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polymer papers

*FT*i.r. studies on reactions of oxazoline functionalised polymer particles

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The reaction between oxazoline-functionalised polymer particles and bis(carboxylic acid)-terminated poly(tetrahydrofuran) (PTHF-COOH) was monitored by means of *FT*i.r. spectroscopy. Parameters such as particle size, content of functional groups, stoichiometry and temperature were varied to study their influence on conversion and reaction rate constants. Oxazoline conversion was primarily affected by particle size and less so by crosslink density. Reactions occurring at particle surfaces and in bulk of the particles were differentiated. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Polymer particles and their dispersions play an important role in polymer technology with applications ranging from coatings to toughening agents and polymer blends[1]. Especially in blend applications surface modification is the key to achieve adequate interfacial adhesion between dispersed polymer particles and the continuous polymer matrix. Preferably interfacial coupling, e.g., by covalent bond formation, is carried out during melt processing. Little is known about reactions on particles during reactive processing. Macosko *et al.*[2,3] investigated the *in situ* formation of block copolymers and dispersed polymer particles by means of reactive blending. Clearly the size of dispersed microphases differs from blending experiments where preformed block copolymers are used for compatibilisation. This was attributed to efficient coupling reactions at the particle/polymer interface. In fact, it appears that accumulation of end-groups at the interface give higher reaction rates with respect to homogeneous reactions.

To study the reaction on particle surfaces, crosslinked oxazoline-functionalised polymer particles, prepared by non-aqueous dispersion polymerisation[4–6], are used as model for 'preformed microphases', which are reacted with bis(carboxylic acid)-terminated PTHF, abbreviated as PTHF-COOH. Such crosslinked, reactive dispersions have the advantage that they can be tailor made and do not alter their size during the course of the reactions. Oxazoline and carboxylic acid are chosen as reactive functional groups because they react in essentially quantitative yield within a suitable temperature range to afford (*Scheme 1*) esteramides[7–10]. Therefore, dispersions of this kind are excellent model systems.

In this study the influence of parameters like particle size, functionality, crosslinking density, reaction temperature and stoichiometry on the kinetics of esteramide formation are investigated.

EXPERIMENTAL

Materials

Bis(carboxylic acid)-terminated-oligo-(tetrahydrofuran), abbreviated as PTHFCOOH, had a number average molar mass of 3000 g mol^{-1}, as determined by means of n.m.r. spectroscopy and was supplied by BASF AG, Ludwigshafen (Germany).

Crosslinked oxazoline-functional particles were obtained by non-aqueous free radical dispersion copolymerisation of methylmethacrylate, 5-oxazolinyl-pentylmethacrylate and ethyleneglycoldimethaerylate in *n*-heptane in the presence of azobisisobutyronitril (AIBN) initiator and polystyrene-block-poly(ethene-alt-propene) (SEP), dispersing agent at 70°C. Experimental conditions are listed elsewhere in more detail[11]. Soluble methylmethacrylate/5-oxazolinyl-pentyl-methacrylate copolymer was prepared by free radical solution polymerisation at 70°C in toluene as solvent. The molecular mass as measured by g.p.c. was $M_n = 40\,000$ g mol^{-1} with $M_w/M_n = 2.0$.

Dispersions were purified by removing the dispersant and residual amounts of monomers and initiator particle dispersions were centrifuged and the diluent replaced by pure THF. After redispersion this procedure was repeated three times. Eventually the dispersion was redispersed in chloroform.

Functionalities, crosslinking densities and the particle sizes, as measured by TEM, are listed in *Table 1*.

Characterisation

For the determination of the particle size by TEM a Zeiss CEM 902 with 80 kV voltage was used. The samples were prepared by spraying approximately 0.01 wt% diluted dispersions onto carbon coated copper grids. Image processing gave the number average of the particle diameter and the standard deviation. The surface/volume ratios listed in *Table 1* were calculated from the whole histograms obtained by image processing.
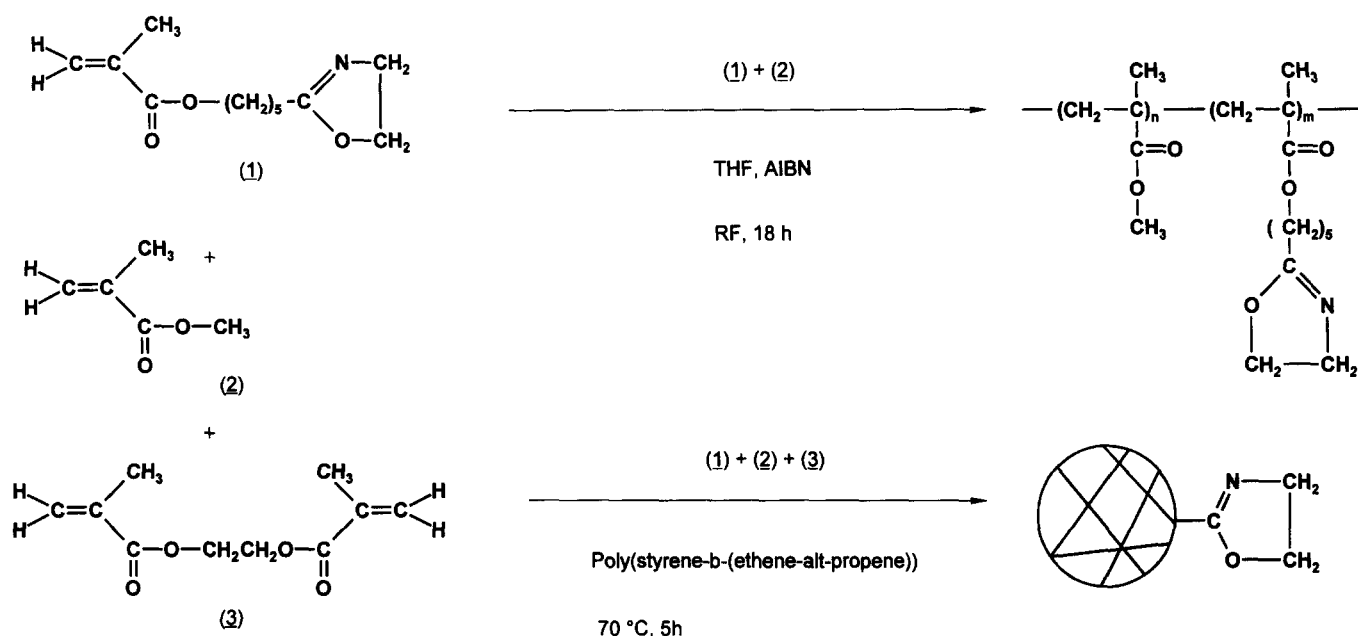
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Scheme 1 Reaction scheme for polymerisations

