ELSEVIER

PII: S0032-3861(96)01052-X

Polymer Vol. 38 No. 17, pp. 4491–4497, 1997

0032-3861/97/$17.00 + 0.00

Crosslinking and drying of a two-component waterborne coating monitored by a functionalized charge-transfer fluorescence probe

Herman J. Verhey, Chris H. W. Bekker and Jan W. Verhoeven*
Department of Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands

and Leo G. J. van der Ven and Johannes W. Hofstraat
Akzo Nobel Central Research, Location Arnhem, Velperweg 76, POB 9300, 6800 SB Arnhem, The Netherlands
(Received 10 April 1996; revised 31 October 1996)

A donor-bridge-acceptor fluorophore with extreme sensitivity to environmental influences has been attached covalently to a polyamino crosslinker. It was found that the progress of the crosslinking reaction with an aceto–acetate functionalized polyacrylate dispersion can be monitored from the fluorescence wavelength shift of the fluorophore. Also formation and drying of films applied from the resulting labelled dispersion induces a significant wavelength shift of the fluorescence of the incorporated label. © 1997 Elsevier Science Ltd.

(Keywords: ceto-acetate functionalization; film formation; polyacrylate dispersion)

INTRODUCTION

Waterborne dispersions and emulsions are widely used in many areas of industry. In the pharmaceutical industry dispersions are used, for example, for diagnostic tests. The coating and adhesives industry is one of the main users of dispersions. Due to the increasing emphasis on environmental aspects, the development of paints with a lower content of organic solvents is forced. High performance waterborne systems penetrate slowly into the market. In order to obtain the desired performance e.g. for automotive application, chemical curing of the film is essential. For waterborne systems this curing process interferes with the film formation process, which causes difficulty in meeting requirements with respect to water sensitivity and solvent resistance.

In this article a new technique is introduced to monitor changes taking place on a molecular level during the curing and film forming process of a polymeric (polyacrylate) dispersion.

As we have shown in a number of earlier publications[1–3], the fluorescent probe molecule 'Fluoroprobe' (*Figure 1*) acts as a very sensitive sensor for (molecular) changes taking place in its environment. It was found that Fluoroprobe does not only display its sensor function in liquid, low molecular weight systems, but can also be applied to monitor a variety of polymeric properties such as polarity, mobility, morphology and penetrability by organic solvents[4–9].

Recently, we have succeeded in extending Fluoroprobe with a maleimido-functionality, yielding 'maleimido-Fluoroprobe' (MFP, *Figure 1*). This system can be covalently attached to (bio)polymers, by conjugation of the maleimide group with reactive groups in such polymers. The maleimido-functionality particularly allows conjugation to amino- and thiol-groups, both important functionalities in (bio)polymers.

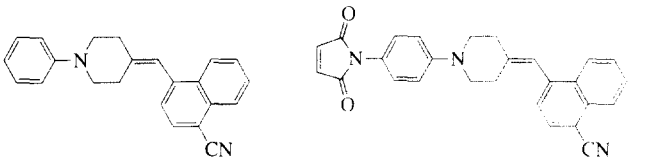
The photophysical properties of MFP and its conjugates have been extensively described elsewhere[10]. It turned out that MFP has the highly desirable property that it is non-fluorescent, whereas its conjugates have fluorescent properties similar to those of Fluoroprobe. Observation of fluorescence thus ensures successful coupling to the host system, furthermore, excess MFP (if present) does not disturb fluorescence of the labelled sites.

Donor–receptor type fluorescent probes have already been used earlier to investigate the properties of polyacrylates[11–13], but the current possibility of specifically introducing the very sensitive 'Fluoroprobe' into these systems opens up a new range of possibilities with regard to the photophysical probing of nanoscale changes in such systems.

In this paper we report the application of MFP to the investigation of a two-component aceto–acetate functional waterborne polyacrylate coating. This class of dispersions is currently of interest because of the increasing amount of environmental regulations, creating the need for coatings which are essentially free of organic solvents.

Key factors for obtaining a coating with certain chemical and physical properties (e.g. solvent resistance)

* To whom correspondence should be addressed



"Fluoroprobe" (FP) "Maleimido-Fluoroprobe" (MFP)

Figure 1 Fluoroprobe and maleimido–Fluoroprobe

are dispersion composition and film formation. Especially the latter is, of course, of the greatest importance in assessing the quality of the film. In the dispersion under investigation the quality of the film is improved by application of a two-component system; one component being aceto–acetate functionalized polyacrylate particles, the second a trifunctional amino-crosslinker[14,15]. The crosslinker can both act to increase the hardness of the particles, after its rapid diffusion into the particles, a process which does not improve the film properties, and, on the other hand, may provide interfacial or interstitial bonds between the particles, which leads to the formation of films with good physical properties.

