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Real-Time NMR. How Fast Can We Do It?

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Summary: Network structure development during cross-linking photopolymerization of polyethylene glycol di-acrylate and its mixture with a mono-functional 2-ethyl-hexyl acrylate was studied using real-time proton NMR T_2 relaxation analysis. The time resolution of the method is typically in the order of seconds. The results reveal largely heterogeneous origin of network build up at the intermediate stages of photocuring. Domains of nano-gel are already formed on initial stages of UV-curing where hardly any change in viscosity is observed. Upon increasing curing time the fraction of gel increases at the expence of sol, the molar mass of network chains decreases and the molar mass of sol increases. The presence of mono-acrylate slows down the curing rate. The curing continues after UV-illumination causing a significant increase in the amount of gel and cross-link density in the gel. Thus, the NMR method is a valuable tool for characterization of the kinetics of photopolymerization, the development of molecular structure and the resultant molecular scale heterogeneity during photocuring.

Keywords: coatings; cross-linking photopolymerization; dark curing; nanoheterogeneity; networks; proton NMR relaxation

Introduction

The photopolymerisation of multifunctional monomers and oligomers is becoming increasingly important not only in coatings but also adhesives and photofabrication of 3-D objects–stereo lithography. This technology offers several advantages, including cure speed, reduced emission (solvent free), low temperature during polymerization and easy to apply. Understanding of photopolymerization and cross-linking kinetics is desired in order to understand how polymerisation and the evolving network structure lead to the required mechanical properties. However, despite numerous studies, the mechanism of photopolymerization is not yet well understood because of its complexity.[1] The type of monomers, photoinitiators and curing conditions largely affect the mechanism of radical reactions and the kinetics of curing. Moreover, a change in molecular mobility during radiation curing largely affects the kinetics of photopolymerization, especially when the resulting material approaches its vitrification temperature. All these phenomena can largely affect the molecular structure of resulting cured materials and its mechanical properties.

Cross-linking photopolymerization (photocuring) of multifunctional monomers and oligomers has been widely studied from the perspective of chemical kinetics via calorimetry[1] and time resolved infrared and near infrared spectroscopy.[2,3] These methods allow determining the chemical conversion of the reactive groups, which can be related to volume average network density of cured material. However, no exact quantitative information on the network structure can be obtained with these methods, since reacted groups can form not only chemical cross-links but also viscoelastically ineffective chains, such as chain branches and chain loops. Furthermore, side reactions, which easily can cause additional cross-links, complicate data

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interpretation due to overlapping of signals from different types of chemical groups in complex mixtures. Moreover, physical network junctions are hardly detected by spectroscopic methods.

The development of mechanical properties upon photocuring is another method that was used for studies of photocuring kinetics.[4–6] This method relies on interpretation of volume average macroscopic properties with a number of assumptions and, therefore, does not provide information about network topology at intermediate conversion of reaction groups.[7] Network structure development during photocuring has received little attention mainly because of a lack of techniques that allow to zoom on nano-scale topology on polymer networks.

NMR T_2 Relaxation Method for Network Structure Analysis

One of the most informative and sensitive methods for network structure analysis is solid state NMR.[8,9] It is well established that NMR transverse magnetization relaxation (T_2 relaxation) is very sensitive to even small differences in the cross-link density, because this relaxation time for rubbery materials is largely governed by constraints on large spatial-scale chain mobility imposed by chemical and physical cross-links. Since chain motion is strongly coupled to elastomer structure, chemical information can be obtained. A comparison of the cross-link density, as measured by T_2 relaxation experiments, with that obtained by traditional methods for the same samples proves that the NMR method provides quantitative data on the cross-link density.[8] In addition to the mean cross-link density, the analysis of T_2 relaxation can provide information on network defects and heterogeneous distribution of network junctions.[9] The sensitivity of the T_2 experiments to the molecular scale heterogeneity of networks is due to the local origin of the relaxation process, which is predominantly governed by the near-neighbor environment and intrachain effects for T_2 relaxation at temperatures well above the T_g. Therefore, the *submolecules* concept can be used to describe the relaxation behaviour. In a simplified picture, the total T_2 relaxation decay for a heterogeneous elastomer is a weighted sum of decays from the different submolecules which are defined as network chains between the chemical and the physical junctions, chain loops and chain-end blocks. These submolecules possess different relaxation behavior due to differences in the large spatial scale mobility. The relative contribution of the submolecules to the total proton T_2 relaxation decay is proportional to the number of protons, which are attached to these chain fragments. A quantitative analysis of the decay shape is not always straightforward due to the complex origin of the relaxation function itself and the structural heterogeneity of the long chain molecules. Nevertheless, several examples of the detection of structural heterogeneity by T_2 experiments have been published, for example the analysis of the gel/sol content in cured and filled elastomers, the estimation of the fraction of chain-end blocks in linear and network elastomers, and the determination of a distribution function for the molecular mass of network chains in cross-linked elastomers. It has been demonstrated that the NMR T_2 relaxation measurements can also be used for the real-time study of cross-linking kinetics.[9]

