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Interrelations between mechanism, kinetics, and rheology in an isothermal cross-linking chain-growth copolymerisation

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Abstract

The free radical chain-growth cross-linking copolymerisation of an unsaturated polyester resin with styrene is investigated in isothermal conditions using different techniques. By modulated temperature differential scanning calorimetry (MTDSC) the rate of polymerisation is observed simultaneously with the (partial) vitrification of the reacting material. An important autoacceleration closely before vitrification corresponds to an accelerating styrene consumption. The autoacceleration occurs long after the gelation of the material, which implies that termination reactions involving small radicals are still important at an advanced conversion. The deceleration of these termination reactions causes the autoacceleration, which is stopped when the propagation reaction slows down due to vitrification. MTDSC proves to be very suitable for studying the interrelations between vitrification and the polymerisation kinetics.

Keywords: Modulated temperature differential scanning calorimetry; Raman spectrometry; Thermoset cure

1. Introduction

The copolymerisation of unsaturated polyester or vinyl ester resins with styrene is a typical cross-linking reaction accompanied by a *Norrish–Trommsdorff* or *gel effect* [1,2]. This gel effect is generally known for the free radical chain-growth polymerisation of certain monomers at an intermediate-to-high conversion as a dramatic increase in the rate of polymerisation, often accompanied by a marked rise in temperature [3–6]. It is well understood in general terms of a diffusion-controlled termination of propagating radicals due to a decrease in mobility of the growing chains, but the detailed mechanism is still a matter of discussion [3]. The importance of the chain-length dependence of the rate coefficients for termination of the propagating radicals was recognised, and a short–long termination concept was introduced [7–11]. According to this concept, the termination reaction would be dominated by shorter chains terminating with longer chains, and this particularly at higher conversion, where the longer chains might become immobile due to e.g. entanglement [3]. The gel effect would then be caused by a depletion of short chains in the system [3].

The gel effect should not be confused with *chemical gelation* [12], which occurs when for the first time covalent bonds connect across the whole volume of the curing material and a macroscopic network is formed [13–16]. Thus, chemical gelation is purely related to network formation and occurs in both step-growth and free radical chain-growth *cross-linking* systems, but by definition not in *linear* polymerisations. In contrast, the gel effect is a typical characteristic of free radical polymerisations and occurs in both linear and cross-linking polymerisations. As a matter of fact, it was first observed and mostly studied for linear systems. At the gelation of cross-linking systems, as a result of the network formation, the steady state shear viscosity tends towards infinity and the resin stops flowing. Nevertheless, unreacted material is still present inside this network, and the overall polymer concentration and the microscopic viscosity can still be very low [12].

In models describing the reaction kinetics for the cross-linking copolymerisation of unsaturated polyester or vinyl ester resins with styrene, the gel effect is seldom included. As a matter of fact, the termination reactions are often neglected [17–21] and the system is treated as if the gel effect is present from the start. One reason for this approach is that in cross-linking polymerisations, a fraction of the propagating radicals is attached to the (growing) network. These *network radicals* are unable to undergo translational diffusion [12], and they will only terminate by *segmental*

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diffusion [22,23] or *reaction diffusion* [24]. Therefore, if upon gelation most active radicals become attached to the growing network, the bimolecular termination rate constant would decrease, and the polymerisation would accelerate. An acceleration as a consequence of network formation (gelation) was e.g. mentioned for a graft copolymerisation in which the active radicals are attached to preformed polymer chains [12]. However, only if termination reactions involving small radicals are negligible, the (overall) termination reaction would be *significantly reduced* upon gelation [19]. In the peroxide-initiated polymerisation of unsaturated polyester with styrene, continuously new (unattached) primary radicals are generated. These small radicals are less influenced by diffusion restrictions [7–9] and they can continue to participate in bimolecular termination reactions long after the gelation of the network.

Diffusion control is not limited to termination reactions only. Upon *vitrification*, when the increasing glass transition temperature reaches the reaction temperature and the material evolves from a rubbery or liquid state to a glassy state [25], the rate of propagation can become diffusion-controlled. In isothermal conditions, the polymerisation may virtually cease, limiting the conversion that can be reached isothermally [20,25].

One of the main problems of accurate measurement of the autoacceleration of the polymerisation is the difficulty of maintaining isothermal conditions in bulky samples during the accelerating heat release. In a recent review, O'Neil and Torkelson [3] point out that isothermal differential scanning calorimetry (DSC) measurements might be advantageous to achieve truly isothermal conditions in bulky samples.

In this work, modulated temperature differential scanning calorimetry (MTDSC) [26–28] was used to study the interrelation between the polymerisation and the rheological changes for the cross-linking of an unsaturated polyester resin with styrene. For studying polymerisation kinetics, a major advantage of MTDSC over conventional DSC techniques is that the heat capacity is measured simultaneously with the (average) heat flow, in both (quasi-) isothermal and non-isothermal conditions. Thus, the vitrification of a polymerising system, can be followed quantitatively in the heat capacity signal, while simultaneously the rate of polymerisation is quantitatively obtained from the heat flow signal [29–33]. In a DSC experiment, vitrification is only observed indirectly, as a decrease in the rate of polymerisation. The phenomenon can be studied by performing partial cure experiments followed by a non-isothermal measurement of the glass transition temperature [34]. Vitrification can be observed in other techniques, e.g. by following the change of mechanical [25,35] or dielectric properties [36]. However, in this case, the conversion or rate of polymerisation is not directly available.