For these reasons the main topics of this study will be investigation of the chemical curing (crosslinking) of the dispersion, and the subsequent drying process. MFP was used to monitor the changes taking place (on a molecular scale) during this chemical curing, and furthermore during the drying of films which were formed from the crosslinked dispersion.

For this purpose an MFP-labelled amino-crosslinking agent was synthesized and applied to both a non-functional (used for reference) and an aceto–acetate functional dispersion. The spectral changes taking place during these reactions will be discussed, as well as those taking place during film formation of the investigated dispersion. The characteristics of the investigated dispersions have been documented elsewhere[14,15].

EXPERIMENTAL

Syntheses and procedures

The reactions of all major compounds described are given in *Schemes 1* and *2*. Jeffamine T403® (tradename of Texaco) was used as received. The syntheses of MFP and compound **2** have been described in detail elsewhere[10], as well as the monomer composition of the dispersions coded AcAc 178 and NF 178[14,15]. In the latter publication the reaction of dispersion AcAc 178 with unlabelled Jeffamine T403 has also been described in detail.

Synthesis of the labelled crosslinker (**1**)

In 50 ml of ethanol 0.20 mmol of Jeffamine and 0.20 mmol of MFP (which corresponds to 1% of the amino groups of Jeffamine) were dissolved. A catalytic amount of acetic acid was added, and the solution was heated to 80°C and refluxed under nitrogen for 2 h. After cooling to room temperature the reaction mixture was concentrated *in vacuo*. A ^{1}H nuclear magnetic resonance spectrum was taken of the product, and because the characteristic maleimido-singlet of MFP at 6.83 ppm had fully disappeared the product was used without further purification.

Reaction of dispersion AcAc 178 and compound **1**

While stirring 1.32 g of a 50 wt% mixture of compound **1** and water was added to a 10 g of dispersion AcAc 178 (a ratio of aceto–acetate groups to crosslinker amino-groups of 1/1).

Swelling of dispersion NF 178 with compound **1**

While stirring 1.32 g of a 50 wt% mixture of compound **1** and water was added to 10 g of dispersion NF 178.

Electronic absorption measurements

Electronic absorption spectra were recorded on a Varian Cary 3 spectrophotometer. The samples were contained in 1-cm pathlength-fused silica cells.

Fluorescence measurements

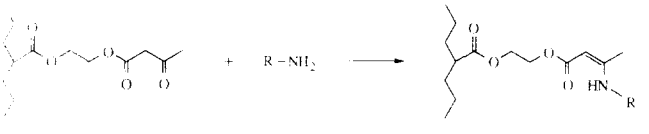
Continuous fluorescence spectra (λ_{ex} = 310 nm) were measured on a Spex Fluorolog 2 spectrofluorimeter in front-face geometry. The samples were contained in 2-mm pathlength-fused silica cells. The spectra were corrected for the detector response.

RESULTS AND DISCUSSION

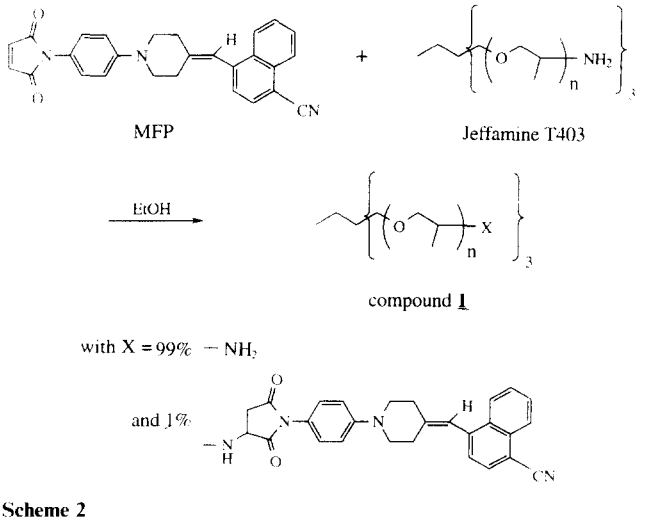
Synthesis of maleimido-Fluoroprobe labelled Jeffamine

In the dispersion under investigation, the trifunctional amino-crosslinker Jeffamine T403® (Texaco) is used to enhance the film properties (such as solvent resistance) of the polyacrylate dispersion (hereafter referred to as 'AcAc 178'[14,15]), which is functionalized with aceto–acetate groups. The chemistry of the crosslinking reaction used (see Experimental) is given in *Scheme 1*, in which, for reasons of clarity, the bulky part of the crosslinker has been designated 'R'.

We decided to label 1% of the amino groups of the crosslinker with MFP. In *Scheme 2* the coupling reaction of Jeffamine T403 with MFP (see Experimental), to yield the labelled crosslinker **1**, is shown.



