are not capable of providing complete and reliable information on the network [30].

Analysis of the heat changes (exothermal) during cross-linking with both

isothermal and dynamic differential scanning calorimetry (DSC) provides insight in the cross-linking kinetics [31–35]. The analysis was based on the assumption that the exothermal processes monitored are caused by the curing reaction and that the heat generation is directly proportional to the rate of cure. This approach was followed for styrene cross-linked with di-vinyl-ester. From the DSC data, molar conversions and average sequence lengths were predicted [36]. The accuracy of these predicted parameters is, however, questionable. Decker and Moussa have demonstrated that thermal treatment can mobilise trapped radicals and giving rise to additional cross-link reactions [37]. Secondly, no additional analysis was performed to support the predicted average sequence lengths of the copolymeric styrene/di-vinyl-ester backbone.

1.3.1.2. Spectroscopic approaches

Another approach to obtain the network density (M_c) is the use of spectroscopic techniques. The molecular mobility of polymer chains can be determined by solid-state nuclear-magnetic resonance (s-NMR) relaxation methods [38,39], which provide quantitative information on the molecular weight between cross-link junctions (M_c) [40].
This approach was used to determine the chemical cross-link density of cured di-acrylates [41] and vulcanised blends [42] and the chemical and physical (temporary and trapped chain entanglements) cross-link density of cured EPDM [43]. Combinations of different s-NMR methods allow the contributions of the addition and combination cross-linking reactions to the total chemical cross-linking of EPDM [44]. However, the magnetic field applied along with inadequacies of the fitting model can lead to misinterpretations in the characterisation of the cross-link density [45].
Other spectroscopic techniques also have been used to measure the cross-link density of networks. Atomic-force microscopy (AFM), in the force modulation mode, has been used to determine the cross-link density of natural rubber [46], styrene-butadiene rubber [47] and EPDM [48], while X-ray microscopy was used for determining the network density of a super-absorbent polymer [49]. Transmission electron microscopy (TEM) was used for determining the cross-link density of vulcanised natural and nitrile/butadiene rubbers [50]. The network density in the mentioned studies is often specified depending on the way it has been determined, such as the optical density for X-ray microscopy measurements [49]. This makes it difficult to compare the different studies.
Besides the physical and mechanical properties and the network density, it is important to determine the cross-linking chemistry and/or the chemical

conversion, preferable in real-time. Time-resolved optical spectrometric techniques, such as infrared (IR) and Raman, are commonly used to monitor the consumption of reactive functionalities during polymerisation as a function of time [51,52]. The use of these real-time techniques provides insight in the chemical conversion during the cross-linking reaction and, thus, the resulting network structure. Various examples of spectroscopic techniques used for the (real-time) determination of the cross-linking chemistry and/or the chemical conversion have been described. The networks studied include EPDM [53,54], phenol-formaldehyde [55], acrylates [56–59] and vinyl-ester-styrene [60]. Local heating by the Raman laser can damage the surface of cross-linked materials and can lead to biased results [61]. When using optical spectroscopy, no distinction can be made between mono- and bi-functional acrylates, although some studies indicate that they have different reactivities [62,63].

The information obtained by these time-resolved techniques can be used to determine the rates of polymerisation. With this information, the number-average molecular weight distribution of the backbone, which is often denoted as the kinetic chain length (*kcl*) of the network, can be estimated [64–68]. Such an estimation involves several assumptions. Often mathematical models are described, which simulate the cross-linking processes and are used to predict network parameters, without any supporting measurements [69–72]. As a consequence, the calculated *kcl* is only an indicative value, which can be used to interpret general trends [64,73].

