Polymer Vol. 38 No. 21, pp. 5455–5462, 1997
© 1997 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/97/$17.00+0.00

PII: S0032-3861(97)00074-8

The structure of a styrene-acrylonitrile/butadiene polymer studied by 2D-i.r. spectroscopy

Paul A. M. Steeman* and Robert J. Meier
DSM Research, PO Box 18, 6160 MD Geleen, The Netherlands

and A. Simon and J. Gast
Bruker Analytische Meßtechnik GmbH, Wikingerstraße 13, D-76189 Karlsruhe, Germany
(Received 23 May 1996; revised 18 November 1996)

2D-i.r. spectroscopy involving mechanical excitation is employed to study the mechanical relaxation phenomena in a styrene-acrylonitrile/butadiene (ABS) sample, revealing detailed information regarding the molecular segments involved in macroscopic mechanical relaxation. From the temperature dependence of the dynamic signals it is corroborated that in the ABS sample the polybutadiene (PB) rubber relaxes entirely independently from the styrene-acrylonitrile (SAN) matrix, and thus is present as a separate phase in the material. The *rapid-scan* variation developed to perform 2D-i.r. experiments offers a significantly reduced measurement time in comparison with the *step-scan* mode of operation. In particular, in relation to research in the polymer field, in which case stress relaxation is expected to occur during the 2D-i.r. experiment, this presents a major advantage. © 1997 Elsevier Science Ltd.

(Keywords: vibrational spectroscopy; styrene-acrylonitrile/butadiene; ABS)

INTRODUCTION

The relation between microscopic properties, down to the molecular scale, and macroscopic properties is a long-standing issue in the field of polymer science. Phrased differently, relations between the polymer chain structure and the morphology of the polymeric material on one hand and the materials macroscopic properties comprise an active field of research. Unfortunately, not many techniques provide direct information on the issue. A hyphenated technique which involves one component probing the microscopic part of the problem and a second component addressing the macroscopic properties of the material under investigation may be an appropriate approach. Two-dimensional infrared (2D-i.r.)† or dynamic linear dichroic infrared spectroscopy[1] (DLIRD) is such a recently developed technique. It involves a combination of dichroic i.r. spectroscopy and an external perturbation applied to the sample, such as an electrical or mechanical modulation. Regarding the investigation into the mechanical properties of materials a sinusoidal mechanical strain may be applied to the sample as external perturbation. This means that effectively i.r. dichroic spectroscopy and dynamic mechanical analysis (d.m.a.) are intimately coupled[2–4]. I.r. dichroic measurements are a well-known tool for determining molecular orientations in materials[5]. In a 2D-i.r. experiment involving mechanical perturbation of the sample, changes in molecular orientation during dynamic deformation of a sample are studied simultaneously using i.r. spectroscopy. This offers the possibility to determine which part of the polymer chains, through the identification of molecular groups via i.r. dichroic spectroscopy, are directly related to relaxation phenomena such as the glass transition and other, secondary, relaxation mechanisms.

2D-i.r. experiments in conjunction with mechanical excitation have been accomplished in, technically, different ways. Early work was performed with a dispersive i.r. set-up[2]. Later step-scan interferometers were applied[6]. In the present paper we present the results of a study involving a continuous, *rapid-scan FT*i.r. spectrometer. This measurement technique relies completely on the utilization of the digital signal processor (DSP) in the *FT*i.r. spectrometer for data acquisition and manipulation, as do the most recently developed step-scan 2D-i.r. instruments[7]. Since no lock-in amplifiers are required, the rapid-scan mode requires a simple experimental set-up. More importantly, it allows for the collection of a 2D-i.r. spectrum within 30 min with a typical noise level of $1–2 \times 10^{-5}$ absorption units, whereas step-scan mode operation typically requires some 10 h of data collection to obtain a similar noise level[8]. This major decrease in data collection time and the accompanying increase in stability of the overall system, i.e. sample plus instrument, significantly increases the applicability of 2D-i.r. with mechanical excitation to polymers.