Fourier transform (FT) Raman spectrometry and dynamic rheometry were employed in this work to obtain complementary information. By FT-infrared (IR) spectrometry, the copolymerisation kinetics of the unsaturated polyester with styrene can be studied [17,18,37,38]. FT-Raman spectrometry offers a high specificity in detecting different functional groups and has a better sensitivity than FT-IR spectrometry for the cross-linking of unsaturated C=C bonds [39]. In literature, the rheological changes during cure have been studied by combining rheological measurements with DSC [40–45]. Chemical gelation was experimentally determined by e.g. steady and small angle oscillating shear flow viscometry (also called dynamic rheometry) [13–16,46–49]. For unsaturated polyester resins, gelation was always observed at the very beginning of the curing reaction, usually at a conversion lower than 5% [17,18,45,50–54].

In this paper, the relative positions of the phenomena on the cure path are discussed for isothermal cure experiments in a relatively small temperature range. The influence of the styrene content on the chemorheological evolution and on the diffusion-controlled copolymerisation kinetics will be discussed in a forthcoming paper [55].

2. Experimental

2.1. Materials

The system under investigation is a commercial unsaturated polyester resin (Polylite 51383, Reichhold) containing 45% by weight of styrene. The polyester prepolymer is made of fumaric acid, maleic acid, tetrahydrophthalic acid, neopentylene glycol, and diethylene glycol. The number average molecular weight equals 1850 g mol^{-1} (by GPC). The molar ratio of styrene versus polyester vinylene bonds equals 4.1:1 (by ^{1}H NMR and ^{13}C NMR). The average number of vinylene bonds per polyester prepolymer chain is 3.5. A small amount of inhibitor is present in the resin. An additional weight fraction of 200 ppm inhibitor (2-methylhydrochinon, DSM) was added for delaying the reaction during sample handling. The resin was cured with a peroxide initiator (36% methyl ethyl ketone peroxide in dimethyl phthalate, Butanox M60, AKZO) and a cobalt octoate accelerator (cobalt 2-ethylhexanoate, 1% cobalt in styrene, NL49S, AKZO) in a ratio of 100:2:1 by weight. The commercial peroxide contains a dimer and a monomer of methyl ethyl ketone peroxide, as well as hydrogen peroxide. The glass transition temperature of the fully cured material is 30 ± 5°C and the transition is circa 50°C wide.

2.2. Procedures

Modulated temperature DSC. The cure reaction was studied using a *TA Instruments* DSC 2920 with MDSC™ option. Hermetic aluminium pans were used. The modulation amplitude was 0.5°C, the period 60 s. The overall, calorimetric conversion x and rate of conversion dx/dt are calculated as:

$$x = \frac{\Delta H_\mathrm{p}}{\Delta H_\mathrm{tot}} = \frac{1}{\Delta H_\mathrm{tot}} \int_0^t (\mathrm{d}q/\mathrm{d}t)\,\mathrm{d}t \qquad \text{or} \qquad \frac{\mathrm{d}x}{\mathrm{d}t} = \frac{\mathrm{d}q/\mathrm{d}t}{\Delta H_\mathrm{tot}} \quad (1)$$

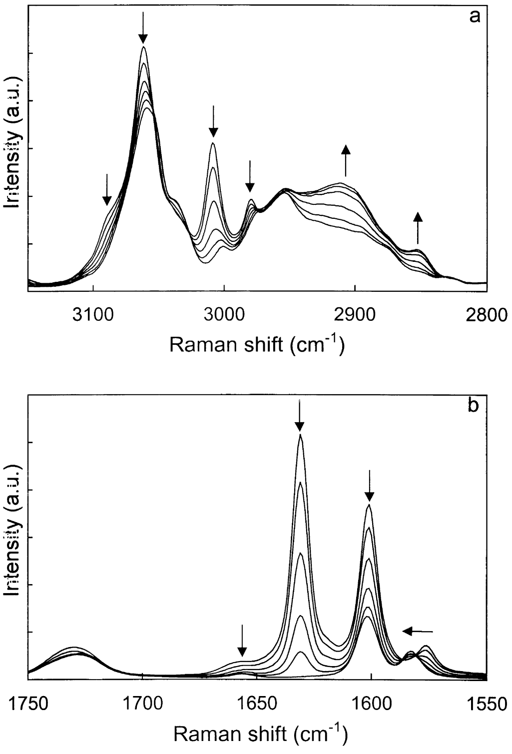

Fig. 1. Time-resolved FT-Raman spectra for the cure of an unsaturated polyester at an average temperature of 28°C. Arrows indicate evolution with cure. Reaction times: 0, 107, 199, 279 and 385 min, and 15 h + post-cure for 4 h at 80°C. Spectra as recorded, not normalised. (a) 3150–2800 cm^{-1}; (b) 1750–1550 cm^{-1}.

with ΔH_p and ΔH_{tot} the partial and total reaction enthalpies, and dq/dt the non-reversing heat flow. This overall, calorimetric conversion determined from MTDSC will be termed *conversion* throughout this text. If the individual conversions of the polyester vinylene groups and the styrene vinyl groups are considered, this will be stated clearly. After a (quasi-) isothermal cure experiment, the glass transition temperature of the isothermally cured material and the residual heat of reaction were determined by cooling the sample to −60 and heating to 225°C at 5°C min^{-1}. In a second cool–heat cycle the final glass transition temperature is obtained.

Dynamic rheometry. A *TA Instruments* AR1000-N rheometer was operated in parallel plates mode using disposable aluminium plates (diameter 4 cm). The oscillation frequency was 1 Hz. For the instrument set-up employed, no quantitative results are obtained if the shear modulus exceeds ca. 7×10^5 Pa. This is due to a significant contribution of the instrument's compliance to the total displacement measured.

