Application Note V-254

Curing of an Acrylate Glue – Rheology with Simultaneous FTIR-Spectroscopy

Klaus Oldörp, Thermo Fisher Scientific, Material Characterization, Karlsruhe, Germany

Introduction

Everybody who has ever worked with glues knows that timing is one of the crucial issues. Subsequently technical leaflets for glues sometimes look like timetables. Terms like pot life, open time, time for minor adjustments, curing time or time to reach maximum bonding strength, are used to describe the properties of glues and to give guidance for their successful application.

For the development of new glues all these times have to fit the application to create a product the market targeted will accept. For example, depending on the method to apply the glue the open time needs to be adjusted to avoid curing before the parts have been joined.

A rheometer is an essential tool to characterise not only the uncured glue but especially the curing process itself. No matter if a drying glue, a 2 component system, a thermally curing glue, or an UV-curing glue is investigated, due to their wide range of accessories the Thermo Scientific HAAKE MARS or the Thermo Scientific HAAKE RheoStress rheometers are the perfect tools to characterize its curing behaviour.

Still, the classical limitation of rheological methods remains: a rheometer can only tell us **what** happens during the curing but it does not tell us **why**. The "why" becomes especially important when we want to understand why a batch of the glue shows other properties than the expected ones or when we want to develop glue for a new application. To overcome this limitation, the rheological data needs to be combined with data from another analytical method able to detect what happens on the molecular scale. A perfect match is the FTIR spectroscopy, a method, which is able to identify and quantify different chemical groups in a substance or in a mixture of substances.

The disadvantage of running tests on two separate instruments is the extra effort it takes to prepare two different samples following different procedures for each method. Plus, as a consequence, this approach makes it virtually impossible to collect both sets of data on two identical samples under exactly the same conditions.

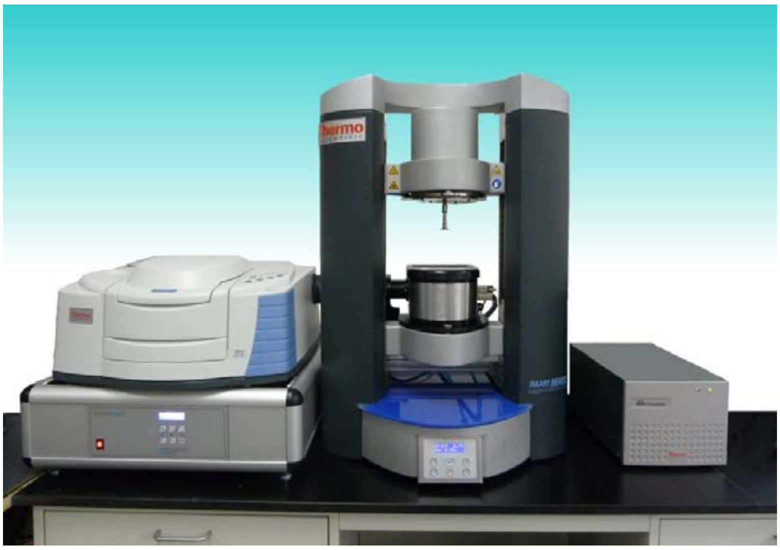


Fig. 1: The Thermo Scientific HAAKE MARS rheometer (centre) with a mounted Rheonaut module* connected to a Thermo Scientific Nicolet iS10 spectrometer (left).

To combine rheological tests with FTIR-spectroscopy avoiding the aforementioned disadvantages, the Rheonaut module has been developed, a unique combination of a temperature control module for the HAAKE MARS rheometer and an Attenuated Total Reflection (ATR) cell with its own IR detector. With the Rheonaut module the HAAKE MARS can be combined with an FTIR spectrometer to one analytical setup (Fig. 1). Only with this unique combination it is possible to record the mechanical changes of the curing glue while at the same time and, even more important, on the same sample IR spectra can be collected to track the chemical changes inside the sample.