Scheme 1



Scheme 2

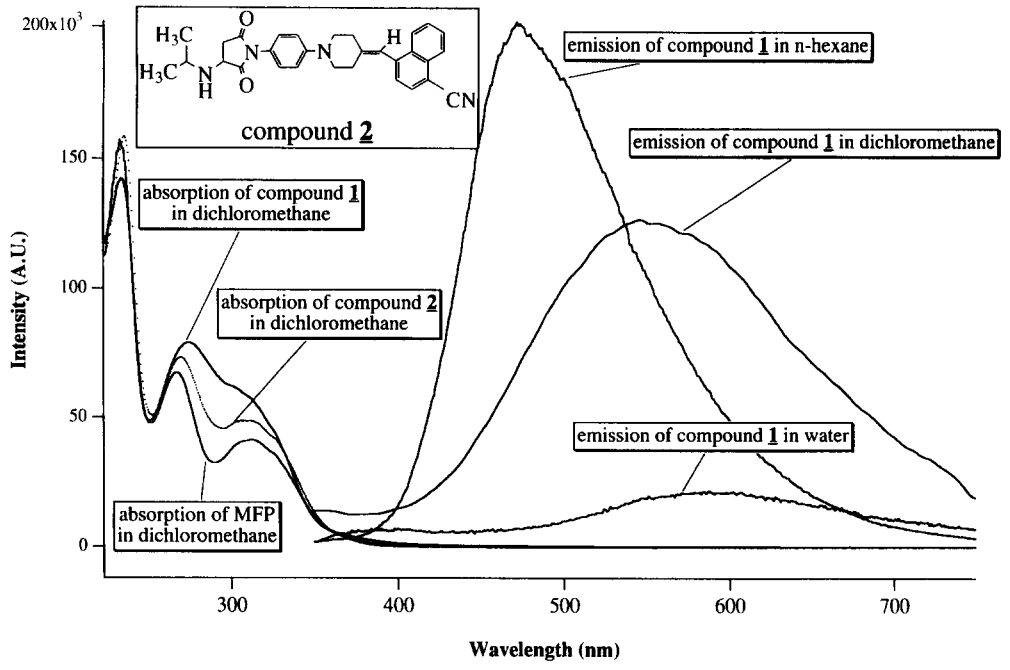


Figure 2 Electronic absorption spectra of MFP and compounds **1** and **2** in CH_2Cl_2 and fluorescence spectra of compound **1** in various solvents

Table 1 Fluorescence maxima of dispersion AcAc 178 during reaction with Jeffamine T403

Reaction time (min)	λ_{max} (nm)	Intensity arbitrary units
0[a]	438	295.5
1	438	219.8
5	438	112.8
60	438	73.4
180	438	51.7
1440	438	39.3

[a] Before addition of Jeffamine

Characterization of the labelled crosslinking agent

The labelled crosslinking agent **1** (see *Scheme 2*) was prepared (see Experimental) to have 1% of the amino groups labelled by reaction with MFP (which itself is non-fluorescent). To ensure that the Fluoroprobe-type photophysical properties of the charge-transfer part of the molecule were restored after reaction, absorption and emission spectra of the labelled compound were taken (*Figure 2*). The absorption spectrum of compound **1** is compared to that of MFP and to that of a model compound consisting of MFP which has reacted with isopropyl amine (compound **2**). The emission spectra are those of compound **1** in *n*-hexane, dichloromethane and water.

From *Figure 2* it can be concluded that, although only a fraction of the Jeffamine has been labelled, the absorption spectrum of compound **1** is dominated by the same absorptions we find in the absorption spectra of MFP and compound **2**. The reason why there is little difference between the absorption spectra of the latter two is explained in detail elsewhere[10]. More important, however, are the emission spectra of compound **1**, it is clearly shown that the solvatochromic properties of the charge-transfer part of the molecule are reinstated after reaction of MFP with Jeffamine. This ensures that compound **1** can be used for probing the mobility and/or polarity of its environment. The observation that compound **1** fluoresces in water is actually quite remarkable, no other CT-type compounds show this behaviour (in protic solvents). It was found, however, that the labelled Jeffamine in water is taken up in micellar structures, so that the CT-part of the molecules is shielded from the aqueous environment, thus enabling fluorescence to occur.

Reference experiments

In order to fully understand the spectral changes taking place during the reaction of the labelled crosslinker **1** and the aceto–acetate functionalized polyacrylate dispersion, two reference fluorescence experiments were carried out. These involved reaction between non-labelled crosslinker and the functional dispersion, and the mixing of the labelled crosslinker **1** with a non-functional polyacrylate dispersion.

First, the reaction between the aceto–acetate functionalizes dispersion (AcAc 178) and the non-labelled crosslinker (Jeffamine T403) was carried out (see Experimental). The fluorescence spectrum was recorded for samples taken from the reaction mixture at various time intervals (see *Table 1* and *Figure 3*). Samples were excited at 310 nm.