To determine the gel point using the method of Winter and Chambon [47–49], multiwave experiments were performed with frequencies of 1, 2, 4, 8, 16 and 32 Hz and torque ratios of 2, 4, 8, 16 and 64, respectively. The displacement was 10^{-4} or 5×10^{-4} rad for 1 Hz. Owing to flow instabilities, the measurement needs to be stopped shortly after gelation.

Raman spectrometry — instrumentation. Raman spectrometry measurements were performed on a Perkin Elmer System 2000 FTIR spectrometer equipped with a System 2000R near infrared FT-Raman accessory. The measurements were performed with back-scattering (180°) collection using a quartz beam-splitter and an InGaAs detector. A capped glass vial containing 1 ml of unsaturated polyester resin was placed in the large-volume liquid-sampling accessory. Spectra were recorded at a resolution of 4 cm^{-1} using a laser power of 250 mW.

The polymerisation was studied in situ in the spectrometer. For performing time-resolved Raman experiments, a *Microsoft Visual Basic* procedure was developed using Perkin Elmer's *Spectrum Procedures* software. Every 13 min, a spectrum of 15 scans was recorded at a laser power of 250 mW. These parameters are a compromise to obtain an adequate signal-to-noise ratio while avoiding large temperature increases resulting from heating by the Raman laser radiation, and while granting the sample enough time to cool down in between the recording of two spectra. The temperature was measured in the centre of the sample using a thermocouple. The temperature increases 2–3°C during the scanning of a single spectrum. The total temperature variation was up to 5°C owing to the exothermicity of the polymerisation reaction.

Raman spectrometry — band assignments and data analysis procedure. Time-resolved Raman spectra for the

Table 1
Raman peak positions and assignments for the unsaturated polyester prepolymer and for styrene and evolution of peak intensity with cure. Assignments based on Refs. [39,56] (ν = stretching; δ = bending; γ = out-of-plane deformation; St = styrene; UP = unsaturated polyester)

Wave number (cm^{-1})	Tentative assignment	Component	Cure evolution
3100–2975	Unsat. νC–H (olefinic and aromatic)	St and UP	↓
2975–2850	Saturated νC–H	UP	↑
1729	νC=O	UP	
1659	νC=C *trans*	UP	↓
1650–1645	νC=C *cis*	UP	↓
1631	νC=C styrene	St	↓
1601	νC=C aromatic ring coupled with νC=C styrene	St and UP	↓
1581	νC=C aromatic ring	St and UP	Shifts

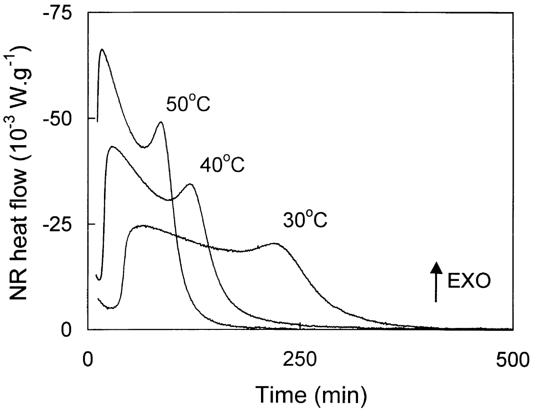

Fig. 2. Non-reversing heat flow for the (quasi-) isothermal cure of an unsaturated polyester at 30, 40 and 50°C.

cure of the unsaturated polyester are given in Fig. 1. With the exception of the post-cured sample, the spectra are given as recorded. Some spectroscopic data are given in Table 1. The conversion of styrene vinyl bonds x_{St} was calculated using the symmetric C=C stretching at 1631 cm^{-1} because: (1) it has a high intensity; (2) the baseline can be readily defined; and (3) the peak width at half height changes little during reaction (Eq. (2)).

$$x_{\mathrm{St}} = 1 - \frac{A_{1631}(t)}{A_{1631}(t=0)} \tag{2}$$

A_{1631} is the peak intensity at 1631 cm^{-1}, normalised by division by the maximum intensity in the region 2955 ± 5 cm^{-1}, which is used as a reference to correct the intensity for slight changes in sample position or scattering. The C=O stretch of the polyester (1729 cm^{-1}) is not a reliable reference band because its intensity varies with reaction (Fig. 1). A plausible cause is the loss of the conjugation of the C=O and C=C bonds of the fumarate units. Yang and Lee [17,18] used the methyne C–H stretch at 2942 cm^{-1} for the normalisation of their FTIR spectra.

For the vinylene bonds, the stretching of the fumarate C=C groups (1659 cm^{-1}) is of low intensity and overlaps with the high-intensity peak of styrene at 1631 cm^{-1} (Fig. 1). The contribution of styrene was subtracted using Eq. (3).

$$A_{1659} = A'_{1659} - 0.028A_{1631} \tag{3}$$

in which A_{1659} and A'_{1659} are the corrected and uncorrected peak intensities, respectively. The correction coefficient 0.028 was determined using pure styrene. After post-curing the unsaturated polyester, an important absorption is left at 1659 cm^{-1} (Fig. 1). This residual absorption is not due to unreacted vinylene bonds: after exposure to bromine, which readily adds to the double bonds, the peak at 1659 cm^{-1} remains present, whereas the peak at 1631 cm^{-1} (residual unreacted styrene) disappears. Thus, the polyester vinylene conversion x_{UP} is calculated as:

$$x_{\mathrm{UP}} = \frac{A_{1659}(t=0) - A_{1659}(t)}{A_{1659}(t=0) - A^{*}_{1659}} \tag{4}$$

with t the reaction time, A^{*}_{1659} the value after bromine treatment, and with A_{1659} corrected for the contribution of styrene using Eq. (3). A spectral deconvolution approach to resolve the overlapping peaks between 1675 and 1550 cm^{-1} (Fig. 1) resulted in too much scatter for quantitative kinetic analysis.