The use of real-time s-NMR methods has been described for the evolution of M_c during cross-linking of sulphur-cured natural rubber [74], sulphur vulcanisation of EPDM [75], and photo-curing of bi-functional acrylates [41]. Palmas *et al.* demonstrated the use of s-NMR (^{1}H-NMR and ^{13}C-NMR) for the study of "specific" structures (chemistry) resulting from aging (oxidation, chain scission) in cross-linked EPDM [76]. To increase the s-NMR sensitivity, ^{13}C-enriched polymers can be used to study the formed structures, as in the case of ^{13}C-enriched ENB-EPDM. This makes it possible to study the structure of the incorporated ENB in more detail [76]. In general, the interpretation of the NMR results depends entirely on the availability of model compounds and only average data for the polymer are obtained [9,43]. Moreover, s-NMR does not yield any detailed information on the network structure in terms of concentration and molecular weight distribution of network chains, such as the kinetic chain-length distribution, *kcl* [58,78].

Different other techniques have been described for the real-time analysis of cross-linked materials, such as real-time di-electric spectroscopy [79,80] and fluorescence spectroscopy [81].

In many cases, the cross-linking kinetic depends strongly on the radical concentration, which is not directly measured by the aforementioned techniques. Consequently, the environment and the structure of the radical species are also not available for analysis with these methods. Electron spin resonance (ESR) spectrometry is a powerful technique which monitors radical species [82] and gives valuable insight in the different processes during cross-linking of acrylates [83,84] and other radical cross-linking systems [85]. Especially, the combined use of ESR and infrared spectroscopy yielded comprehensive insights in the population of various radicals, such as propagation radicals, termination radicals, but also "trapped" and persistent radical populations during cross-linking of bi-functional acrylates [37,86].

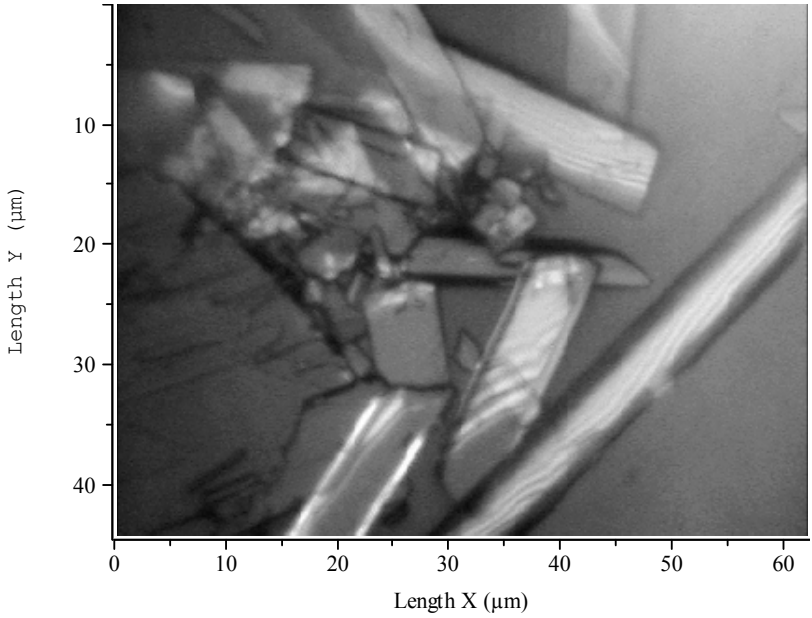

Fig. 1.8. Elongated particles of peroxide degradation products in cross-linked EPDM analysed by microscopy.

Hyphenation of real-time dynamic mechanical analysis and near-infrared spectroscopy allowed the simultaneous monitoring of acrylate photo-polymerisation with regard to both the chemical conversion and mechanical properties [51,87,88]. Steeman *et al.* showed that the modulus build-up did not linearly follow the chemical conversion, but the modulus increased greatly during the final stage of conversion [87]. Another example of hyphenation is the simultaneous analysis of the volume change (shrinkage) and the acrylate conversion [89,90].