From *Table 1* and *Figure 3* it can be concluded that – unexpectedly – the functional dispersion itself fluoresces rather strongly at ≈440 nm. This fluorescence slowly decreases in intensity when the dispersion reacts with the Jeffamine crosslinker. Apparently this fluorescence is caused by side products derived from introduction of the aceto–acetate groups. Also the observation that the non-functional dispersion (which has the same structure as the functional dispersion, except for the aceto–acetate groups) does not show this strong blue fluorescence supports this hypothesis. The excitation spectrum of the functional dispersion (λ_{em} = 440 nm) indeed shows a broad signal which extends to below 310 nm (see below). From the intensity decrease during the crosslinking reaction, it can be concluded that the fluorescing species disappears due to reaction with the amino groups of the crosslinker. However, it is also clear (from the spectrum

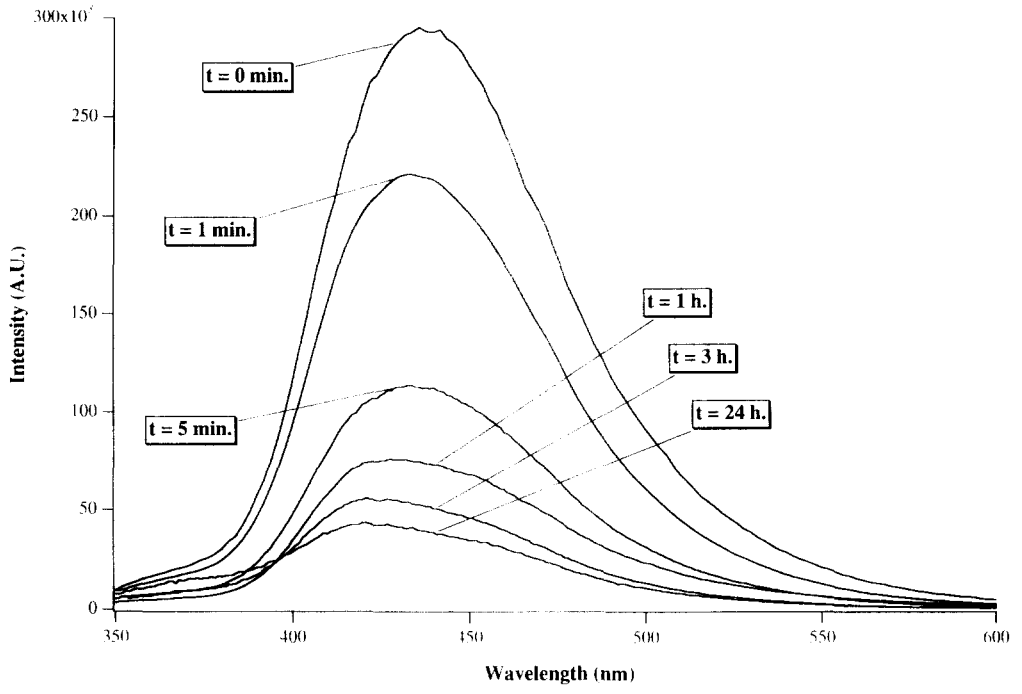


Figure 3 Fluorescence spectra of the functional dispersion during reaction with Jeffamine T403

Table 2 Fluorescence maxima of dispersion NF 178 during reaction with labelled Jeffamine T403 (compound **1**)

Reaction time (min)	λ_{max} (nm)
0[a]	380
1	510
15	512
60	512
120	516
180	516
1440	516

[a] Before addition of compound **1**

Table 3 Fluorescence maxima of dispersion AcAc 178 during reaction with labelled Jeffamine T403 (compound **1**)

Reaction time (min)	λ_{max} (nm)
0[a]	438
1	534
10	527
30	522
70	516
180	512
300	511
1440	511