Table 1 Polymers used and their abbreviations

Abbreviation[a]	Parameter	$D(\sigma)^b$ (nm)	Oxa[c] (mol%)	EGDMA (mol%)	Surface/volume[d] ($m^2 cm^{-3}$)
P20-Da	Particle-size	110 (22)	20	5	56
P20-Db	(diameter)	270 (51)	20	5	24
P20-Dc		520 (90)	20	5	12
P10	Oxazoline	200(61)	10	5	33
P20	functionality	270 (51)	20	5	24
P40		230(34)	40	5	27
P95		260 (41)	95	5	23
P20-Ea	Crosslinking	200 (27)	20	1	31
P20-Eb	density	210 (58)	20	10	31
S10		–	10	0	–

[a]The materials are abbreviated according to the following scheme: PX-Var$Y$. P means particle and X is the content of the oxazoline methacrylate. Var represents the varied parameter: E for [EGDMA] and D for diameter. The letter Y denotes the degree of variation in alphabetical order. Samples P20, P20-Ec and P20-Dc are identical
[b]Particle diameter and standard deviation as measured by TEM
[c]Content of 5-oxazolinyl-pentyl-methacrylate

Sample preparation for FTi.r. studies

A 3 wt% dispersion of oxazoline functionalised particles and a 10 wt% solution of PTHF-acid in $CHCl_3$ were mixed in appropriate amounts and one droplet of this mixture was placed on a KBr plate. This sample was placed quickly in an oven at 70°C for 5 min. After evaporation of the solvents a thin film was formed on the KBr plate. The thickness of the film was optimised in order to provide the best absorbance unit. For the infrared measurements the sample was covered with another KBr plate. Various methods of sample preparation are described by Koenig[12].

Measurements

For the kinetics measurements on polymer surfaces and interfaces a special infrared vacuum thermocell was designed to afford possibility for applying vacuum and to control temperature (*Figure 1*). This FTi.r. application allows very accurate on-line measurements, even over long periods of time. Additionally the time which the sample needs to be isothermal is very short, because the sample is placed in a pre-heated oven. Typically, first the sample,

covered on both sides with KBr plates, was placed in the movable sample holder and the cell was evacuated. The sample was positioned with the external sample mover in the cold (!) oven to record a reference. Then the sample was removed from the oven. When the oven reached the required temperature, the sample was mounted again in the oven. The sample reached the isothermal temperature quickly and the kinetic measurement was started.

FTi.r. spectroscopy

The FTi.r. spectra were obtained on a BRUKER IFS 88. For signal averaging 100 scans were taken. Over several time domains the spectra were taken every 30 s to follow esteramide formation. A liquid nitrogen cooled MCT detector was used at a resolution of $4 cm^{-1}$. The peak integration program was included in OPUS software and a method with two baseline points was used.

RESULTS AND DISCUSSION
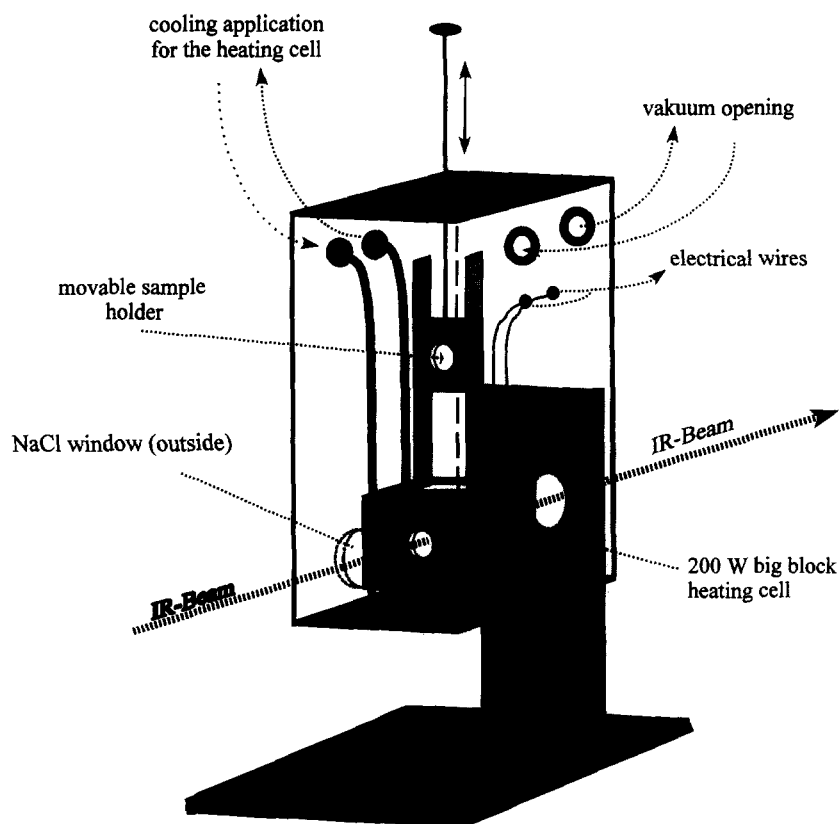
Figure 2a shows the spectrum of pure PTHF-acid. At