Time-resolved techniques do not provide direct information on the network density and network structure, since reacted groups can form chemical cross-links, but also ineffective chains and other defects. Moreover, side reactions can cause additional cross-links, which complicate data interpretation.
Spectroscopic techniques can also be used for the determination of spatial heterogeneity of cross-linked systems [91]; s-NMR can give information regarding the molecular heterogeneity of different phases [92,93].
Surface techniques, such as light microscopy (see *Fig.* 1.8), AFM, scanning electron microscopy (SEM, after cryo-facing and ruthenium-staining), wide-angle X-ray diffraction (WAXD), small-angle X-ray scattering (SAXS), and electron spectroscopy (ESCA), can all give information on the surface composition, surface morphology, domain-size distribution, shape of the domains, and ligament thickness of cross-linked materials [94–99]. Other imaging techniques, such as Raman microscopy and secondary-ion mass spectrometry (SIMS) are also capable of collecting spatially resolved chemical images (chemical structure information) of the surface [100].

1.3.1.3. Analysis of the starting materials

Insight in the network structure can also be obtained by analysis of the starting compounds and prepolymers. Their characterisation (*e.g.* purity, structures, distributions of molecular weight, functionality, *etc.*) gives insight in the expected network structures, extractables, *etc.* and is often needed for a proper interpretation of the data obtained by the aforementioned techniques.
The chemistry of polymers, especially copolymers, is very complex, due to the molecular-weight distribution, but also to the many different types of chemical structures incorporated in the polymer. Depending on the molecular weight, different chromatographic techniques can be applied. The most commonly applied chromatographic technique is size-exclusion chromatography (SEC) for the determination of the molecular-weight distribution [101]. In the case of poly-electrolytes, aqueous SEC can be used to estimate the molecular-weight distribution [102,103]. The functionality-type distributions (FTD) of polymers can be obtained by liquid chromatography at critical-conditions (LCCC) [104–106]. Pasch *et al.* demonstrated the use of LCCC followed by matrix-assisted laser desorption ionisation time-of-flight mass spectrometry (MALDI-TOF-MS) for the characterisation of the molecular weight and functionality-type distributions of epoxy resins [107]. SEC coupled to more than one detector or a specific detector can also provide information on the average chemical composition as a function of molecular weight. Typical examples are SEC

coupled to UV and refractive-index detection [108], SEC-NMR [109], SEC-FT-IR [110,111], and SEC-MS [112], while two-dimensional separations can be used to unravel different distributions of a polymer. For example LCCC×SEC has been applied for block copolymers [113], tacticity separations [114] and complex grafted systems [115]. Valuable information (*e.g.* functionality-type distribution) on polymers can also be obtained by MALDI-TOF-MS directly [116,117]. However, the quantitative aspects are questionable [118].
Field-desorption mass-spectrometry (FD-MS) has been used to determine the molecular weight and structure of oligomers in a polymer mixture [119]. Another example is the uses of interaction chromatography that allows polymers to be separated into different oligomers. Although this approach is limited to low-molecular-weight samples (oligomers), it can give highly detailed information [120,121].
Structural characterisation of the polymers can be performed by NMR, which yields information on the polymer composition, such as the concentration of diene incorporated in EPDM [122], ethylene/propylene copolymers sequence information [123], and fully quantitative structural characterisation in the case of phenol-formaldehyde resins [124,125]. Another example is the use of ^{13}C-enriched polymers, to study the grafts in polyolefins functionalised with maleic anhydride [126]. Zhang *et al.* demonstrated the use of ^{1}H-NMR for the determination of different maleic anhydride structures on polyethylene and found indications of chain scission reactions [127]. Characterisation of the composition can also be performed by different optical techniques, such as IR and Raman. Besides chromatographic and spectroscopic techniques, differential scanning calorimetry or dynamic mechanical analysis can be used to determine physical and mechanical properties of polymers (*e.g.* T_g) prior to cross-linking.