Experimental

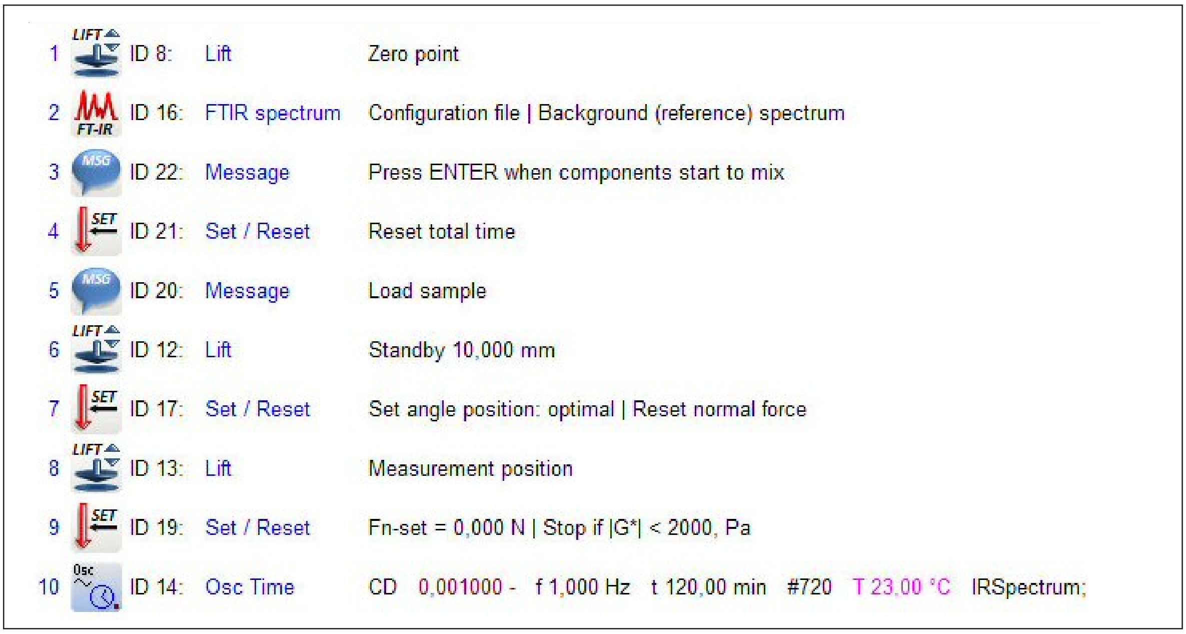
A consumer-grade 2 component acrylate glue was prepared by mixing both components outside the rheometer according to its technical leaflet. Part of this mixture was transferred into the rheometer.

When designing the test method, two important facts about curing materials have to be kept in mind:

1. The curing reaction starts already outside the rheometer. To be able to compare different datasets, the test method contains an element to reset the internal time the moment the 2 components mix (Fig. 2, step 3 and 4). Otherwise, any deviation in the loading procedure would lead to an undefined offset on the time axis.
2. The biggest changes happen during the first moments of the curing process. The test method has been optimized to start the test as quickly as possible after the sample was put onto the lower plate. The upper geometry is lowered to 10 mm before loading the sample to shorten the time to reach the measuring gap (Fig. 2, step 6). The test itself starts immediately after the measuring gap has been reached without any time for thermal or mechanical equilibration.

The rheological part of the test method is an oscillation time curve (Fig. 2, step 10) i.e. the oscillation parameters are kept constant to detect only changes in the sample due to the curing. Since drastic changes of the moduli are ex-

* Resultec developed the Rheonaut module for exclusive resale by Thermo Fisher Scientific.



1	ID 8:	Lift	Zero point
2	ID 16:	FTIR spectrum	Configuration file | Background (reference) spectrum
3	ID 22:	Message	Press ENTER when components start to mix
4	ID 21:	Set / Reset	Reset total time
5	ID 20:	Message	Load sample
6	ID 12:	Lift	Standby 10,000 mm
7	ID 17:	Set / Reset	Set angle position: optimal | Reset normal force
8	ID 13:	Lift	Measurement position
9	ID 19:	Set / Reset	Fn-set = 0,000 N | Stop if |G*| < 2000, Pa
10	ID 14:	Osc Time	CD 0,001000 - f 1,000 Hz t 120,00 min #720 T 23,00 °C IRSpectrum;

Fig. 2: Test method for 2 component glues in Thermo Scientific HAAKE RheoWin measuring and evaluation software. In step 3 and 4 the time is reset when the 2 components mix outside the rheometer. In step 6 the upper geometry moves to a 10 mm gap to minimize lift travel after the sample is put onto the lower plate. Step 8 moves the upper geometry to the measuring gap and step 10 starts the test without waiting for temperature equilibration.

pected during the test, the rheometer's CD-mode is used to ensure optimum signal quality throughout the whole test. A small amplitude from the sample's linear viscoelastic range (LVR) is selected, which still yields data with a good signal-to-noise-ratio from the uncured glue.