Figure 1 Special *FTi.r.* vacuum cell for isothermal investigations

1738 cm^{-1} the carbonyl i.r. absorption band of the acid group can be seen. *Figure 2b* shows the spectrum of P95 which is typical for the oxazoline-functional particles. The characteristic oxazoline band is the C=N vibration at 1668 cm^{-1}. A scheme of the investigated esteramide formation is shown in *Scheme 2*. *Figure 3* shows the reactive sample at room temperature before heating (*Figure 3a*) and after 43 min at 200°C (*Figure 3b*). It can be seen that the characteristic peaks are not totally separated, so difference spectroscopy is necessary. The difference spectrum after a reaction time of 43 min is shown in *Figure 4*. There are several peaks which reflect the esteramide formation very clearly. The band at 1731 cm^{-1} is the characteristic carbonyl vibration of the acid group and this band decreases because the carboxylic acid reacts with oxazolines. The band at 1712 cm^{-1} is characteristic for the carbonyl vibration of the newly formed ester group. The band at 1687 cm^{-1} is an amide I band, especially for the surface reaction of the particles, as discussed in more detail below. At 1668 cm^{-1} the well known oxazoline band decreases, thus reflecting oxazoline conversion. Another amide I vibration can be seen at 1648 cm^{-1} which is complementary to the band at 1687 cm^{-1} and is also discussed below. The amide II band at 1514 cm^{-1} increases and also the –CH$_2$ deformation band, which is located next to the newly formed ester group. The characteristic bands are very well separated in the difference spectrum, so peak integration can be performed. The spectra are taken every 30 s and the kinetics of esteramide formation can be measured accurately. To elucidate the important parameters for the reaction the temperature, functionality, size and crosslinking density of the particles, and the stoichiometry of the reactants were varied. This investigation was carried out at a reaction temperature of 200°C and stoichiometry of carboxylic acid/oxazoline = 1 mol%/2 mol%.

Variation of particle size

In this series particle sizes were varied from 110 to 520 nm at constant oxazoline functionality of 20 mol%, constant EGDMA crosslinking agent content of 5 mol% and temperature of 200°C. The qualitative results can be seen in *Figure 5*. In contrast to other oxazoline/carboxylic acid reactions, this system shows two different amide I bands at 1687 and 1653 cm^{-1}. These band locations have been observed earlier in many polymeric systems containing amide groups[13–15] in the temperature range 30–210°C. Coleman *et al.* found amide I bands between 1650 and 1680 cm^{-1} varying with temperature. They explained this effect with different degrees of crystallinity influencing hydrogen bonding, thus modulating the double bond character of the carbonyl group.

The intensity of the band we found at 1687 cm^{-1} increased much faster at the beginning of the reaction and reached its final absorbance after approximately 10 min. In contrast, the intensity of the band at 1653 cm^{-1} increased steadily for a long period of time, indicating a diffusion controlled process. For P20-Dc (520 mm diameter, 12 m^2 cm^{-3}) the amide I band at 1653 cm^{-1} dominates (*Figure 5a*), for P20-Da (110 nm diameter, 56 m^2 cm^{-3}) the peak at 1687 cm^{-1} has higher absorbance (*Figure 5c*) and for P20-Db (270 nm, 24 m^2 cm^{-3}) an intermediate situation can be seen (*Figure 5b*).

In contrast to Coleman *et al.*, the amide I band locations were essentially the same at room and reaction temperature. Most likely, these bands result from different surroundings of the formed esteramide groups located at particle surface or in the bulk. At the surface the interactions of the formed esteramide groups are supposed to be weaker than inside the particles, where the amount of carbonyl groups is larger and the crosslinking density limits the mobility of PTHF-acid.
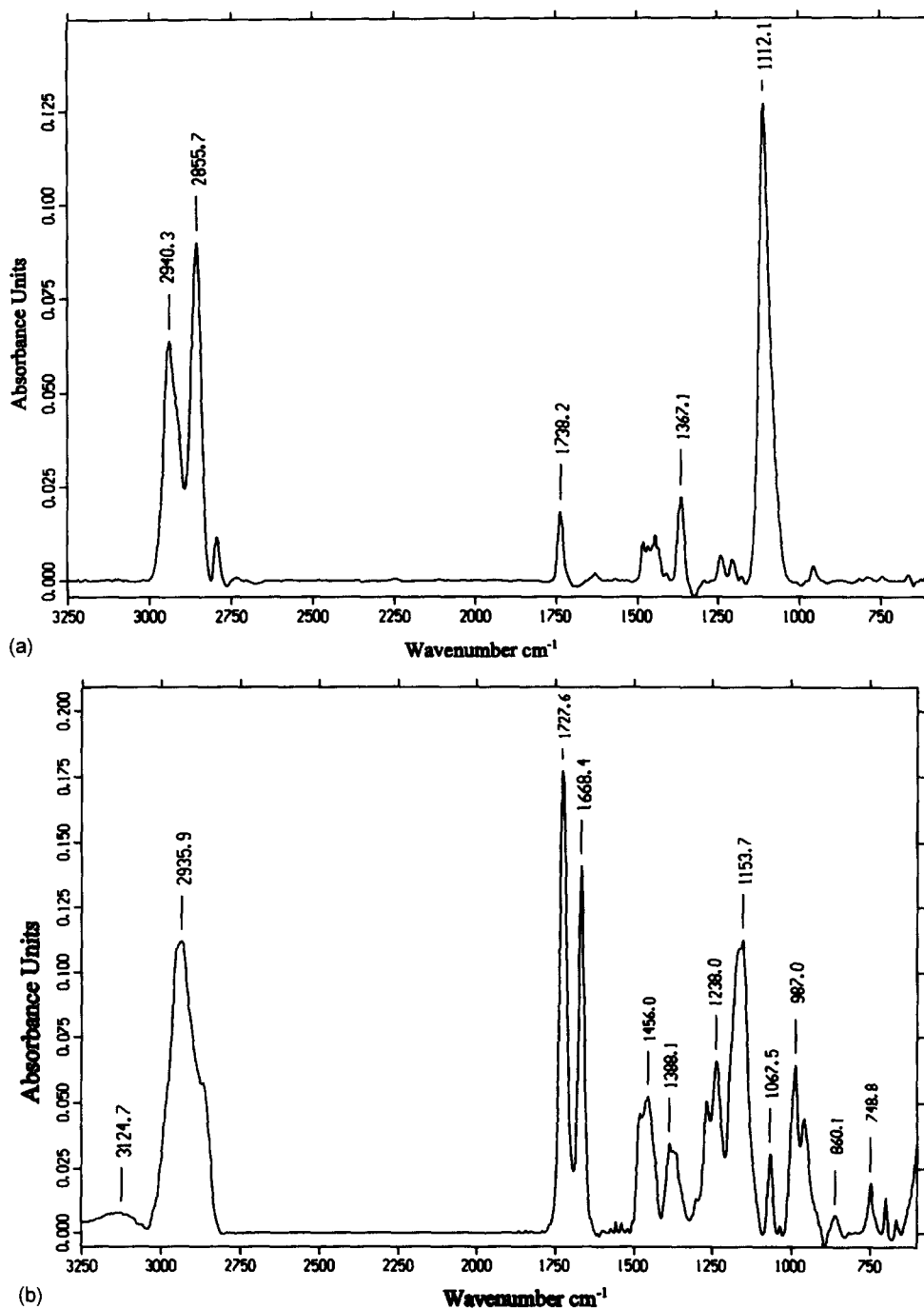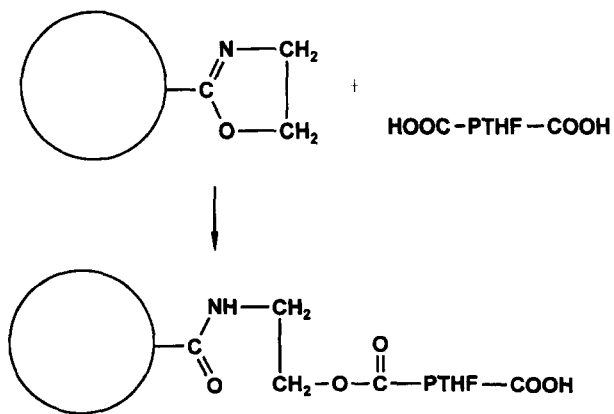
Figure 2 (a) *FT*i.r. spectrum of PTHF-acid at room temperature. (b) *FT*i.r. spectrum of P95 at room temperature