---

* To whom correspondence should be addressed
† Unfortunately, an ambiguity has arisen as far as the terminology 'two-dimensional spectroscopy' is involved. Regarding the optical spectroscopies, the term is sometimes applied to two-dimensional spatial spectroscopic imaging

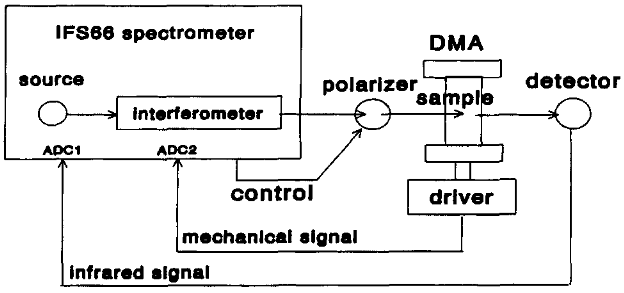

Figure 1 The rapid-scan 2D-i.r. set-up

It has been demonstrated before that separation of components in a blend can be demonstrated by applying 2D-i.r. For the polystyrene/polyethylene (PS/PE) blend this was shown at room temperature only[9]. Preliminary experiments on a styrene–butadiene–styrene (SBS) triblock copolymer performed at various temperatures were reported and brought in connection with the glass transition of the rubbery phase[10]. In the present work we report in more detail on the application of 2D-i.r. with mechanical excitation on ABS, a styrene-acrylonitrile copolymer with polybutadiene (PB) rubber inclusions, using a rapid scan *FT*i.r. set-up.

EXPERIMENTAL

2D-i.r. spectroscopy and dynamic mechanical analysis

Sample films were mounted in a Rheometrics RSA-2 dynamic mechanical analyser. The oven doors of the mechanical analyser were modified to allow for optical access. After static pre-straining of about 0.4–0.45%, the samples were sinusoidally deformed in tension with a dynamic strain amplitude of 0.3% and a frequency of about 0.1 Hz. Since polymers often show stress relaxation after applying a step strain, some adjustment of the static pre-strain before the start of the i.r. measurements may be necessary. As will be shown later, a typical acquisition cycle for the rapid-scan i.r. measurements takes about 5 min, which offers the ability to control and preserve an adequate level of pre-strain during the experiment. This ability assures reliable dynamic measurements. For acquisition times of several hours, as is often the case with step-scan instruments[8], thus lacking the ability to preserve the pre-strain, this is a critical factor which may seriously affect the results.

Synchronous dichroic i.r. measurements in transmission with a spectral resolution of 4 cm^{-1} were performed with a Bruker IFS66 *FT*i.r.-spectrometer, equipped with a MCT detector, in the *rapid-scan* mode. The experimental set-up is shown in *Figure 1*.

The acquisition parameters of the i.r.-spectrometer were set such that exactly three i.r. spectra were acquired during one period of the mechanical modulation. According to the Nyquist criterion this number of samples per period is sufficient to determine the dynamic signals. The i.r.-spectra collected during subsequent periods were co-added to the set acquired during the first period in order to reduce the noise level. Simultaneously with the i.r.-acquisition the mechanical strain signal was sampled, one data point for each i.r. spectrum. Thus, three low-noise i.r. spectra together with the matching mechanical modulation signals were available after a certain measurement time. During post-processing, linear regression analysis was performed on the series of mechanical data points and i.r. spectra in order to extract the static and the dynamic i.r. signals. From this analysis the static i.r. spectrum and two dynamic i.r. spectra are obtained: the *in-phase* dynamic i.r. spectrum which contains the changes in the spectra which occur in-phase with the mechanical deformation and the *out-of-phase* dynamic i.r. spectrum which contains the changes in the spectra which occur a quarter period out-of-phase with the mechanical deformation.

A rotatable wire-grid polarizer was installed which could be automatically switched between perpendicular and parallel directions, compared to the direction of mechanical deformation. This allowed the extraction of the so-called *dynamic dichroic spectra* (i.e. the difference spectra between the two-directions) which contain information on the molecular orientations induced by the mechanical deformation.