Experimental

Materials

Polyethylene glycol *di*-acrylate with $M_n = 700$ g/mol (PEG700DA) and its mixture with a mono-functional 2-ethylhexyl acrylate (EHA) (70:30 w/w%; the molar ratio 1 : 1.2). 1 mass % of photoinitiator 1-hydroxycyclohexyl phenyl ketone (HCPK) was added as photoinitiator.

Equipment for Photocuring

An UV-light source: A Macam UV cure flexicure lamp fitted with a 400W medium pressure Hg halide lamp. The energy at the sample position was 1.1 mW/cm^2 (Figure 1).

Figure 1.
Picture of real-time NMR equipment. NMR tube with inserted UV-light guide and with the monomer coated disc at the bottom is magnified of the right side of the figure.

Solid State NMR Experiments

The Carr-Purcell-Meiboom-Gill pulse sequence with a Bruker Minispec NMS-120 spectrometer operating at a proton resonance frequency of 20 MHz. (Figure 1). The decays of the transverse magnetisation relaxation (T_2 decays) were analysed with a single exponential function for uncured materials and with a linear combination of two exponential functions coatings at different stages of curing.

Photocuring

A auarz disc of 15 mm diameter was covered with 0.1 mm layer of the monomers using a coating bar. Sample temperature was 40 °C. Oxygen was removed by flushing of the NMR tube with a flow of dry nitrogen.

Results and Discussion

Proton NMRT_2 experiment synchronized with an UV-light source is used for the analysis of the growth of the network structure during of UV-curing of PEG700DA and its mixture with EHA (70:30 w/w%). The sampling rate of the data points was determined by the rate of the spin-lattice relaxation (T_1) and equals 0.4 sec ($4 \times T_1$).

A single exponential T_2 relaxation is observed for the uncured compounds (Figure 2). A second relaxation component with a significantly shorter decay time (T_2^s) appears shortly after switching on the UV-light (Figures 2–4). This component is

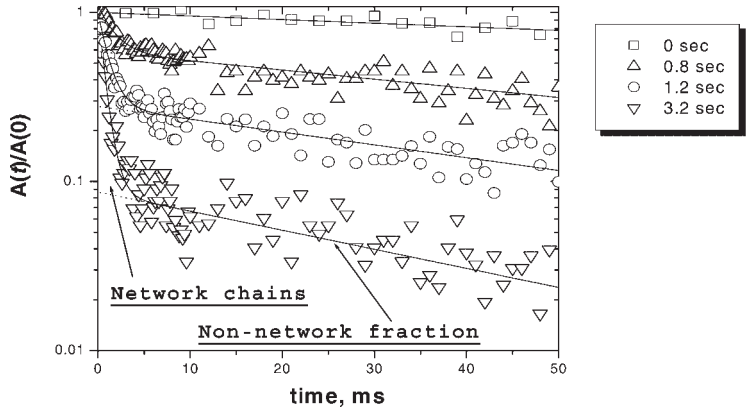

Figure 2.
The decay of the transverse magnetization relaxation (T_2 decay) for uncured PEG700DA and partially cured sample at different curing times.

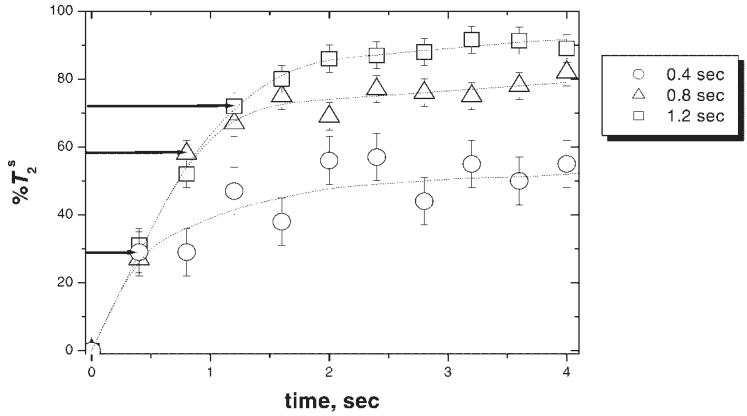

Figure 3.
The amount of nano/micro-gel as a function of curing time, as determined by the fraction of T_2^s relaxation component (%T_2^s) for PEG700DA. Arrows denote duration of UV-light irradiation that is also given on Figure insert.