Scheme 2 Reaction scheme for esteramide formation

Therefore, the band at higher wavenumbers ($1687\,\mathrm{cm^{-1}}$) could correspond to the esteramide groups at the surface because interactions could diminish the force constant, thus shifting the peak maximum to lower wavenumbers. The intensity increase of the band at $1687\,\mathrm{cm^{-1}}$ confirms this assumption because the oxazoline groups at the surface are more easily accessible by PTHF-COOH than the oxazoline groups in the polymer network inside the particles. The much slower increase of intensity of the band at $1653\,\mathrm{cm^{-1}}$, on the other hand, is typical for diffusion controlled reactions which are expected in a polymer network. Additional experimental evidence results from the influence of the diameter on reaction kinetics. Because the surface/volume ratio increases with decreasing diameter of the particles, the absorbance of the amide I band at the surface should also increase, as found in this set of experiments.
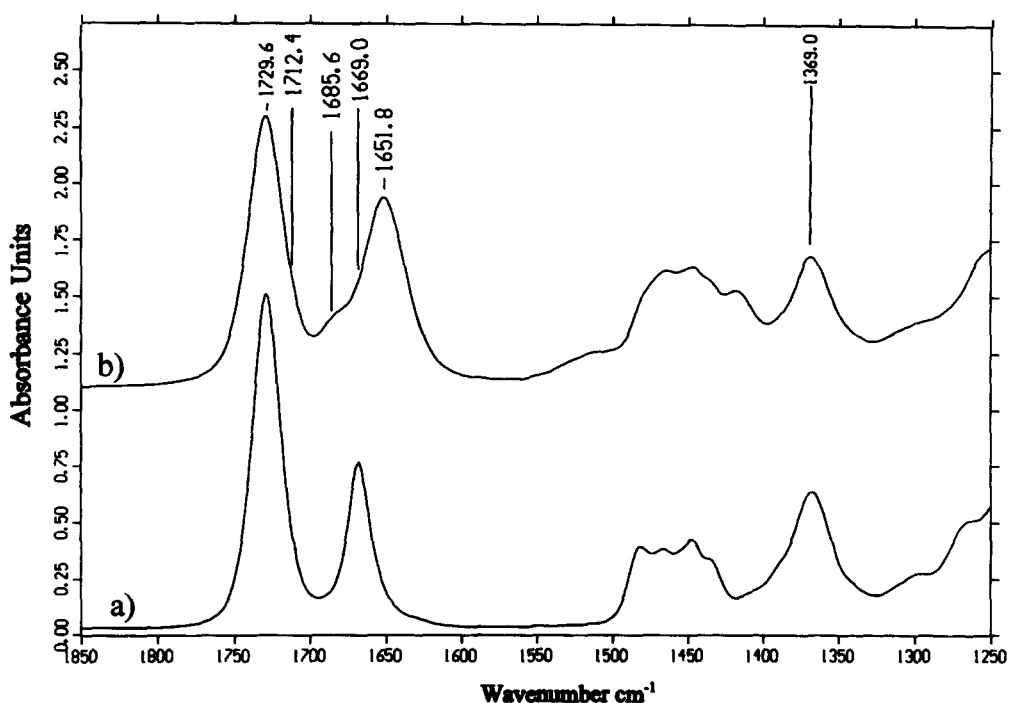
Figure 3 *F*7i.r. spectra of the system P95/PTHF-acid (a) at room temperature before chemical reaction and (b) after 43 min at 200°C
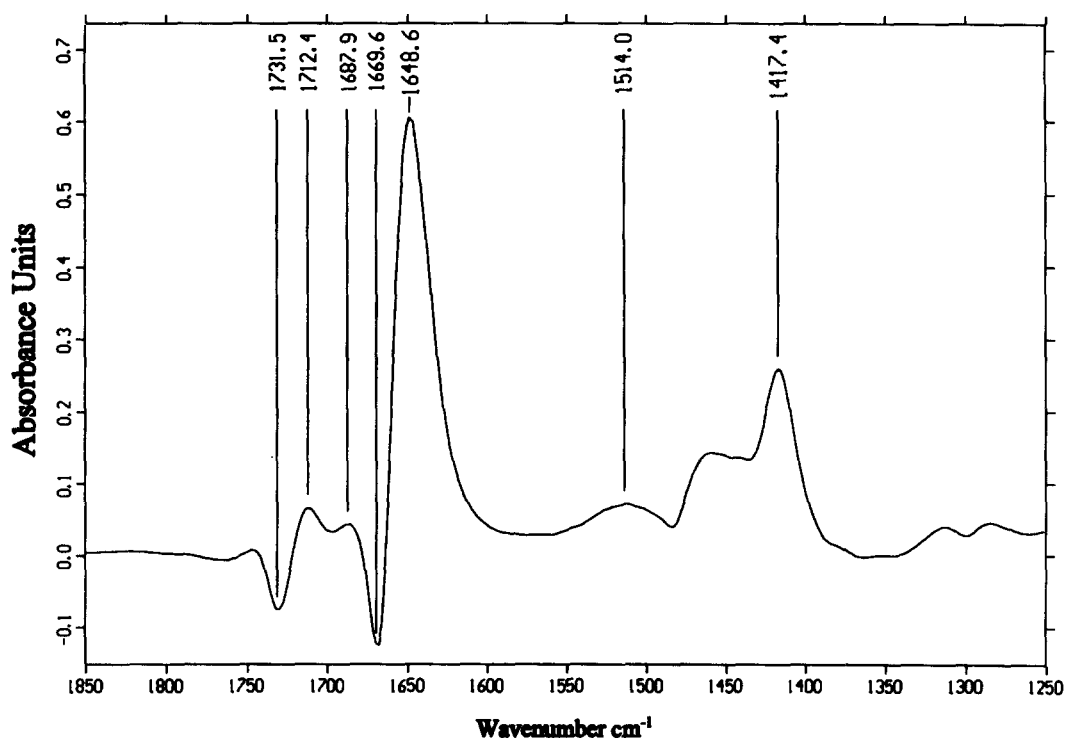