Spectra were acquired during 5 min in each direction, i.e. with parallel and perpendicular polarization of the incoming i.r. light, respectively, taking in total about 10 min measurement time for a single dynamic dichroic experiment. Data acquisition, manipulation and extraction of the dynamic dichroic spectra was performed with a specially developed program running in the spectrometer control software package OPUS™. Three consecutive dynamic measurements were performed in order to improve the signal-to-noise quality, taking in total about 30 min of measurement time. Details about the experimental procedure are discussed in the Appendix.

Materials

An experimental acrylonitrile-butadiene-styrene (ABS) copolymer consisting of a styrene-acrylonitrile (SAN) copolymer matrix containing about 40 wt% of polybutadiene (PB) rubber inclusions, was investigated. Films with a thickness of about 25 μm were compression moulded at a temperature of 200°C. From these films samples with dimensions $25 \times 6\,\mathrm{mm}^2$ were cut which were used for the 2D-i.r. experiments. The samples were roughened with type 600 abrasion paper in order to reduce the surface smoothness, thus suppressing internal reflections in the sample which may cause major disturbances in the dynamic infrared signals.

RESULTS AND DISCUSSION

Room temperature experiments

Figure 2 shows the static absorption spectrum at room temperature (23°C) of the material studied. For the assignment of the vibrational bands employed in the present work we refer to Socrates[11]. The absorption in the 765 cm^{-1} range is mainly due to the out-of-plane C–H ring vibrations of the styrene aromatic rings, the absorptions close to 970 cm^{-1} originates from 1,4-polymerized polybutadiene units, the absorption band just below 1500 cm^{-1} is due to C–C stretching vibrations within the aromatic rings of the styrene, while finally the absorption of the CN group of the acrylonitrile at 2240 cm^{-1} is clearly visible.

Figure 3 shows the dynamic dichroic spectra of the material at room temperature, both in-phase with the