assigned to the relaxation of *network chains*, i.e. acrylic chains attached to both chain ends to tri-branching points (*cross-link junctions*) (Figure 5). These network chains are the precursor of the *microgel* and ultimately the '*macrogel*' that is formed at a latter stage of photocuring by coalescing of growing nanogel particles. Nano-gel is already formed on initial stages of UV-curing where hardly any change in viscosity is observed, as was shown by real-time rheological studies of UV-curing of acrylates.[6] The component with long decay time (T_2^1) corresponds to the relaxation of non-network fraction and unreacted oligomers. The distinction between a non-network ('*sol*' and *network defects*) fraction and network chains is made in this study on the basis of the distinct differences in molecular mobility, as reflected by the T_2 relaxation behaviour.

Fast increase in the amount of nano-gel is observed in the initial stage of UV-curing, when hardly any change in viscosity is

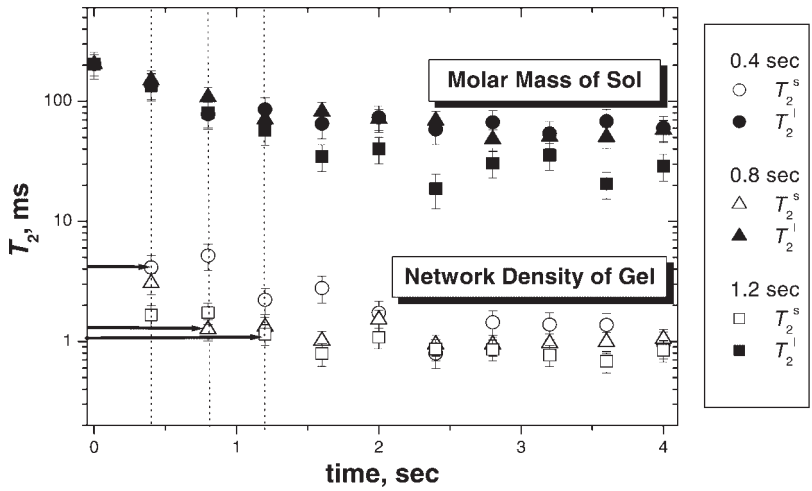

Figure 4.
Proton T_2 relaxation time for sol fraction (T_2^1) and nano/micro- gel (T_2^s) as a function of curing time for PEG700DA. Arrows and dotted lines denote duration of UV-light irradiation that is also given on Figure insert.