3. Results and discussion

3.1. Polymerisation kinetics

3.1.1. Inhibition, polymerisation, and autoacceleration

Quasi-isothermal MTDSC cure experiments were made at 30, 40 and 50°C. The reaction exotherm is observed in the (non-reversing) heat flow (Fig. 2). Table 2 gives some numerical characteristics. Previous studies of cure and vitrification showed that the non-reversing heat flow from a modulated experiment corresponds well with the heat flow measured in a conventional DSC [29–31]. Three stages can be identified. An *inhibition period* is observed before the main reaction exotherm sets in. This delay of the start of the polymerisation is due to a fast inactivation of the generated radicals by the inhibitor that is present in the reaction mixture. At higher temperatures, the inhibitor is consumed more quickly because the peroxide initiator decomposes faster into radicals. At 50°C, the reaction exotherm starts before the temperature modulation reaches a steady state. For the other temperatures, the significant and slightly decreasing exothermic heat flow during the inhibition period can be attributed to a competition between monomer and inhibitor to react with free radicals generated by initiator decomposition.

When there is no inhibitor left for scavenging the free radicals, their concentration sharply increases. The polymerisation accelerates, and the *main reaction exotherm* is observed. The maximum heat flow rate is attained around a (calorimetric) conversion x of 10–14%. Subsequently, the heat flow decreases owing to the decreasing monomer concentration. However, after reaching a minimum near a conversion x of 57–58%, the rate of reaction accelerates towards a second heat flow maximum.

At first sight, the *autoacceleration* might seem to be rather limited. However, the concentration of reactive double bonds is continuously decreasing and the autoacceleration more than compensates this decrease. The decreasing monomer concentration is accounted for by calculating the reduced rate of conversion R_{r}:

$$R_{\mathrm{r}} = \frac{\mathrm{d}x/\mathrm{d}t}{(1-x)} \approx -\frac{1}{[\mathrm{M}]}\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} \approx k_{\mathrm{p}}[\mathrm{R}^{\cdot}] \tag{5}$$

with [M] and [R$^{\cdot}$] the concentrations of monomer and propagating radicals, respectively, and with x the conversion. The

Table 2
MTDSC results for the isothermal cure of an unsaturated polyester system at cure temperatures T_{cure}. Time, conversion x, and non-reversing heat flow dq/dt are given for the onset of the main reaction exotherm, at the first maximum, at the minimum, and at the second maximum in the non-reversing heat flow, and at the onset of the final decrease in heat capacity

T_{cure} (°C)	Onset exotherm	First maximum			Minimum			Second maximum			Onset decrease in C_p	
	Time (min)	Time (min)	x	dq/dt (mW g^{-1})	Time (min)	x	dq/dt (mW g^{-1})	Time (min)	x	dq/dt (mW g^{-1})	Time (min)	x
30	37	65	0.14	25	177	0.58	19	219	0.73	20	248	0.83
40	15	29	0.11	42	95	0.57	30	121	0.72	34	131	0.82
50	–	15	0.10	66	62	0.58	43	80	0.74	49	95	0.82

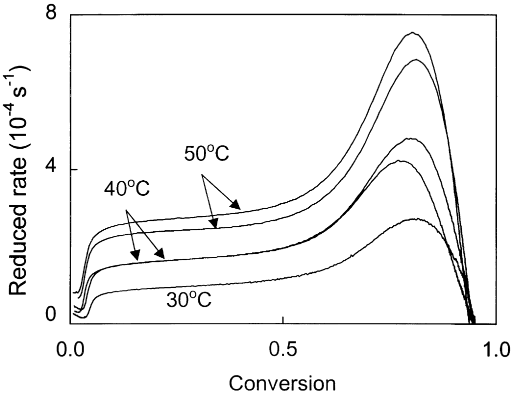

Fig. 3. Reduced rate of reaction versus conversion for the isothermal cure of an unsaturated polyester at 30, 40 and 50°C. At 40 and 50°C, results for two independent measurements are shown.

principles of free radical polymerisation show that R_r reflects the change in [R$^{\cdot}$] and in the (apparent) rate constant of propagation k_p (Eq. (5)).

In Fig. 3, R_r is given versus the conversion x for the experiments of Fig. 2. Results for two additional independent experiments indicate the reproducibility of these curves. A few percent of reaction occurs during the inhibition period. When the inhibitor has been consumed, R_r sharply increases owing to the strong increase in the concentration of propagating radicals. For a conversion x between 10 and 50% R_r shows a slowly increasing plateau. Near 50% conversion, the onset of a threefold autoacceleration is observed. The maximum in R_r is attained for x equal to 80%. The shape of the curves is little affected by the (limited) variation in temperature.

The evolution of the heat capacity, which is measured simultaneously with the reaction exotherm, will be discussed in the following paragraphs. First, the conversion of the two comonomers measured with FT-Raman spectrometry will be discussed.