[a] Before addition of compound **1**

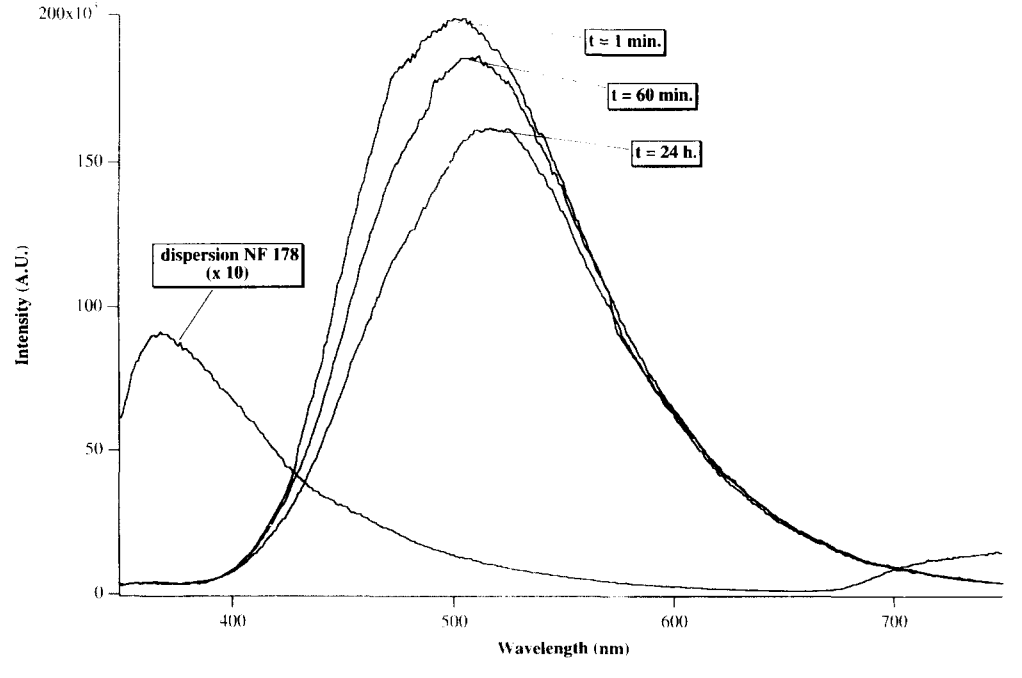


Figure 4 Fluorescence spectra of the non-functional dispersion during interaction with labelled Jeffamine T403 (compound **1**)

taken after 24 h) that not all of these groups have reacted when the crosslinking has finished. The fluorescence maximum seems to slowly shift hypsochromically (from $t = 60$ min onwards), but this is caused by an emission which starts to appear around 400 nm, and slowly increases in intensity. Although the rather strong (impurity) fluorescence of the functional dispersion may seem problematic, it will be shown below that is does not in fact interfere with the Fluoroprobe labelling studies.

The second reference experiment (see Experimental) was the mixing of a non-functionalized dispersion (code NF 178; its contents are the same as those of dispersion AcAc 178, except for the aceto–acetate groups[14,15]) and the labelled Jeffamine (compound **1**). The data of this experiment are compiled in *Table 2* and *Figure 4*. The fluorescence spectrum was recorded for samples taken from the reaction mixture at various time intervals, and samples were excited at 310 nm.

Also the non-functionalized dispersion shows some background fluorescence, but significantly weaker and at a shorter wavelength (≈380 nm) than the functionalized dispersion. Upon addition of the labelled Jeffamine (**1**) the background fluorescence is quenched and substituted by the much stronger and longer wavelength fluorescence of **1**. While the fluorescence of **1** in an aqueous medium is rather weak and located above 600 nm (see *Figure 2*), it thus displays a quite strong and hypsochromically shifted emission in the presence of the dispersion particles. This appears a typical result of penetration of **1** into the polyacrylate particles, which brings the fluorophoric label groups in a less polar environment.

Interestingly, although the interaction of **1** with these non-functional acrylate particles must be purely physical in nature, still a small bathchromic shift (i.e. from 510 to 516 nm) of the fluorescence occurs during the first hours of contact. This phenomenon can probably be attributed to the slow diffusion of polar material into the particles[9].

Reaction of the functional dispersion with the MFP-labelled crosslinker

After the experiments described above (conducted for reference purposes) the main reaction, namely that between the aceto–acetate functional dispersion (code AcAc 178) and the labelled Jeffamine crosslinker (compound **1**) was carried out (see Experimental). The data of this experiment are compiled in *Table 3* and *Figure 5*. The fluorescence spectrum was recorded for samples taken from the reaction mixture at various time intervals, and samples were excited at 310 nm.

As with the non-functional dispersion, the addition of **1** immediately quenches the impurity background fluorescence of the functional dispersion. This fortuitous phenomenon appears to be related to efficient energy transfer from the chromophoric sites in the dispersion to the fluorophoric sites in the label molecules, which are absorbed by the dispersion particles. This was substantiated by recording excitation spectra of the dispersion before, during and after the reaction (*Figure 6*).

After 1 min of reaction the fluorescence of the probe is induced to a large extent by excitation of the fluorescent species present in the dispersion as is substantiated by the similarity of the excitation spectra obtained before (at $\lambda_{em} = 440$ nm) and after (at $\lambda_{em} = 530$ nm, which is the emission wavelength of the probe) addition of compound **1**. The observation that there is, at the same time, no longer an emission present at 440 nm thus makes the occurrence of energy transfer highly probable. After 24 h of reaction the normal excitation spectrum of the probe is restored, which indicates that, as observed in the reference experiment without label, the fluorescing species present in the AcAc 178 dispersion has disappeared after reaction with the amino functionalities of the crosslinker.