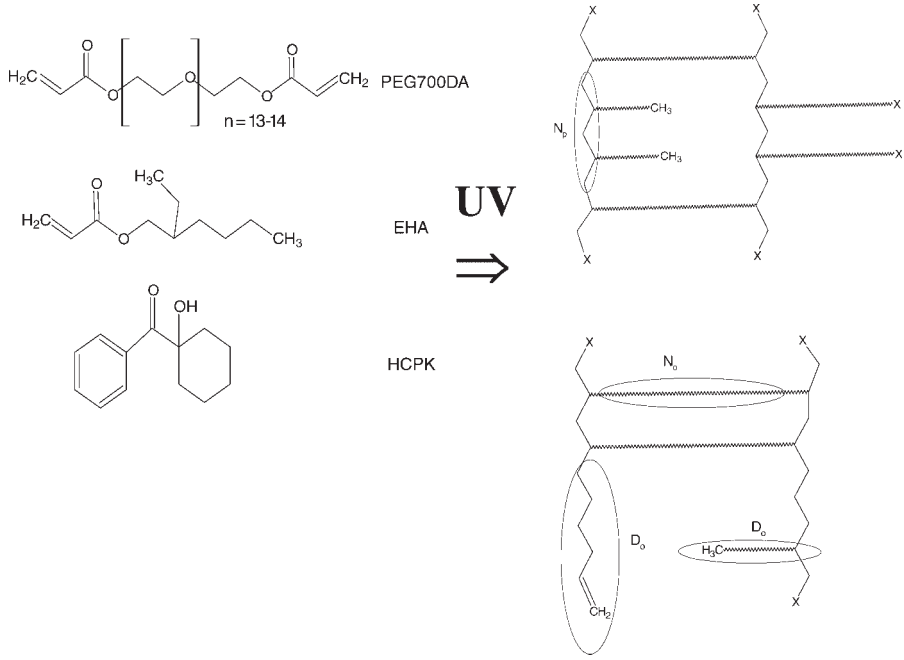

Figure 5.
The chemical structure of initial composition that is used in this study and schematical drawing of network structure at intermediate stages of UV-curing of a mixture of mono- and di-acrylates. Do–*network defects*: dangling chain ends, linear, branched and comb-like molecules; Np–*network chains from polymerisation*; No–*network chains from oligomer*; X–*cross-link points*. As expected, photocuring continues in the dark via chain propagation and chain transfer mechanisms until the reaction is terminated by radical recombination and trapping (Figures 3, 4).

observed at curing of acrylates.[6] The fraction of gel increases at the expense of the sol fraction with increasing curing time. The rate of increase in gel content slows down with the reaction time (Figure 3). This is attributed to the increasing influence of the diffusion-controlled limit of the photocuring with degree of the conversion.

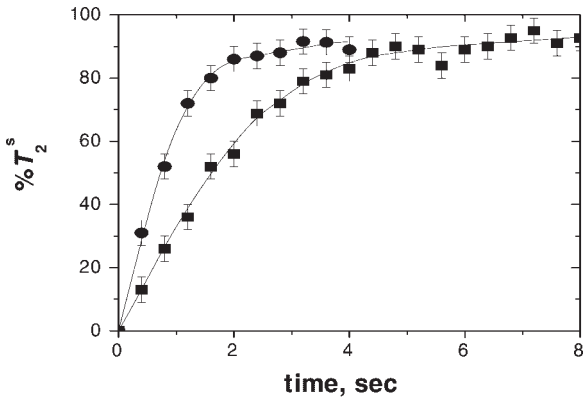

Figure 6.
The amount of nano/micro-gel as a function of curing time for PEG700DA (circles) and for the mixture of PEG700DA and EHA (squares), as determined by the fraction of T_2^s relaxation component.

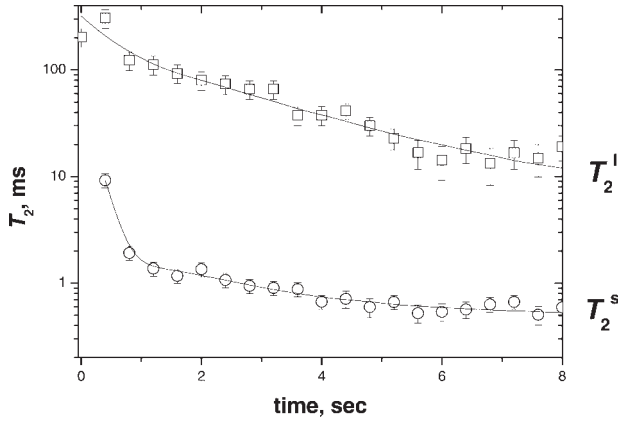

Figure 7.
Proton T_2 relaxation time for sol fraction (T_2^l) and nano/micro- gel (T_2^s) as a function of curing time for mixture of PEG700DA and EHA (70 : 30 w/w%).

The T_2 relaxation time for the gel and sol fractions differs more than one order of magnitude, which allows separate characterization of gel and sol fraction at different curing times. A change in the T_2 relaxation time for network chains and non-network material (Figure 4) allows one to follow a relative change in average molar mass of network chains and the sol fraction as a function of UV exposure. The T_2^s relaxation time decreases by a factor of 3–4, which corresponds to a decrease in the molar mass of network chains, as was shown previously.[7] Since T_2 for linear and branched polymers decreases with increasing the molar mass,[10] a significant decrease in T_2^1 upon curing corresponds to an increase in the molar mass of the sol fraction and network defects.

The presence of the monoacrylate slows down the curing rate, as can be seen from results in Figures 6, 7.

Conclusions

Real-time NMR T_2 relaxation experiment allows one to follow the network structure development during photocuring. The time resolution of this method is typically in the order of seconds. Thus, it is applicable in photocuring applications that occur over multiple seconds, i.e. dental cements, ophthalmic hydrogels (contact lenses), medical coatings, etc. It appears that this method lends itself to characterization of the kinetics of photopolymerization, the development of molecular structure and the resultant molecular scale heterogeneity during photocuring.

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