3.1.2. Mechanistic information

Raman spectrometry provides information about the individual consumption of the reactive C=C bonds in the prepolymer and the reactive solvent. In Fig. 4, conversion and rate of conversion versus time profiles for the polyester vinylene and styrene vinyl groups are reported for a cure at 28°C. Data presented for two experiments indicate a good reproducibility. Initially, the vinylene rate of conversion is higher. After passing through a maximum, it decreases monotonously towards zero level. The styrene rate of conversion increases to a first maximum, which is half as high as for vinylene. Then, the rate slowly decreases, reaches a minimum, and increases again to reach a second maximum (of similar height as the first one). At the onset of the acceleration of the styrene consumption, the vinylene rate of conversion has decreased to less than 20% of its maximum. Finally, the styrene rate of conversion decreases to zero level. However, although after 400 min both rates

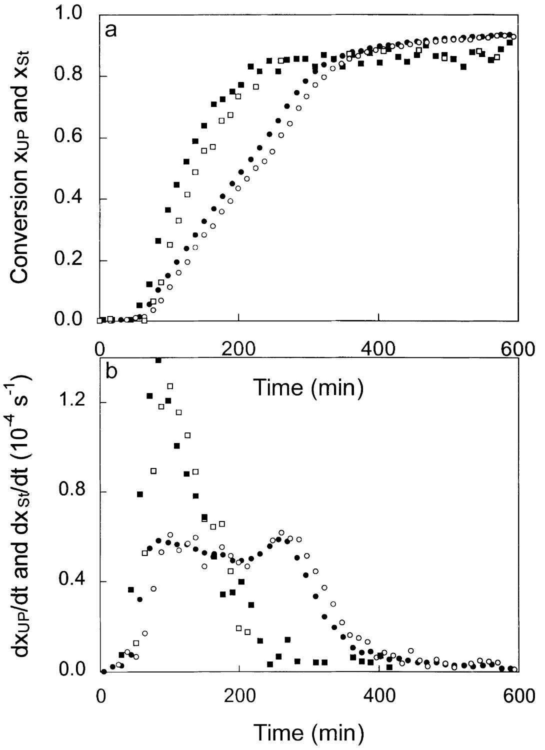

Fig. 4. Conversion and rate of conversion versus time for the cure of an unsaturated polyester. (■□) polyester vinylene units; (●○) styrene; filled and unfilled symbols denote two experiments at an average reaction temperature of 28°C.

are close to zero, a slow but continuing increase in styrene conversion is still observed (Fig. 4).

As the calorimetric conversion x proceeds from zero to more than 75%, C_p decreases linearly (Fig. 5). This slow decrease can be attributed to the chemical changes upon curing. If the C_p of the polymer is lower than the C_p of the uncured resin, then the C_p will decrease if monomer units are transformed into polymer. Sometimes, mechanistic information can be deduced from these conversion-related heat capacity changes [32]. For conversions around 80%, a sharp decrease in C_p is observed, which will be discussed in the next paragraph.

3.1.3. Final cure stages and vitrification

After reaching the autoacceleration maximum, R_r sharply decreases (Fig. 3) and simultaneously a sharp decrease in C_p sets in (Fig. 5). The latter decrease points to the occurrence of vitrification [29–31]. This is supported by final isothermal conversions below unity. The calorimetric conversion x attained isothermally is about 93% for an isothermal cure of 600 min at a temperature of 30°C (Fig. 3). The final conversions x_{ST} and x_{UP} measured by Raman spectrometry are also lower than unity (Fig. 4).

Vitrification occurs when a resin is cured below the glass transition of the fully cured resin ($T_{g\infty}$). For the unsaturated polyester resin studied, this transition stretches from 10 to 60°C, as can be seen in Fig. 6. The heat flow phase ϕ (expressed in degrees) given in Fig. 6 is defined as the phase lag between the modulated heat flow output and the modulated heating rate input [28]. Upon changing from the (fully) rubbery to the (fully) glassy state, the heat flow phase ϕ passes through a minimum (Fig. 6 and [28–31]).

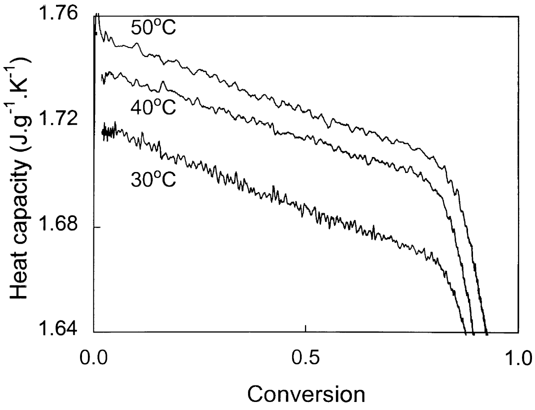

Fig. 5. Heat capacity versus reaction conversion for the isothermal cure of an unsaturated polyester at 30, 40 and 50°C.

The isothermal cure temperatures of 30, 40 and 50°C are within the glass transition of the fully cured resin ($T_{g\infty}$). Hence, the final state reached upon cure at these temperatures is in between the fully glassy and the fully rubbery state and only *partial vitrification* occurs, as was already noted for epoxy resins in a much narrower range of cure temperature [32]. The lower the cure temperature, the closer is the final state of the material to the fully glassy state, and the larger is the characteristic decrease in C_p (Fig. 7).