1.3.2. Indirect approach

Soluble (non-cross-linked) polymers are widely characterised through chromatographic and spectroscopic techniques, such as SEC and NMR, as described above. However, cross-linked polymers pose problems, since they are inherently insoluble. This limits the applicability of chromatographic and spectroscopic techniques. Chemical or thermal degradation are often used as methods for the structural analysis of these non-soluble (cross-linked) polymers. Both techniques are used to reduce the molecular weight of the polymers, forming monomers or other “small” soluble degradation products. These traditional methods of degradation are followed by chromatographic and/or spectroscopic analysis. Besides degradation of polymeric networks, low-

molecular-weight model compounds can be used to mimic cross-linking reactions, followed by chromatographic and/or spectroscopic analysis of the "cross-linked" model compounds.

1.3.2.1. Pyrolysis

Degradation of the cross-linked materials can be performed by pyrolysis, which is the "controlled" thermal degradation of a complex material in an inert atmosphere or vacuum (absence of air). It causes molecules to cleave at their weakest points to produce smaller fragments, the collection of which is called pyrolysate [128].
Pyrolysis (Pyr) followed by analysis of the degradation products can be either performed directly by mass-spectrometry (Pyr-MS) or by separation of the degradation products with gas chromatography, followed by mass-spectrometric detection (Pyr-GC-MS) [129]. A classic example of Pyr-GC-MS is the determination of the composition of ethylene/propylene copolymer [130–132]. Pyr-GC-MS of EPDM cured with sulphur showed several compounds, such as C_7H_6S, which has been supposed to be formed from the addition of sulphur bridges to 5-ethylidene-2-norbornene residue in the polymer chain through cyclisation. Based on these observations the mechanisms of the sulphur-less vulcanization of EPDM rubber has been discussed [133,134]. Cross-linked natural rubber devulcanised uniformly by cleavage of the S-S bond, while peroxide cross-linked EPDM showed frequent chain scission of the C-C backbone [135]. In case of peroxide cross-linked EPDM the main products in the pyrolysate are branched and linear alkanes and alkenes arising from intramolecular H-transfer accompanied by unzipping (radical chain scission of the ethylene/propylene backbone)[136,137]. Random chain cleavages followed by intermolecular H-abstraction reactions yield a series of *n*-alkanes, α-alkenes, 2-methyl-alkenes, 2,4-dimethyl-alkanes, and even higher branched alkenes, as well as degradation products from the dienes and the peroxide (see *Fig.* 1.9). Besides these degradation products, "unexpected" compounds, such as benzene and toluene are observed, as a result of rearrangement reactions upon pyrolysis. The decomposition products can be interpreted in terms of composition (ethylene/propylene ratio, diene concentration) and ethylene/propylene sequence distribution [138]. However, more-detailed information on the cross-linked structures formed in terms of addition and combination cross-linked structures in the case of EPDM cannot be obtained. Pyrolysis studies on cross-linked rubbers are therefore mostly performed to obtain insight in the application range of cross-linked materials, such as thermal recycling of EPDM [139].

The number average sequence length in a copolymeric (cross-linked) backbone chain is an important parameter in the copolymer microstructure characterisation of a polymeric network. The determination of the number-average sequence length of EPDM [139] by Pyr-GC-MS is one of the few examples of the copolymer microstructure characterisation of a polymeric network. Wang *et al.* [140] described the number-average sequence length determination by Pyr-GC-MS of various non-cross-linked copolymers: styrene-butyl acrylate, chlorinated polyethylene, styrene-methyl methacrylate copolymer, vinyl-chloride-vinylidene chloride and styrene-maleic anhydride copolymer. However, no supporting data has been given that the monomer arrangement as determined by Pyr-GC-MS is similar as that determined by *e.g.* NMR. Moreover, the authors suggested that the number-average sequence length will suffer a relative large error using Pyr-GC.