The evaluation can be based on the storage modulus G' representing the elastic part of the viscoelastic properties and the loss modulus G" representing the viscous part (Fig. 3).

The freshly prepared glue is mainly viscous, G" dominates over G' with phase angle (δ) values around 70° (purely viscous: δ = 90°, purely elastic: δ = 0°). The curing reaction proceeds quickly, after 3.2 min the cross-over point where G" = G' or δ = 45° is reached. From this so-called gel time on, the glue behaves mainly elastic because a wide-meshed network has developed throughout the sample. Joining the parts has to be done well before the gel time is reached. Otherwise any movement in the glue line is either not possible any more or would reduce the final bonding strength.

After 10 min δ drops to 3° and G' reaches an almost constant value when the glue reaches its final strength. Although, strictly speaking, acrylate glues continue to cure at a slow rate, reaching their final strength after 12 – 24 h.

Simultaneously with the rheological data FTIR spectra have been collected about every 13 s yielding 115 IR-spectra during the 25 min the rheological test lasted. The spectra show several characteristic signals, which can be correlated with the progress of the chemical reaction (Fig. 4). The signal at 1637 cm^{-1} for example is characteristic for the C=C-bond of the acrylate monomer. Its decrease over time illustrates the consummation of the monomer during the curing reaction. The signal at 1241 cm^{-1} on the other hand is, amongst others, characteristic for the O=C-O-C ester bond in the polymeric acrylate formed during the curing of the glue (Fig. 5).

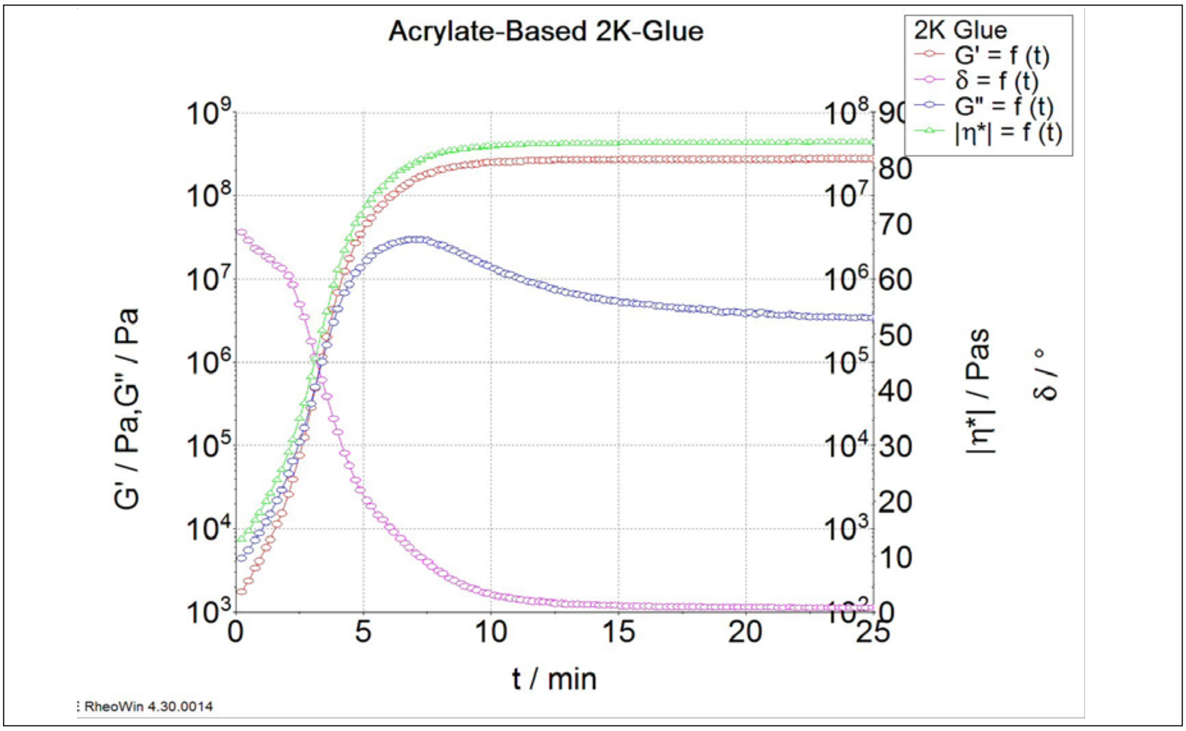


Fig. 3: Curing of an acrylate glue: development of the moduli G' and G", the complex viscosity |η*| and the phase angel δ over time.