Figure 4 *F*7i.r. difference spectrum from P95/PTHF-acid at 200°C after 43 min

As shown in *Figure 6*, only one amide I band is found if the same experiment is carried out with a chemically equivalent non-crosslinked MMA/5-oxazolinyl-pentyl-methacrylate copolymer S10 containing 10 mol% of oxazoline functional monomer. This is explained by the fact that there is only one kind of chemical environment for the esteramide groups.

For quantitative evaluations of reaction kinetics the two amide I bands must be taken into account. Total conversion is equivalent to the sum of integration values of both peaks. However, it is nearly impossible to calibrate this two band spectrum. For the following investigations the peak at

$1653 \, \text{cm}^{-1}$ is used. For all systems the maximum conversion is normalised, i.e. all curves can be compared with each other.

Quantitative information about the amide I band at $1653 \, \text{cm}^{-1}$ is displayed in *Figure 7*. For small particles of 110 nm diameter the apparent conversion inside the particle is much lower than for 270 nm and 520 mn particles. In contrast, the oxazoline conversions of large and medium particles are very similar. Obviously the maximum conversion in the bulk does not only depend on the surface/volume ratio. With increasing diameter the increasing diffusion distance causes decreasing bulk conversion.
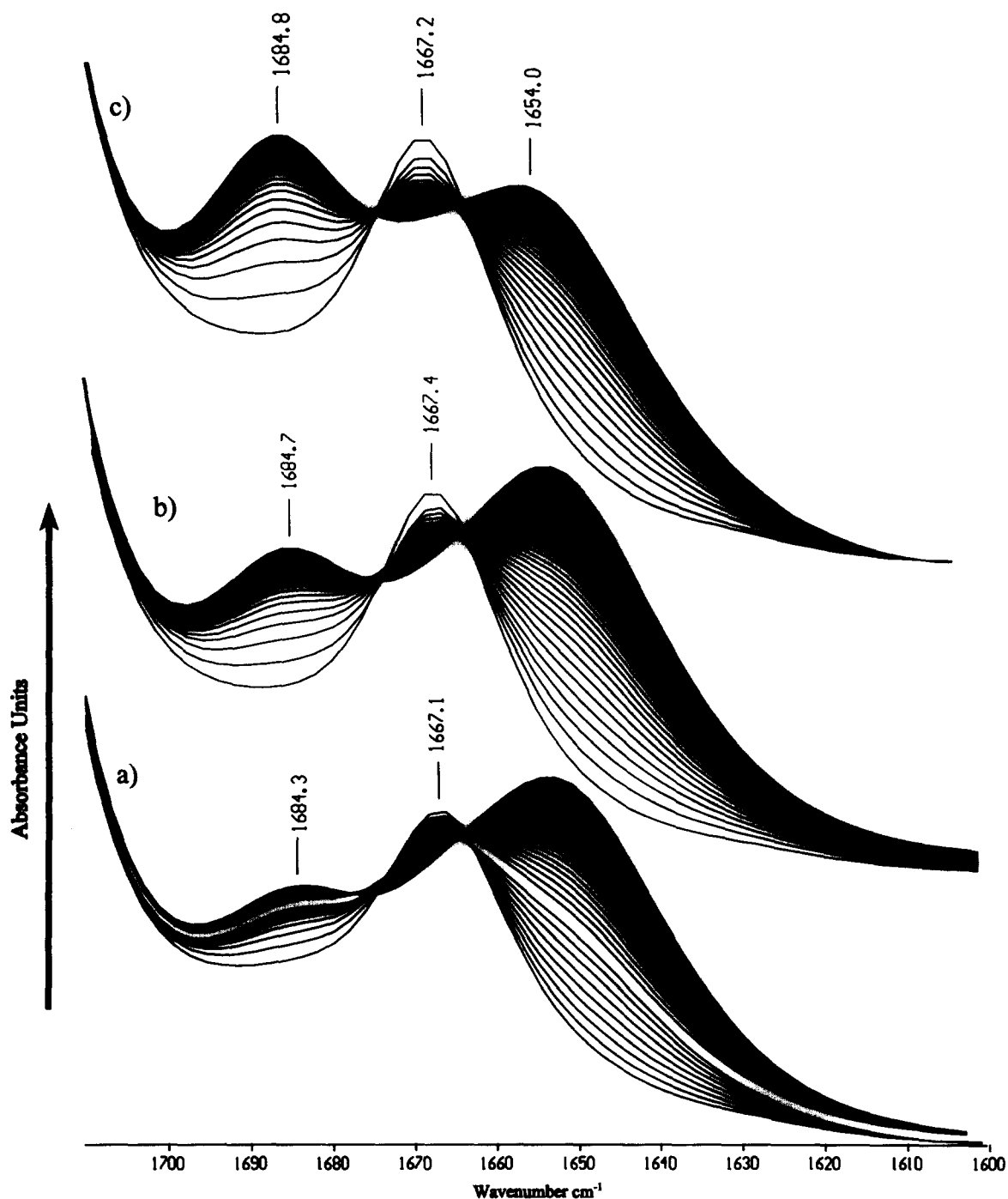
Figure 5 *F*T i.r. spectra from the systems P20-Da (a), P20-Db (b), P20-Dc (c) /PTHF-acid from 60 s to 20 min every 30 s

Variation of the reaction temperature

The reaction kinetics for the heterogeneous systems P10 and S10 with PTHFCOOH were measured at 170, 180, 190 and 200°C. The experiment was done as described above. As is apparent in *Figure 8*, only the temperature-independent amide I band at 1687 cm^{-1}, which is assigned to the amide on the surface, is evaluated quantitatively for S10.