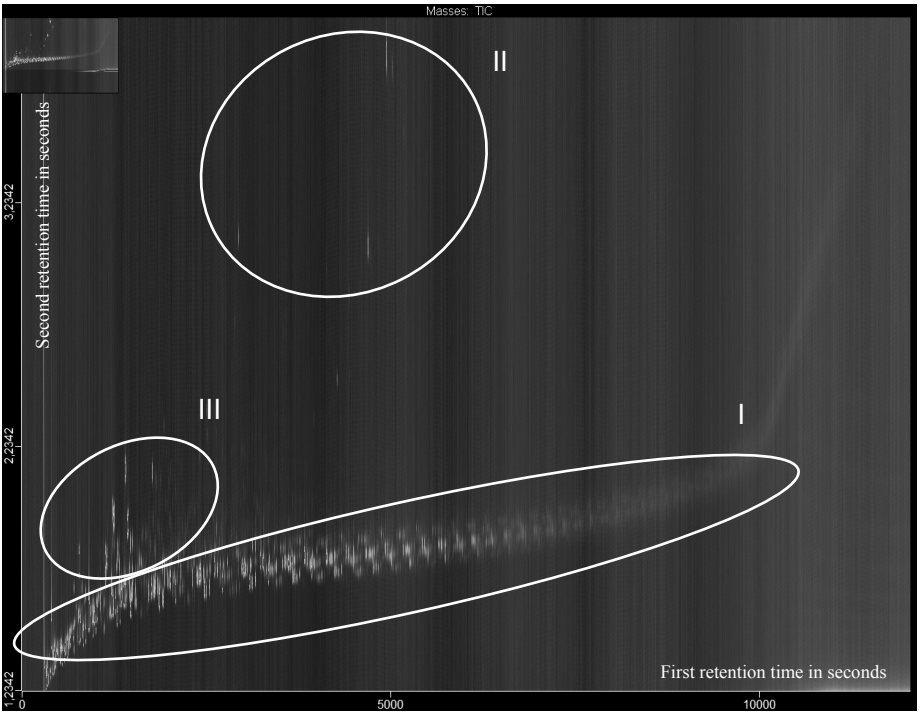

Fig. 1.9. Pyr-GC×GC-MS chromatogram of peroxide cross-linked ENB-EPDM with branched, linear alkanes and alkenes (I), peroxide decomposition products (II) and diene degradation products (III), as a result of pyrolysis.

The characterisation of an UV-cured acrylate network structure in terms of chain-length distribution of network junctions by Pyr-GC-MS has been

described by Matsubara *et al.* [141,142]. Thermo-chemolysis, in the presence of tetramethyl-ammonium hydroxide, shows "quantitative" cleavage of the ester-linkage and limited pyrolytic cleavage of C-C and C-O bonds. The authors suggested that the chain-length distribution of the repeating acryloyl groups could be determined from their results. However, the low recovery of acrylate polymer in GC due to their low volatility and the possible C-C cleavage make the determination of the *kcl* in the UV-cured resin unreliable.
Only volatile degradation products of a relatively low molecular weight can be analysed with Pyr-GC-MS, which makes this techniques not applicable for oligomeric pyrolysis degradation products. Liquid chromatography instead of gas chromatography can be used for the analysis of such oligomeric compounds, to obtain more information about the structural composition. This has been demonstrated by van der Hage *et al.*, who used pyrolysis, coupled to LC-MS for the analysis of collagen-based materials [143]. Another approach to determine oligomers of *e.g.* polyurethanes is the use of off-line pyrolysis followed by MALDI-TOF-MS [144] or the use of SIMS to "pyrolyse" the surface (top monolayer) of various cross-linked polymers, such as EPDM [145].
Besides the use of pyrolysis for the determination of structure, pyrolysis can also provide information regarding the thermal stability of cross-linked polymers. Kurdikar *et al.* [146] determined the thermal stability of highly cross-linked acrylate polymers and revealed that highly cross-linked acrylates have a better thermal stability than loosely cross-linked acrylates. However, they suggest that spatial heterogeneity causes the thermal instability, however, it seems more logical that the concentration of network junctions plays an important role with respect to thermal stability. Another example of TGA is an study of the thermal stability of collagen, with the use of lignin model compounds [147].