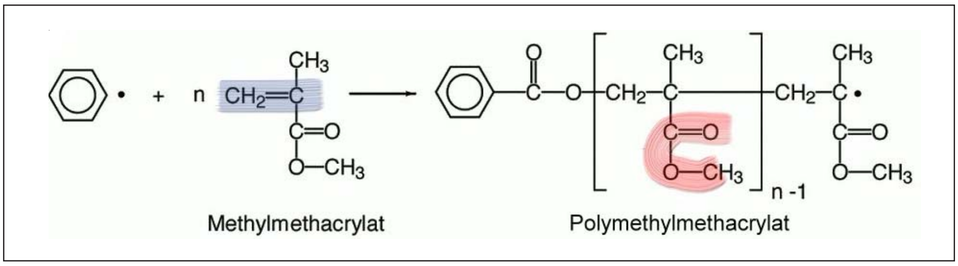


Fig. 4: Radical polymerization of Methylmethacrylate (MMA) to Polymethylmethacrylate (PMMA). Marked in blue: C=C-bond of the monomer, marked in red: ester bond in the polymer.

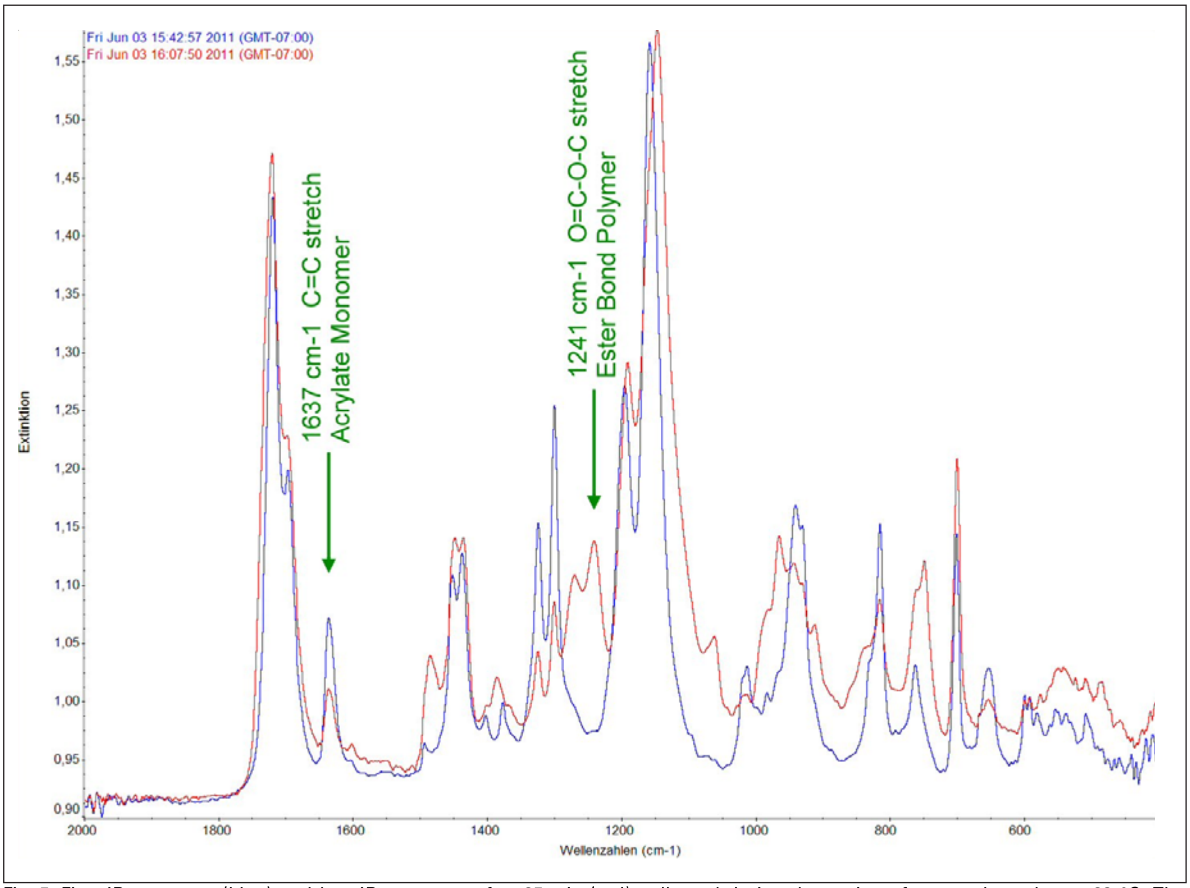


Fig. 5: First IR-spectrum (blue) and last IR-spectrum after 25 min (red) collected during the curing of an acrylate glue at 23 °C. The signal at 1637 cm^{-1} decreases over time while the signal at 1241 cm^{-1} increases.

The Thermo Scientific OMNIC software with its optional OMNIC Series add-on allows to line-up the spectra in chronological order in a 3D-graph and to evaluate how characteristic signals change during the time of the test (Fig. 6).

Cutting through the data set along the characteristic wavenumbers results in absorbance profiles, which show the changing amounts of the corresponding chemical groups in the sample.