Returning to *Table 3*, it is clear that whereas in the non-functional dispersion **1** was found to fluoresce around 510 nm, in the functional dispersion its fluorescence initially appears at a significantly longer wavelength (534 nm). This is consistent with a more polar environment in the latter due to the presence of the aceto–acetate groups. Upon reaction of the two compounds, however, a significant hypsochromic shift occurs (from 534 to 511 nm), in contrast to the small bathchromic shift (512 to 516 nm) observed upon prolonged interaction of **1** with the non-functional dispersion. Clearly the hypsochromic shift must be related to the crosslinking reaction in which the aceto–acetate groups are transformed (see *Scheme 1*), while at the same time the rigidity of the polymer matrix increases, which is known to induce a hypsochromic shift of the fluorescence for embedded fluorophores of the present type[4–6]. The slow increase in fluorescence intensity during the reaction can also be explained satisfactorily by the decreasing mobility (and, to a lesser extent, the polarity) of the environment of the labels.

The observed shift of the fluorescence wavelength indicates that after 1 h of reaction about 70–80% of the reaction has been completed, after 3 h it has been fully terminated. For comparison, in *Figure 7* the fluorescence data as compiled in *Table 3* are plotted, together with those obtained by monitoring the progress of the reaction via titration of the aceto–acetate groups[14,15].

Clearly a good agreement exists between the reaction of the aceto–acetate groups (and the resulting increase in rigidity of the particles) and the fluorescence wavelength of the labels. These results indicate that significant crosslinking occurs within the functionalized polyacrylate particles, and that this can be quantitatively monitored by the present fluorescence technique.

Film formation and drying process

The quality of a coating, as has already been pointed out in the Introduction, hinges on the formation and on the composition of the film. Much research is therefore directed towards chemical curing processes which enhance the physical properties of such films (e.g. solvent resistance), while simultaneously attempting to limit the drying time. In the literature several models are presented to describe this process[16].

After investigation of the curing process, which occurs mainly within the polymer particles (as described in the earlier sections), we also attempted to monitor the drying process of films, made from the dispersion which was investigated in the previous section. On quartz slides films were applied, using samples taken from the reaction mixture at different points (A, B, C) in time. The fluorescence spectrum of these films was recorded at regular time intervals ($\lambda_{ex} = 310$ nm) during drying and film formation. The data of this experiment are compiled in *Table 4* and *Figure 8*.

As expected from the data obtained for the crosslinking reaction, the starting wavelength of film A,

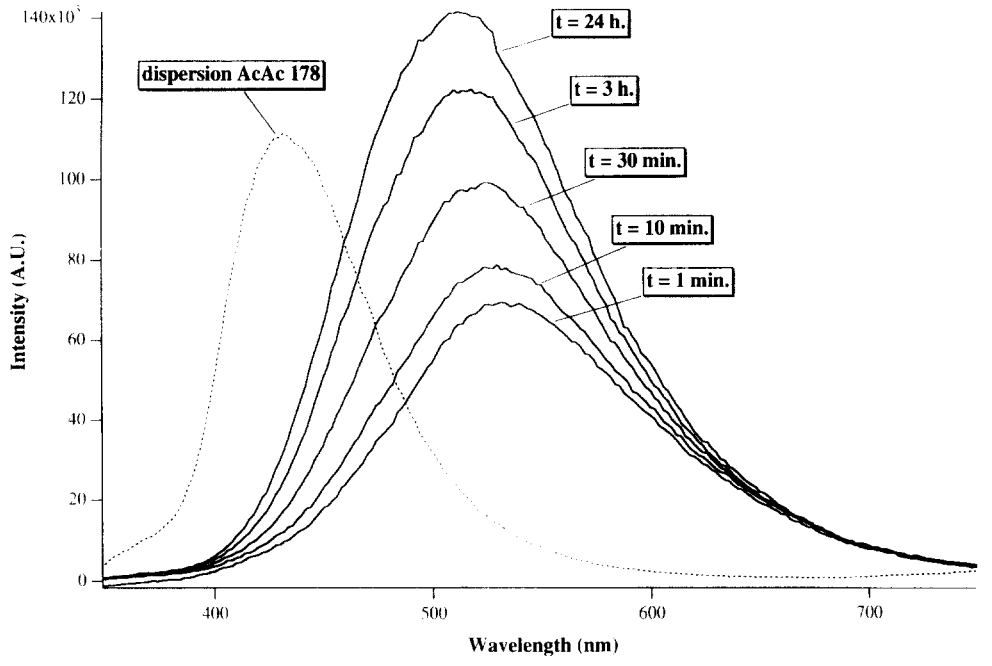


Figure 5 Fluorescence spectra of the functional dispersion before (- - -) and during reaction with the labelled crosslinker **1**