Clearly the initial slope of the curves is steeper for higher temperatures. Next to that the slope gets very small after a certain amount of time, which can be assigned to a diffusion controlled reaction inside the particles. The initial slope is proportional to the reaction rate constant. It changes from $k = 4.2 \times 10^{-1}$ s^{-1} at 200°C to $k = 4.0 \times 10^{-4}$ s^{-1} at 170°C (see *Table 2*). With these data an apparent activation energy is calculated to be 140 kJ. The corresponding activation

energies for P10 particles are determined for both amide I bands separately. *Figure 9* shows the Arrhenius plot for four different temperatures. From the slope of the curve the apparent activation energies were calculated with 61 kJ mol^{-1} for the band at 1687 cm^{-1} and 79 kJ mol^{-1} for the band at 1653 cm^{-1}. It is only an apparent activation energy, because of the diffusion controlled reaction in the melt. Earlier investigations from melt reactions in heterogeneous systems showed an activation energy in the same range[16]. The difference of 18 kJ mol^{-1} between the activation energies of the two amide I bands for P10 can also be explained by the location of the functional groups at the surface or in bulk because oxazoline groups at the surface are easier to access. The higher activation energy of 140 kJ mol^{-1} calculated for S10 is remarkable. Possibly the domain size which is in the micrometre range of this phase
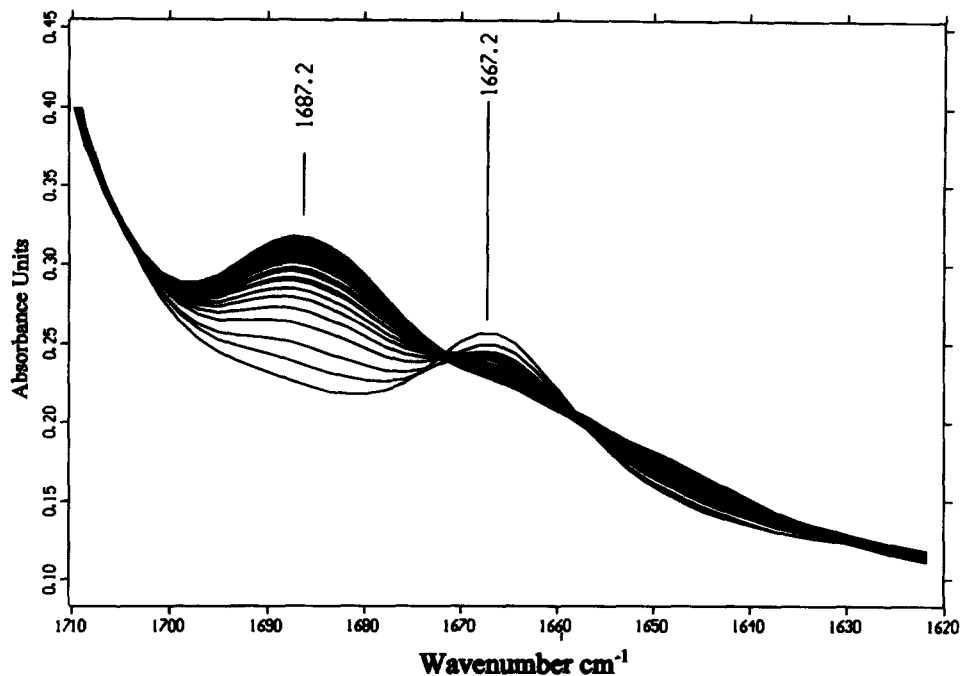
Figure 6 *FT*i.r. spectra from the system S10/PTHF-acid from 60 s to 20 min every 30 s
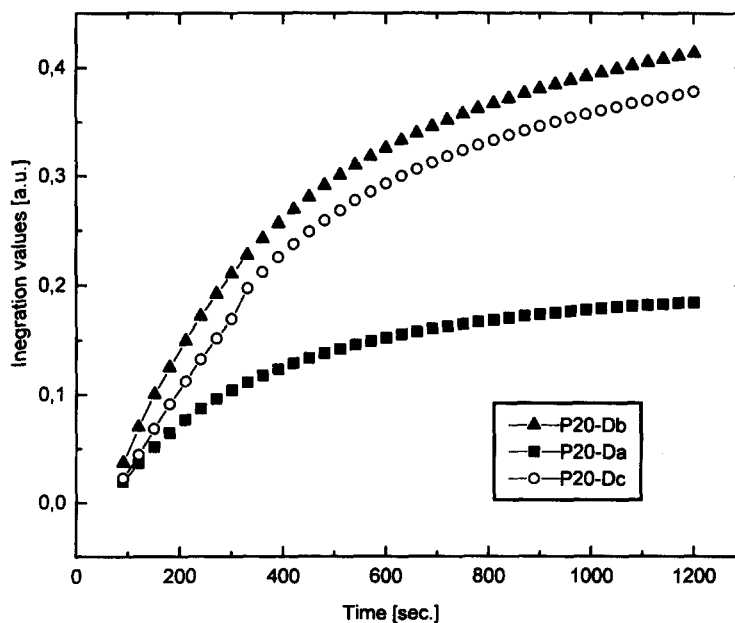

Figure 7 Kinetics of P20-Da,b,c/PTHF-acid at 200°C calculated from the band at 1653 cm^{-1}

separated system is so large that the apparent activation energy increases because of diffusion.

A control experiment with the homogeneous system S10/stearic acid showed that this reaction proceeds much faster but unfortunately the band locations disabled a more detailed evaluation.

Variation of oxazoline functionality

Oxazoline content was varied from 10 to 95 mol% at a reaction temperature of 200°C at steady crosslinking density particle sizes ranging from 210 to 270 nm. The results concerning the reaction of oxazoline functional particles with PTHF-COOH are listed in *Table 1*. For a higher oxazoline functionality, a higher conversion is expected. According to *Figure 10* the kinetics with respect to the amide I band at 1653 cm^{-1} demonstrate that both the initial

slope and the maximum of the curve are higher for high oxazoline contents. The upper curve represents the largest amount of functional groups and it can be seen that there is still no plateau after 1750 s in contrast to the other experiments.