Combining the rheological data with the spectroscopic profiles shows that the initial increase of the moduli corresponds with the decreasing amount of monomer (Fig. 7). When G' reaches its plateau value after 10 min the decrease of the monomer slows down significantly due to the reduced mobility of the monomer in the solidifying glue. The increase of the ester bond in the polymer is also reduced but still continues with twice the speed of the monomer's decrease. This indicates that intramolecular processes are more important for the final curing stage compared to reactions of the free monomer, which dominated the initial part of the curing.

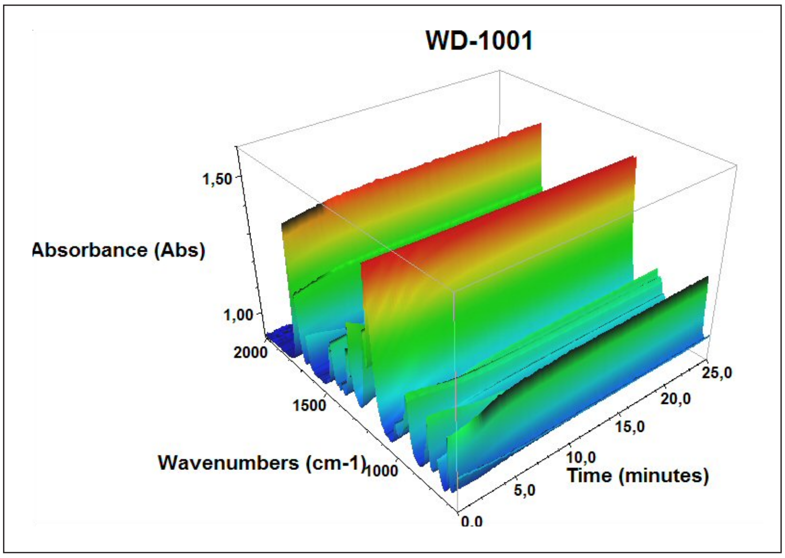


Fig. 6: 3D-Profile illustrating the time-dependant change of the IR-spectra collected during the curing of the sample in the rheometer, created with the OMNIC Series add-on.