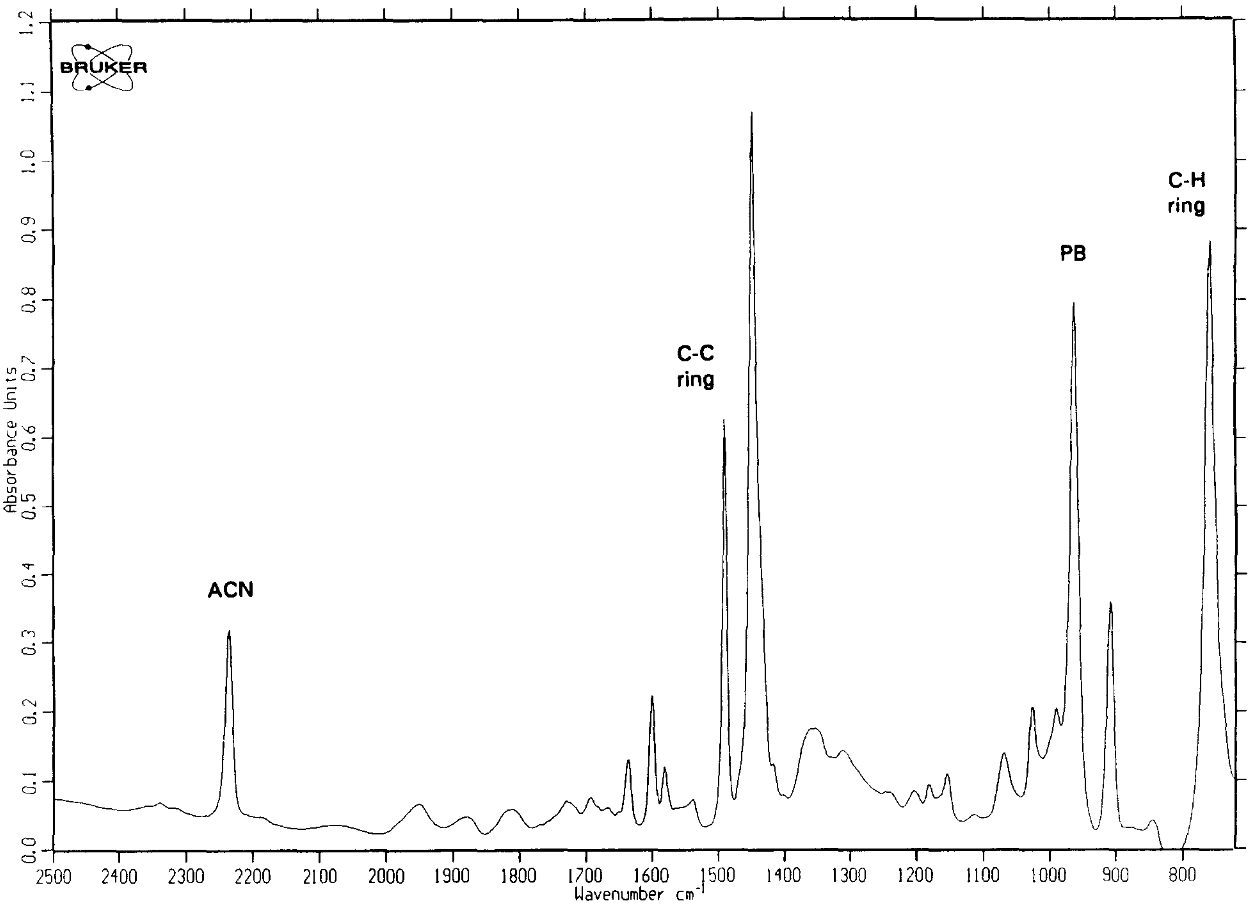

Figure 2 The static absorption spectrum of ABS at room temperature

mechanical deformation and out-of-phase with the mechanical deformation.

From the lack of any significant bands in the out-of-phase spectrum it must be concluded that, at least at room temperature, all molecular groups probed by the i.r. absorption exhibit elastic behaviour with respect to the external mechanical strain, i.e. molecular orientation and macroscopic deformation are in-phase. In addition, while referring to the in-phase spectrum, the absence of dynamic bands due to the polybutadiene (PB) rubber (e.g. 970 cm^{-1}) is striking. Only the bands from the styrene-acrylonitrile (SAN) matrix copolymer show dynamic orientation effects due to the mechanical deformation.

From the dynamic dichroic intensities of the various absorption bands the dynamic orientation factor *f* of the corresponding molecular segments, at a mechanical strain of 0.3%, can be calculated according to

$$\tilde{f}(\nu) = \frac{\tilde{A}_{\parallel}(\nu) - \tilde{A}_{\perp}(\nu)}{\bar{A}_{\parallel}(\nu) + 2\bar{A}_{\perp}(\nu)} \tag{1}$$

in which $\tilde{A}_{\parallel}$ and $\tilde{A}_{\perp}$ are the dynamic and $\bar{A}_{\parallel}$ and $\bar{A}_{\perp}$ the static absorbances of the studied absorption band in the parallel and the perpendicular directions, respectively.

Table 1 lists the dynamic orientation factors obtained for the different molecular segments in ABS. It appears that the dynamic orientation factors of the various bands coupled to the SAN-chain segments are of comparable magnitude, while no dynamic orientation is observed for the PB-segments.

Table 1 Dynamic orientation factors at 23°C and 0.3% strain of several groups in ABS

Group	Dynamic orientation factor *f*
765 cm^{-1} (C–H phenyl ring)	$(1.6 \pm 0.2) \times 10^{-3}$
970 cm^{-1} (polybutadiene)	$(0.0 \pm 0.2) \times 10^{-4}$
1490 cm^{-1} (aromatic C–C styrene)	$(-5.0 \pm 0.2) \times 10^{-4}$
2240 cm^{-1} (CN acrylonitrile)	$(6.6 \pm 0.2) \times 10^{-4}$

At room temperature the PB-phase is in its rubbery state, and therefore much more mobile in comparison with the SAN-phase which at room temperature is still in its glassy state, which might explain the observed differences between the dynamic SAN and the PB absorption bands. This was studied in more detail by varying the temperature at which the 2D-i.r. measurements were performed between −130°C and +23°C, while focusing attention on the temperature range around −85°C, where the glass–rubber transition of the PB-phase is found.