Variation of the crosslinking density and stoichiometry

Particles of the same size, with the same amount of oxazoline groups but different crosslinking densities with EGDMA content varying between 1 and 10 mol% were reacted with PTHF-COOH at 200°C. In contrast to the other parameters it can be seen in *Figure 11* that the effect on the amide I band at 1653 cm^{-1} of changing the crosslinking density is very low. The maximum conversion as well as the initial slope are quite similar for all samples. In conclusion, crosslinking density in the observed range only marginally
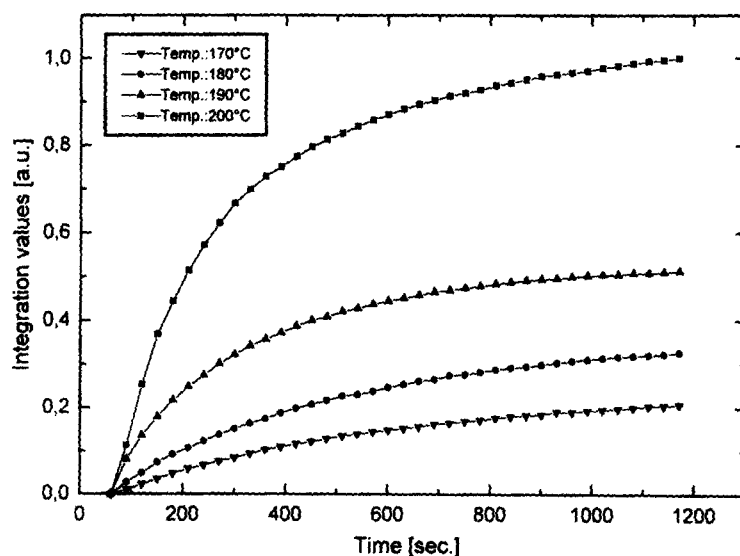
Figure 8   Kinetics of S10/PTHF-acid calculated from the band at 1687 cm^{-1} for four different temperatures
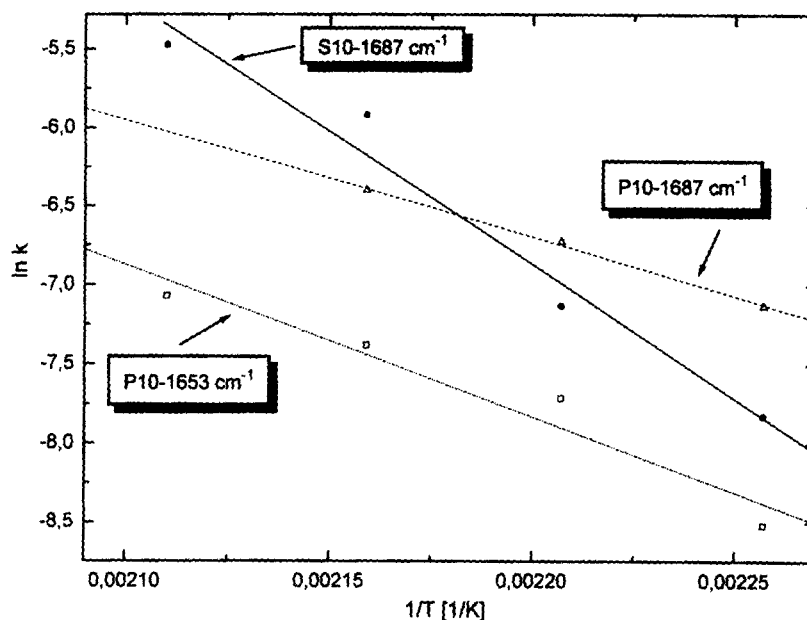

Figure 9   Arrhenius plot of the systems P95/PTHF-COOH (1653 cm^{-1}, 1687 cm^{-1}) and S10/PTHF-COOH (1687 cm^{-1})
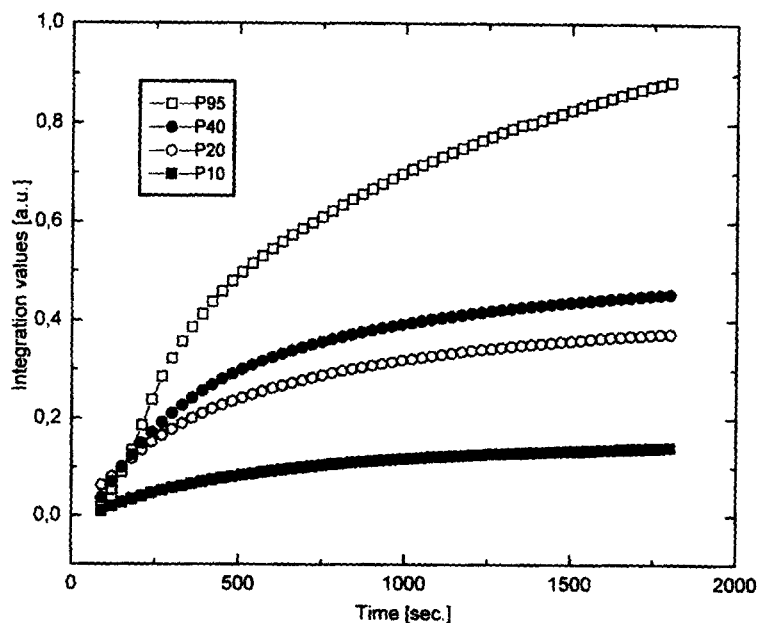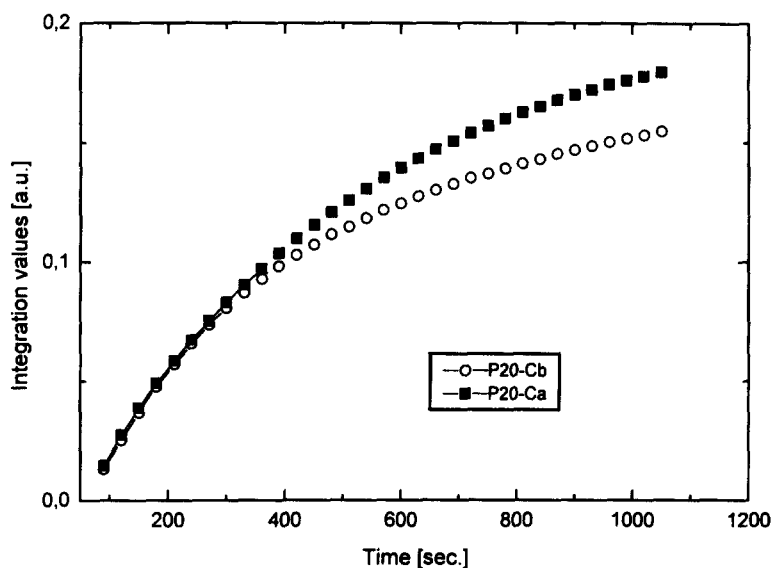