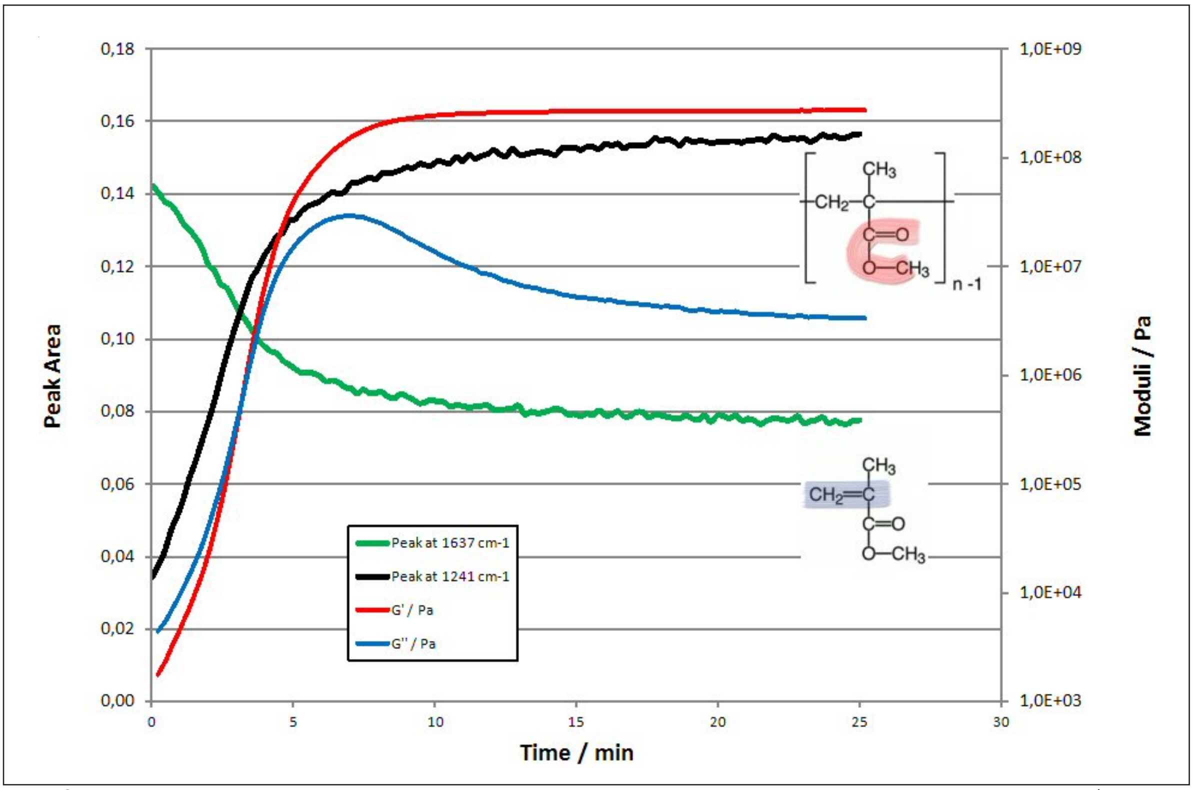


Fig. 7: Curing of the acrylate glue monitored with rheology and simultaneous FTIR. The increase of the sample's moduli (red and blue) corresponds with the decreasing signal of the monomer (green) and the increasing signal of the polymer's ester bond (black).

With this information it is possible to understand why the curing process runs the way it does. Subsequently a targeted approach to optimize a glue or to design a completely new formulation is now possible, knowing for example if it would be better to add more monomer or to increase the temperature to increase the mobility of the existing monomer.

Summary

An oscillation time sweep is a well established method to characterize the curing of glues and similar curing materials. It shows the transition from the liquid to the solid state based on the mechanical properties of the glue. The rheological results can answer questions about the dosing and application properties of the liquid glue and the toughness of glue bond. The evaluation of the changing rheological properties gives the characteristic time spans like the pot life, the curing speed and the time to reach maximum strength of the bond.

Using the Rheonaut module the HAAKE MARS rheometer can be combined with an FTIR spectrometer to simultaneously record on the same sample what happens during the curing process and why it happens on a molecular level. This reduces significantly the time for sample preparation and analysis and excludes any uncertainties due to different sample composition or sample treatment when running both analysis separately.

This unique combination of methods not only increases the quality of the data collected but also increases the time efficiency and cost efficiency of an analysis like the one described in this report.

Material Characterization

International/Germany
Dieselstr. 4,
76227 Karlsruhe
Tel. +49(0)721 40 94-444
info.mc.de@thermofisher.com

Benelux
Tel. +31 (0) 76 5 87 98 88
info.mc.nl@thermofisher.com

China
Tel. +86 (21) 68 65 45 88
info.mc.china@thermofisher.com

France
Tel. +33 (0) 1 60 92 48 00
info.mc.fr@thermofisher.com

India
Tel. +91 (20) 66 26 7000
info.mc.in@thermofisher.com

Japan
Tel. +81 45 453 9167
info.mc.jp@thermofisher.com

United Kingdom
Tel. +44 (0) 1606 54 81 00
info.mc.uk@thermofisher.com

USA
Tel. 603 436 9444
info.mc.us@thermofisher.com

www.thermoscientific.com/mc

V-254_11.11