If the resin is cured at a temperature below the heat flow phase minimum in Fig. 6, a minimum is observed upon vitrification [29–33]. This is illustrated in Fig. 8 for a cure at 0°C. At this temperature, the rate of reaction is too slow for a quantitative analysis of the polymerisation kinetics, but nevertheless the vitrification can be studied quantitatively by MTDSC. At 30, 40 and 50°C (Fig. 7), the evolution of ϕ

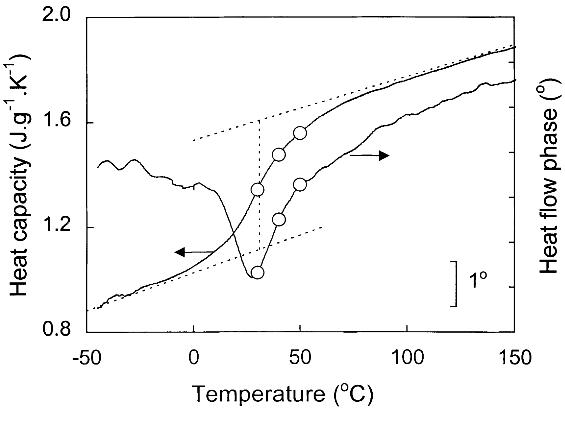

Fig. 6. Heat capacity and heat flow phase for the fully cured unsaturated polyester in a heating at 5°C min^{-1}. The symbols (○) indicate the selected temperatures of 30, 40 and 50°C.

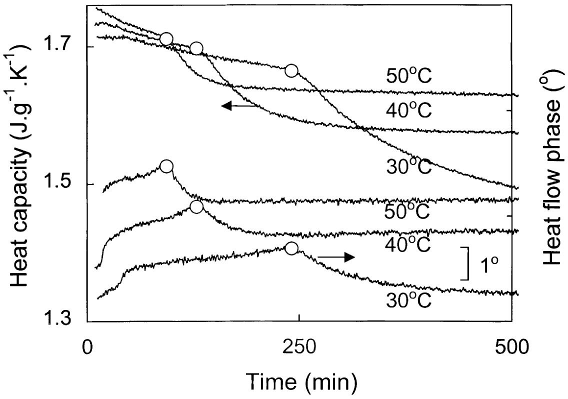

Fig. 7. Heat capacity and heat flow phase for the isothermal cure of an unsaturated polyester at 30, 40 and 50°C. The heat flow phase curves were shifted vertically to avoid overlap. The symbols (○) indicate when the maximum reduced rate of reaction is attained.

is somewhat different: upon vitrification, ϕ decreases and then remains at a low (more negative) value without passing through a minimum. The minimum is not observed because these cure temperatures are located above the minimum in heat flow phase for $T_{g\infty}$. Thus, the partial vitrification is also detected in the heat flow phase.

3.2. Interrelations between chemorheology and cure kinetics

The evolution of viscosity with the progress of polymerisation, the resulting decrease in molecular mobilities, and its effect on the rate of the polymerisation reaction strongly depend on the polymerisation mechanism. This will be illustrated by comparing the rheological evolutions for cross-linking step-growth and chain-growth polymerisation systems.

In a cross-linking step-growth (bifunctional) epoxy–(tetrafunctional) amine system, the complex viscosity rises continuously with extent of polymerisation (Fig. 9). The size distribution of the reacting species is continuous and gradually increases. Therefore, the diffusion limitations will be non-specific (*overall diffusion control* [57]) and the decrease in the rate of polymerisation upon vitrification parallels the decrease in molecular mobility observed in the heat capacity [29–33,58]. Gelation occurs when ca. 60% of the epoxy groups has reacted, and it does not markedly affect the rate of cure [58].

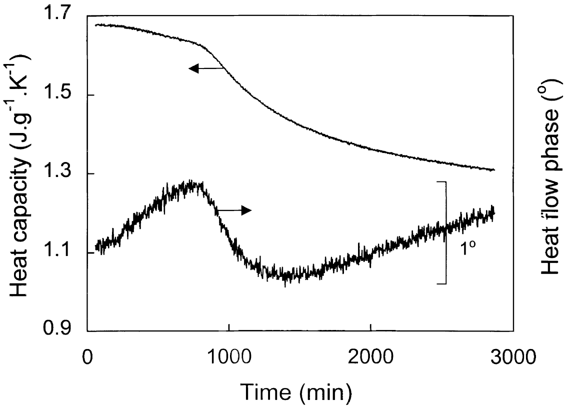

Fig. 8. Heat capacity and heat flow phase for the isothermal cure of an unsaturated polyester at 0°C. No extra inhibitor added to formulation.

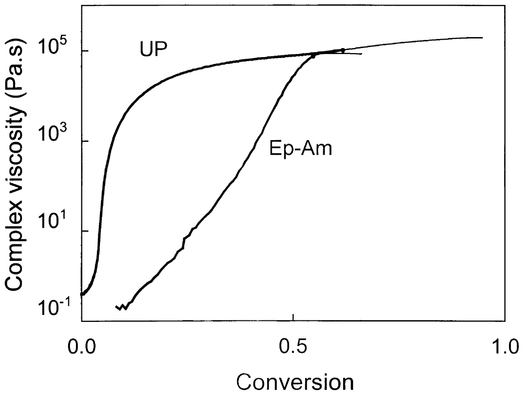

Fig. 9. Complex viscosity versus conversion for the isothermal cure of an epoxy–diamine system at 60°C (Ep–Am, results from Ref. [58]) and for the isothermal cure of an unsaturated polyester at 40°C (UP). Viscosity is plotted on a logarithmic scale.