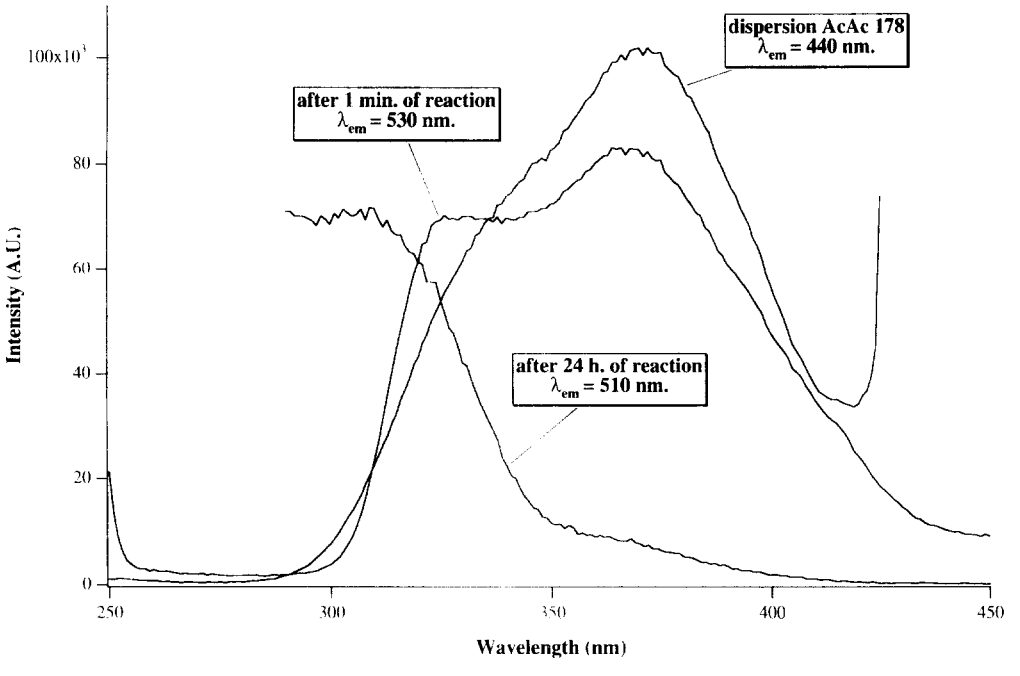


Figure 6 Excitation spectra of the functional dispersion before, during and after reaction with **1**

applied immediately after addition of the (labelled) crosslinker, is longer than that of the other two films. It is difficult, however, to draw any conclusions from the change in fluorescence wavelength observed during the drying of film A, because the crosslinking reaction, also giving rise to a fluorescence shift to shorter wavelengths, is still taking place. The other two samples, taken at 3 and 24 h respectively, behave very similarly throughout the drying process, which is consistent with the earlier conclusion[14] that after 3 h the crosslinking reaction has been virtually completed. In both B and C the drying process induces a hypsochromic shift of about 20 nm.

From the fact that the fluorescence wavelength of all three samples after 3 h of drying is much shorter than that in the dispersion after even 24 h of reaction (551 nm), we can conclude that, even though the labels are mainly embedded inside the particles, they still respond markedly to the disappearance of the water from the film.

CONCLUDING REMARKS

The functional probe molecule MFP can be coupled to an amino-crosslinking agent. Because the labelled crosslinking molecules diffuse rapidly into the particles of an aceto–acetate functionalized polyacrylate dispersion, the progress of the reaction between a crosslinker and the

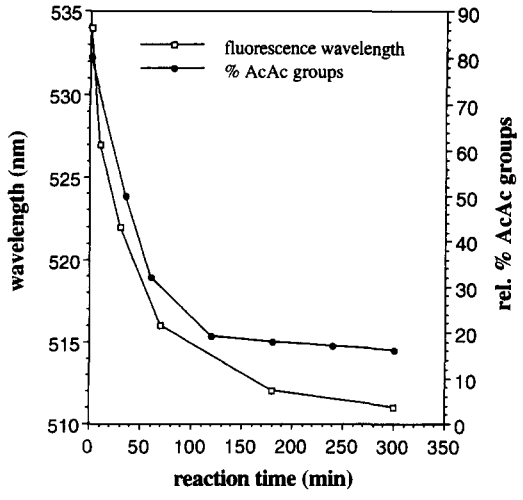


Figure 7 Fluorescence maxima of the labels and relative % of AcAc-groups during the reaction of the functional dispersion AcAc 178 with; (a) Jeffamine T403 (titration); (b) compound **1** (fluorescence)

Table 4 Fluorescence maxima of films, applied from dispersion AcAc 178 during and after its reaction with labelled Jeffamine T403 (compound **1**)

Drying time (min)	λ_{max} (nm)		
	Film A	Film B	Film C
0[a]	534	512	511
1	524	506	504
5	522	500	499
10	508	499	496
15	499	494	495
60	497	493	491
120	496	492	490
180	496	492	489