1.3.2.2. Chemical degradation

The chemical degradation of polymers can be performed by acid or base hydrolysis or by other specific reactions of the ester- or amide-group. Chemical degradation is limited to cross-linked polymers which have a hydrolysable group. As a consequence, rubbers (*e.g.* EPDM) cannot be hydrolysed.
Different chemical degradation methods for polymers are published over the years. The polymers are mostly acid hydrolysed with subsequent separation of the reaction products by gas chromatography [148,149]. The Zeisel-reaction (cleavage of acrylate ester-linkage of non-cross-linked polymers by hydrolysis with hydriodic acid) has also been applied to acrylate resins [150] and for acrylic polyesters [151]. The individual alkyl-halides were separated using gas

chromatography. Publications of chemical degradation of non-cross-linked polymers include acid hydrolysis of polyurethanes [151], polyethers [152], polysiloxanes [153] and polyamides [154].

In general, hydrolysis of esters to a carboxylic acid is promoted by bases, acids and temperature [155]. Acid hydrolysis is reversible and follows a reaction mechanism similar to base hydrolysis, which is irreversible. Besides the disadvantages of the reversible reaction, acids can cleave the ether-linkage, while the ether-linkage is quite stable toward bases and reducing agents. Conclusions about the network structure can be drawn from the nature and concentration of the hydrolysis products. A typical example of the added value is the characterisation of the final chemical structure of the styrene/vinyl-ester networks using hydrolysis as a sample preparation method. Funke *et al.* [156] carried out extensive studies on the chemical degradation of styrene/vinyl-ester networks; the network has been hydrolysed and the hydrolysis products have been made soluble by esterification/methylation with diazomethane. The derivatised degradation products have been analysed by several techniques such as osmometry, viscometry [157,158], and IR [158] and NMR [159-161] spectroscopy. ^{13}C-NMR analysis of the dervatised hydrolysis products revealed a pattern of resonance due to the quaternary carbon atoms of the styrene group, which originated from the different type of sequences in the styrene/vinyl-ester enchainment [162]. These peaks can be used for the determination of the monomer distribution and, thus, the mean styrene sequence length in the copolymer. This has also been shown by several liquid-state NMR [163-165] and s-NMR spectroscopy studies [166-169] on copolymers of styrene with different unsaturated and/or vinyl-ester oligomers. The monomer distribution of the backbone chains is usually determined after hydrolysis of the network followed by derivatisation of the formed hydrolysis products with diazomethane [160,161].

Another example of the use of chemical degradation is the determination of the kinetic chain length (*kcl*) in highly cross-linked acrylate networks. Polyacrylic acid (PAA) or polymethacrylic acid (PMAA) is one of the (biodegradation) products after hydrolysis of cross-linked (meth)acrylates. Both the *kcl* and the endgroups are of great interest; PAA and PMAA with a high molecular weight (5-200 *kDa*) can be accumulated in the body's circulatory system [73,170–172]. The hydrophilic PAA chains can be characterised by different techniques, such as MALDI-TOF-MS, NMR and SEC. The PAA molecular weight distributions, after hydrolysis of similar acrylate networks, found by SEC contradict to MALDI-TOF-MS and ^{1}H-NMR results [65]. These observations, own experiences and other studies indicates that MALDI-TOF-MS can only be used

for very low molecular weight PAA (<<5 *kDa*) [173].