Figure 10   Kinetics of P10,20,40,95/PTHF-acid at 200°C calculated from the band at 1653 cm^{-1} for four different functionalities

Table 2 Reaction rate constants at different temperatures for the system P95/PTHF-acid

Temperature (°C)	ln k S10 (1687 cm^{-1})	ln k P10 (1687 cm^{-1})	ln k P10 (1654 cm^{-1})
170	−7.824	−7.131	−8.517
180	−7.131	−6.725	−7.710
190	−5.915	−6.400	−7.380
200	−5.473	–	−7.070

Figure 11 Kinetics of P20-Ca,b/PTHF-acid at 200°C calculated from the band at 1653 cm^{-1} for two different crosslinking densities
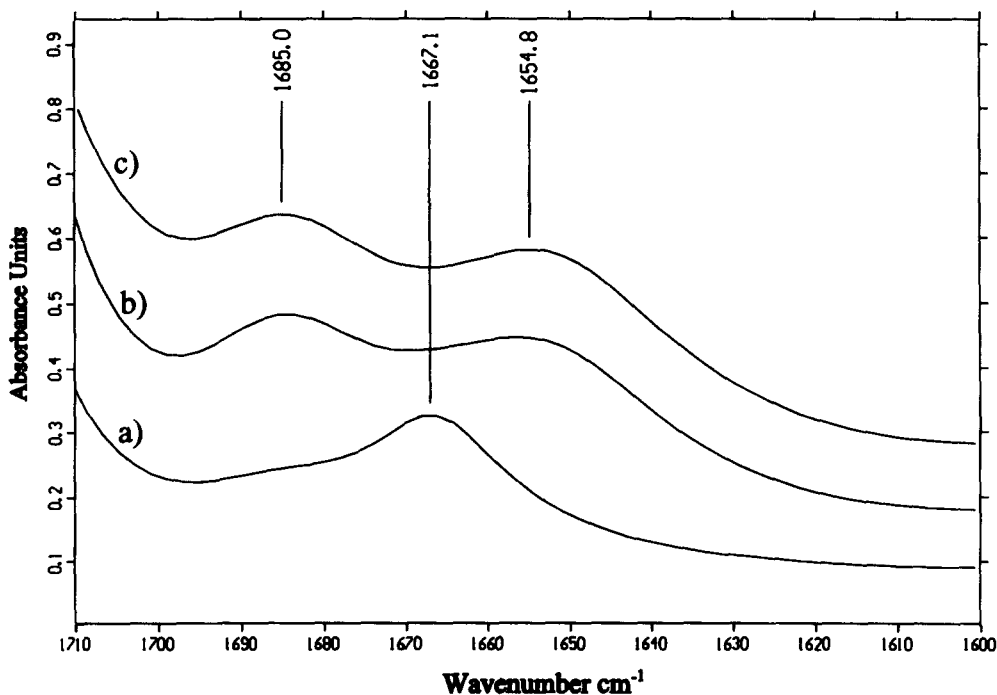
Figure 12 *F*Ti.r. spectra of the system PTHF-COOH/P20 at 200°C after 20 min, with acid:oxazoline ratios of (a) 1:10, (b) 1:1 and (c) 1:0.5

affects rate constant and diffusion of PTHF-COOH molecules.

The molar ratio of carboxylic acid to oxazoline groups varied from 1:0.5 to 1:10. For all other reactions the ratio of 1:2 is used. *Figure 12* shows the final spectra after 20 min. The lower curve (*Figure 12a*) represents the sample with 10 mol% of PTHF-COOH with respect to oxazoline groups. Only the amide I band at 1687 cm^{-1} can be detected in extremely low absorbance. Therefore, at low PTHF-COOH/

oxazoline molar ratios oxazoline groups at the surface were converted. For molar ratios of 1:1 and 1:0.5 both amide I bands at 1687 cm^{-1} and 1653 cm^{-1} can be seen clearly in the middle (*Figure 12b*) and upper (*Figure 12c*) curve. There are no significant differences between the samples with PTHF-COOH/oxazoline molar ratios varying between 1:0.5 and 1:1. Fast formation of the amide I band at 1687 cm^{-1} and typical diffusion controlled reaction, reflected by amide I band formation at 1653 cm^{-1} is

observed. The variation of stoichiometry clearly indicates that PTHF-COOH reacts first with oxazoline groups at the surface, followed by diffusion into the particle to react with bulk oxazoline groups.

CONCLUSIONS

Oxazoline functional polymer particles with controlled diameter, functionality and crosslink density are model systems to study the kinetics of the reaction of functionalised polymer particles with a reactive telechelic polymer. On-line *FT*i.r. spectroscopy is a powerful tool to monitor such reactions in bulk and at interfaces. In the case of oxazoline functional acrylic particles and bis(carboxylic acid)-terminated oligo(tetrahydrofuran) it was possible to identify the influence of parameters like particle size, crosslinking density, functionality, stoichiometry and reaction temperature on reaction kinetics. It was found that two amide I bands at $1687\,cm^{-1}$ and $1653\,cm^{-1}$ reflect the reaction occurring at the surface or in the bulk of the particles. The ratio of bulk to surface reaction is primarily dependent on the average particle size. The activation energy for the surface reaction with $61\,kJ\,mol^{-1}$ was found to be $18\,kJ\,mol^{-1}$ lower than for the bulk reaction. In contrast, the uncrosslinked polymer showed an apparent activation energy of $140\,kJ\,mol^{-1}$, possibly because of the large domain size of the heterogeneous system.

ACKNOWLEDGEMENTS

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