For (cross-linking) free radical chain-growth polymerisations, a sudden increase in complex viscosity is noticed (Fig. 9). Note that for linear free radical polymerisations, the highest average degree of polymerisation of the polymer chains formed is attained at the start of the reaction (once the inhibitor is consumed). Thus, in cross-linking free radical chain-growth polymerisations: (1) different reaction steps occur (initiator decomposition, propagation, termination); and (2) species with very different molecular sizes are involved (styrene monomer, polyester prepolymer, small active radicals, radicals attached to growing chains or to the growing network,…). For each reaction step, the diffusion limitation depends on the size and structure of the molecules or radicals involved (*specific diffusion control* [57]). Therefore, a complex interrelation exists between the reaction kinetics and the changing rheology.

3.2.1. Initial cure stages

According to literature [17,18,45,50–54], for unsaturated polyester resins chemical gelation occurs within the first few percent of reaction. For the present system, this was confirmed by dynamic rheometry. In Fig. 10, cure experiments at 30, 40 and 50°C are presented. Near the end of the inhibition period, (chemical) gelation results in a sharp increase in complex viscosity η^* (with more than four orders of magnitude, Fig. 10(a)). The mechanical loss angle δ, the phase lag between the sinusoidal strain rate input and the resulting oscillating shear stress, drops from more than 85° to less than 5° (within a 5-min interval, Fig. 10(b)).[1] The cross-over point of the storage shear

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[1] The mechanical loss angle is 90° for a purely viscous liquid and 0° for a purely elastic solid [59].

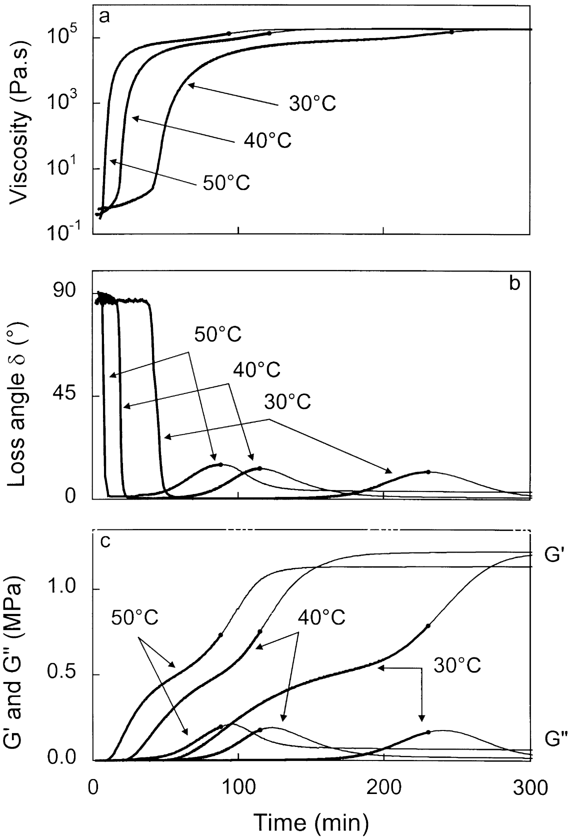

Fig. 10. Dynamic rheometry experiment for the isothermal cure of an unsaturated polyester at 30, 40 and 50°C. (a) Complex viscosity plotted on a logarithmic scale; (b) mechanical loss angle δ; (c) storage and loss shear moduli G' and G''.

modulus G' and the loss shear modulus G'' corresponds to δ equal to 45°. It is often used as a measure of the gel point [15,16]. Note that the cross-over itself is not clearly seen in Fig. 10(c) because it occurs at very low values of the shear modulus. According to Winter and Chambon [47–49], the gel point in a cross-linking polymerisation is more correctly determined as the instant that the mechanical loss angle is frequency independent. For the unsaturated polyester system studied, multiwave experiments (see Section 2) show that a frequency-independence is reached for the time at which the mechanical loss angle δ has decreased to 77°, which is just before δ equal to 45° (Fig. 10). Hsu and Lee [50–53] determined the gel point of an unsaturated polyester system by gel fraction measurements; they also found that it occurs before the cross-over of G' and G''. This being said, it is worth noting that due to the sharpness of the transition (Fig. 10(b)), the criterion used to define the gel time has little influence on the gel time determined, and the corresponding calorimetric conversions agree within the experimental errors (Table 3). The conversions at the gel point might seem to be rather low, but predicted gel conversions for unsaturated polyester resins tend to be even lower than the experimental values [17,18], which is usually attributed to extensive intramolecular cyclisation and non-ideal polymerisation behaviour [17,18,60].

Table 3
Dynamic rheometry results for the cure of an unsaturated polyester system at different isothermal cure temperatures (T_{cure}). Time at the cross-over point of storage shear modulus G' and loss shear modulus G'' and at a mechanical loss angle δ of 77° (gel point determined using the method of Winter and Chambon [47–49]), and corresponding calorimetric conversion x

T_{cure} (°C)	$t_{\delta=77°}$ (min)	x MTDSC (%)	$t_{G'=G''}$ (min)	x MTDSC (%)
30	41	5	44	5
40	18	3	19	4
50	7	2	8	2

Most important here is that all results confirm that: (1) the calorimetric conversion x at gelation is 5% or less (in agreement with literature [17,18,20,50–54]); and (2) gelation occurs before the first maximum of the reaction exotherm ($x = 10$–12%), and long before the autoacceleration (second maximum in heat flow, $x = 72$–74%) and vitrification effects (compare Tables 2 and 3).

At higher reaction times, the onset of vitrification is observed as a further increase in η^* and G', and a maximum in G'' and δ is observed (Fig. 10) [25]. However, the final η^* and G' obtained by dynamic rheometry are much too low for a glassy solid: the instrument's compliance dominates the response in this region. MTDSC is more suited to study the vitrification transition quantitatively.