1.3.2.3. Model compounds

Cross-linking can be studied indirectly by analysing "cross-linked" low-molecular-weight model compounds. Because of their low-molecular-weight, the corresponding model cross-links are soluble, which allows chromatographic and spectrometric analysis. The added value of this approach has been demonstrated by several cross-linking studies with model compounds, which led to elucidation of the mechanisms of accelerated sulphur vulcanisation of natural [174,175] and synthetic rubbers [176]. These studies resulted in an extended sulphur vulcanisation scheme. Van Drumpt and Oosterwijk [177] used model compounds to obtain kinetic data and insight into the peroxide cross-linking mechanism of polyethylene (PE). Although the study has been performed on PE, the results provide valuable insight on EP(D)M cross-linking. Camara *et al.* used electron spin resonance (ESR) spectroscopy to study the cross-linking of (branched) alkanes [178] in terms of radical selectivity and rate constants for H-abstraction. Similar studies with model compounds have been performed on esters as model compound for lubricants [179] and on saccharides as model compound for biomolecules [180]. Low-molecular-weight model compounds have also been used to study the effect of the type and amount of the third monomer on the peroxide-curing efficiency of EPDM [181]. Since model compounds only mimic the cross-linked polymer system, the results of the model compound studies should be translated carefully to real network systems.

1.4. Scope of the thesis

As discussed above it is essential to understand the network topology, which determines the final functional properties of the polymer. This thesis deals with the analysis of the chemical network structure of peroxide cross-linked rubber networks and chemically cross-linked di-acrylate systems, using an indirect approach. Different indirect approaches and analytical techniques are described to obtain insight in the chemical network structures of these cross-linked systems.

In chapter 2, the analysis of the network structure of UV-cured mixtures of polyethylene glycol di-acrylate and 2-ethylhexyl acrylate is described. The cross-linked films are analysed, after hydrolysis, by aqueous-SEC on-line

coupled to reversed-phase liquid-chromatography. The chemical network structure for the different UV-cured acrylate polymers is obtained and is expressed in network parameters such as the degree of cross-linking and the network density, expressed as the molar concentration of effective network chains between cross-links per volume of polymer. The network density, expressed as the number-average molecular weight of polymers between cross-links, is similar to that found by s-NMR and mechanical analysis.

An integrated approach, involving the use of different analytical techniques to study the chemical network structure of cross-linked styrene/di-methacrylate polymers, is discussed in chapter 3. The cross-linked materials are hydrolysed at optimised conditions and without additional sample preparation subsequently analysed by both SEC and NMR analysis. Detailed insight into the chemical network structure is obtained by combining the results of all the different analyses used.

Chapter 4 focuses on the complex degradation processes of chemically cross-linked poly-(*D,L*-lactide-*co*-glycolide 50/50)-di-acrylate film. Liquid-chromatographic analyses are employed to identify and quantify the various oligomeric and polymeric degradation products from the soluble fraction, which gives detailed insight into the chemical changes at the different stages of degradation; extraction, network attack, network penetration, bulk degradation, and finally release of persistent network fragments.

The study of the network structure of peroxide cross-linked rubbers (EPDM) is described in chapter 5 and 6. The peroxide cross-linking of EPDM is mimicked using low-molecular-weight compounds. Both GC-MS and comprehensive two-dimensional GC–MS (GC×GC–MS) analyses have been employed to analyse the isomeric reaction products. The MS-fragmentation patterns and the GC-elution pattern are investigated in detail. This study with model compounds has led to a more accurate description of the peroxide cross-linking scheme of EPDM and valuable insight in the cross-linking mechanism (H-abstraction reactivities, steric hindrance, *etc*.).

Chapter 7 focuses on the thermal degradation of UV-cured mixtures of polyethylene glycol di-acrylate and 2-ethylhexyl acrylate. The use of pyrolysis for cross-linked acrylates was reviewed. The cross-linked acrylates are analysed by Pyr-MS, MALDI-TOF-MS and pyrolysis-LC-MS. The degradation products are studied in detail and are related to the overall network structure.

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