[a] Dispersion before application to the slide

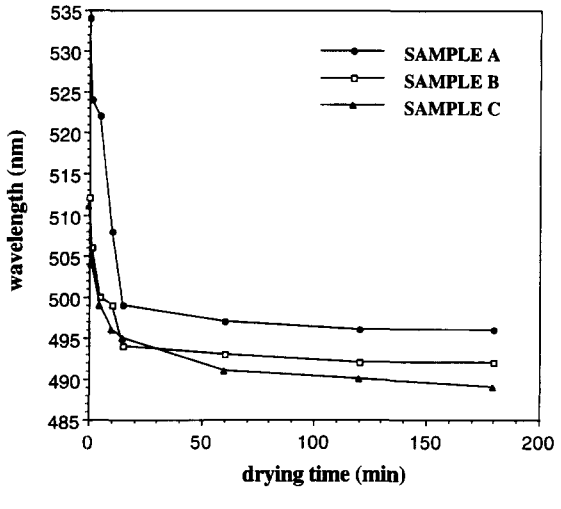


Figure 8 Fluorescence maxima observed during the drying process of films made from the functional dispersion

aceto–acetate groups within the particles can be followed by monitoring the changes in the fluorescence spectrum of the labels. From comparison with other techniques[14,15] it was found that these changes in the fluorescence spectrum give a quantitative indication of the progress of the reaction where the changes in fluorescent wavelength are proportional to the disappearance of aceto–acetate groups (see *Figure 7*).

The fluorescence of films made by application of material taken from the reaction mixture at different times during the reaction provides further information above the relative speed and degree of drying of these films. While clear indications are found that changes taking place on the particle interfaces during drying and film formation also lead to a response of the embedded fluorophore, as yet no quantitative separation of these inter-particle effects from intra-particle effects has been achieved.

The scope of MFP and related charge-transfer probes as fluorescent labels in other macromolecular systems is presently under investigation. These investigations will especially be directed at systems in which the MFP is not – as in the present case – attached to a crosslinking reagent, but rather to the backbone of artificial polymers and proteins.

REFERENCES

1. Mes, G. F., De Jong, B., van Ramesdonk, H. J., Verhoeven, J. W., Warman, J. M., De Haas, M. P. and Horsman van den Dool, L. E. W., *J. Am. Chem. Soc.*, 1984, **106**, 6524.
2. Hermant, R. M., Bakker, N. A. C., Scherer, T., Krijnen, B., Verhoeven, J. W., *J. Am. Chem. Soc.*, 1990, **112**, 1214.
3. Scherer, T., Hielkema, W., Krijnen, B., Herman, R. M., Eijckelhoff, C., Kerkhof, F., Ng, A. K. F., Verleg, R., van der Tol, E. B., Brouwer, A. M. and Verhoeven, J. W., *Recl. Trav. Chim. Pays-Bas*, 1993, **112**, 535.
4. Jenneskens, L. W., Verhey, H. J., Van Ramesdonk, H. J., Witteveen, A. J. and Verhoeven, J. W., *Macromolecules*, 1991, **24**, 4038.
5. Van Ramesdonk, H. J., Vos, M., Verhoeven, J. W., Möhlmann, G. R., Tissink, N. A. and Meesen, A. W., *Polymer*, 1987, **28**, 951.
6. Jenneskens, L. W., Van Deursen, J. P. B., Verhey, H. J., Van Ramesdonk, H. J. and Verhoeven, J. W., *Appl. Fluor. Technology*, 1991, **3**, 11.
7. Jenneskens, L. W., Verhey, H. J., Van Ramesdonk, H. J. and Verhoeven, J. W., *Macromolecules*, 1992, **25**, 6365.
8. Jenneskens, L. W., Verhey, H. J., Van Ramesdonk, H. J., Verhoeven, J. W., Van Malssen, K. F., and Schenk, H., *Recl. Trav. Chim. Pays Bas*, 1992, **111**, 507.
9. Verheij, H. J., Gebben, B., Hofstraat, J. W. and Verhoeven, J. W., *J. Polym. Sci., Part A: Polym. Chem.*, 1995, **30**, 399.
10. Verheij, H. J., Bekker, C. H. W., Verhoeven, J. W. and Hofstraat, J. W., *New J. Chem.*, 1996, **20**, 809.
11. Loutfy, R. O., *J. Polym. Sci., Part B: Polym. Phys.*, 1982, **20**, 825.
12. Paczkowski, J. and Neckers, D. C., *Macromolecules*, 1992, **25**, 548.
13. Schaeken, T. C. and Warman, J. M., *J. Phys. Chem.*, 1995, **99**, 6145.
14. Van der Ven, L. G. J., Lamping, R. R., Geurink, P. J. A., and Van Dalen, L., *Proceedings of Twenty-second Fatipec Congress*, Budapest, 1994, pp. 105–118.
15. Geurink, P. J. A., Van Dalen, L., Van der Ven, L. G. J. and Lamping, R. R., *Progress in Organic Coatings*, 1996, **27**, 73.
16. Daniels, E. S. and Klein, A., *Progress in Organic Coatings*, 1991, **19**, 359.