3.2.2. *Autoacceleration and partial vitrification — MTDSC*

The autoacceleration can be attributed to a (further) increase in the concentration of propagating radicals due to diffusion limitations on the termination reaction. Indeed, if the quasi-stationary state hypothesis is applied to the free radical concentration, this results in:

$$R_{\mathrm{r}} = k_{\mathrm{p}}[\mathrm{R}^{\cdot}] = k_{\mathrm{p}}\sqrt{\frac{2fk_{\mathrm{i}}[\mathrm{I}_2]}{k_{\mathrm{t}}}} \qquad (6)$$

with f the initiator efficiency, k_{i} the rate constant for the initiator decomposition, $[\mathrm{I}_2]$ the initiator concentration, and k_{t} the (apparent) rate constant for termination. A decrease in mobility of the growing radicals, resulting from a densifying network, leads to a decrease in k_{t}, and thus to a higher radical concentration and polymerisation rate.

The fact that the autoacceleration occurs long after gelation points out that termination reactions are still important at these advanced conversions, although the network structure is present. This is an indication for the importance of terminations involving small (mobile) radicals after gelation. Thus, a (conversion-dependent) termination reaction step should be included when modelling the cure kinetics. The fact that a plateau in R_{r} is observed indicates that after gelation, the main termination reactions are at first little influenced by the increasing cross-link density of the network (up to the onset of the autoacceleration at a calorimetric conversion of 57–58%).

Although the system under investigation is a cross-linking system, the autoacceleration shows characteristics of linear free radical polymerisations. Firstly, the autoacceleration is mainly an acceleration of the styrene consumption, the vinylene rate of conversion is near zero (Fig. 4). Secondly, the autoacceleration is not caused by a network effect (which would occur near gelation [12]) but rather by a depletion of the residual styrene monomer that causes a further increase in the (micro)viscosity.

Comparison of Figs. 3 and 5 shows that upon the onset of vitrification, the autoacceleration is stopped and R_r suddenly decreases. This can be attributed to the onset of diffusion limitations on the propagation reaction resulting in a strong decrease in k_p. As a result, the polymerisation reaction is frozen out before full cure is reached. Thus, while diffusion limitations on the termination reaction accelerate the polymerisation, limitations on the propagation reaction retard or even halt the cure process. If a termination and a propagation reaction involve reactive units of similar mobilities, e.g. the recombination of a small radical with a radical located on the network, and the propagation of a styrene monomer with a radical located on the network, the termination reaction is expected to become diffusion-controlled *before* the propagation reaction because the (chemical) rate constant of the former is much higher than for the latter [61].

3.2.3. Diffusion control and copolymerisation kinetics

Indications for the influence of different molecular mobilities on the diffusion control of the propagation reaction can also be seen in the evolution of the conversion of the polyester vinylene and the styrene monomer for more advanced conversions. Fig. 4 shows that at first polyester vinylene bonds are more quickly consumed than styrene, which is usually attributed to a higher reactivity ratio [17,18]. However, the consumption of polyester vinylene slows down at an earlier stage than the styrene consumption, and attains a lower final level. This can be related to a different influence of the network formation on the propagation reaction of the two monomers. The polyester vinylene bonds are located within polymer chains that in turn are likely to be part of the growing network. The densifying network structure will hinder the movement of the reactive sites (mainly by segmental diffusion) at an earlier stage than the diffusion of the small styrene molecules. Thus, the propagation of polyester vinylene bonds with radicals located in longer chains, or on the growing network, will become diffusion-controlled at an earlier stage than the propagation of the (more mobile) styrene monomer with these radicals. This propagation version of the short–long effect might contribute to the higher amount of residual vinylene groups buried in the network. This leads to the observed faster increase of the styrene conversion x_{ST} with respect to the polyester vinylene conversion x_{UP} at an advanced stage of the reaction (Fig. 4 and e.g. Ref. [37]. According to Dusek [62], residual vinylene groups may be buried inside microgel particles due to *molecular shielding*, which reduces the number of polyester vinylenes available for further cross-linking. The rate of conversion for styrene drops when vitrification sets in.

Because diffusion control effects seem to influence the vinylene consumption at an early stage in the reaction, the evolution of the individual monomer conversions should not be used for a detailed discussion of the reactivity ratios of polyester vinylene and styrene vinyl bonds [1,2]. The influence of the styrene content on the copolymerisation kinetics and its effect on the interrelation between chemorheology and diffusion control will be discussed in a forthcoming paper [55].

4. Conclusions

Gelation, vitrification, and an autoacceleration or gel effect were studied for the cure of an unsaturated polyester resin by combining modulated temperature DSC, Raman spectrometry, and dynamic rheometry.

Just before vitrification, an important autoacceleration occurs. The fact that the effect is observed long after gelation indicates that short–long termination reactions are significant at a more advanced conversion. The decrease in the overall rate constant for termination, caused by a depletion of small radicals and a continuing increase in viscosity, would cause the autoacceleration effect. Thus, the termination reaction should not be neglected when modelling these polymerisations.

The autoacceleration is restricted by the onset of vitrification. Using MTDSC, the partial vitrification can be studied simultaneously with the evolution of the polymerisation kinetics. This ability is an important asset for investigating and modelling diffusion-controlled reactions. The accelerating effect of (decreasing) molecular mobilities on the rate of the cure process is related to the specific features of the cross-linking free radical chain-growth polymerisation mechanism and contrasts with addition step-growth polymerisation thermosetting systems. For the system investigated, effects of diffusion or mobility limitations on both termination and propagation reactions need to be taken into account to model the autoacceleration and the influence of vitrification.

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