Experiments at lower temperatures

Figure 4 shows the in-phase dynamic dichroic spectra obtained at a series of temperatures starting from −130°C, at which both the SAN-phase and the PB-phase are vitrified, up to room temperature.

At the lowest temperatures dynamic dichroic bands due to the PB-rubber are observed, which disappear sharply in the temperature range of the PB glass transition (−85°C). Meanwhile, the out-of-phase spectra show significant intensities at 970 cm^{-1} at temperatures around −85°C only, as can be seen from *Figure 5*.

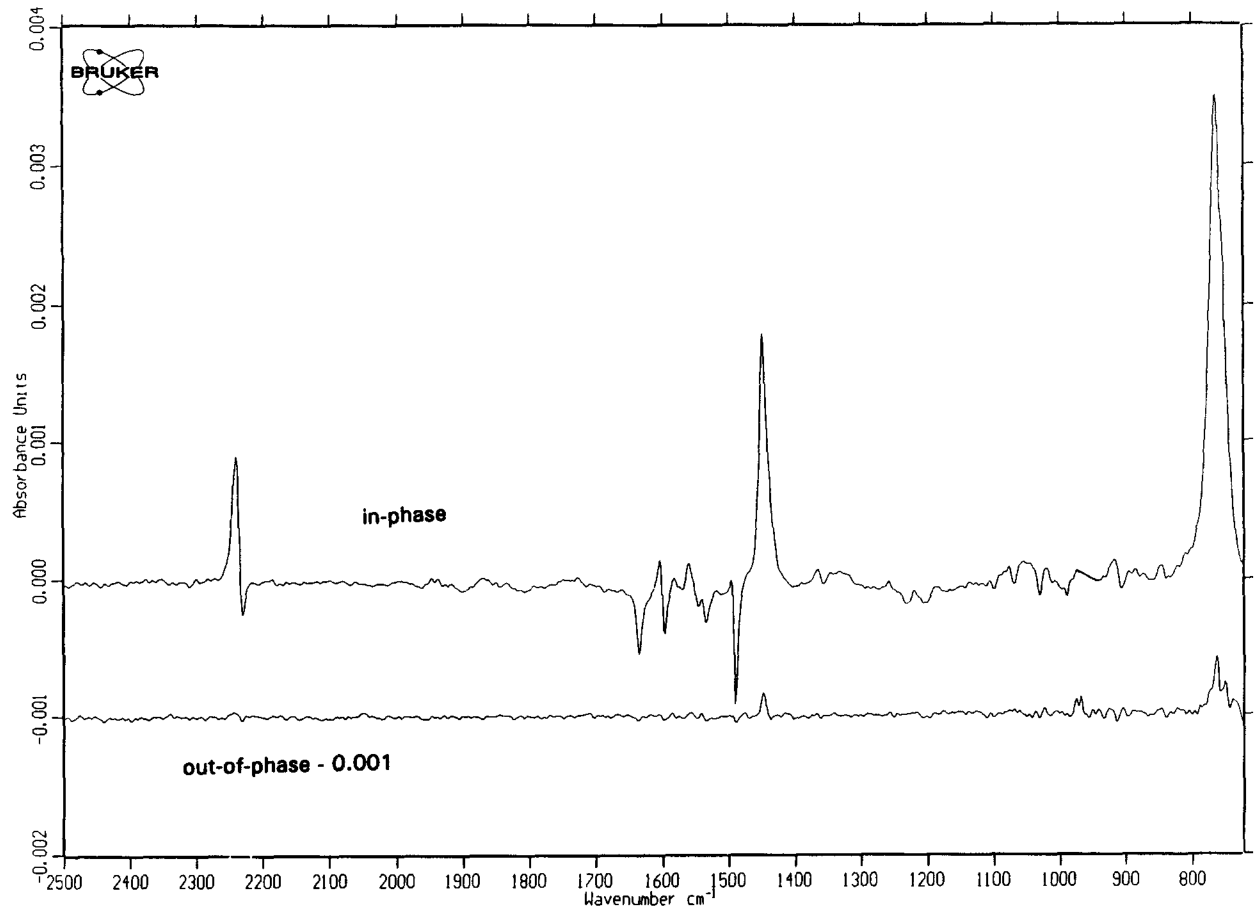

Figure 3 The dynamic dichroic spectra of ABS at room temperature

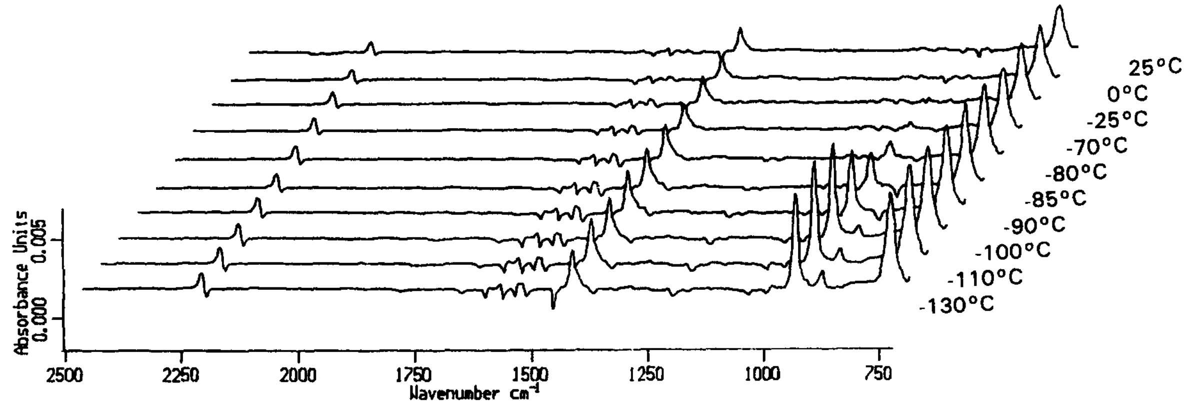

Figure 4 The in-phase dynamic dichroic spectra of ABS at various temperatures

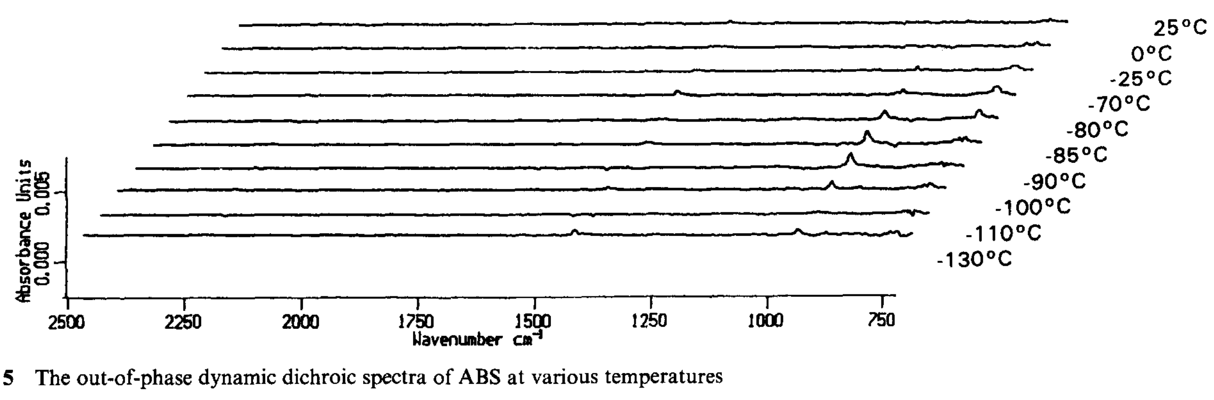

Figure 5 The out-of-phase dynamic dichroic spectra of ABS at various temperatures

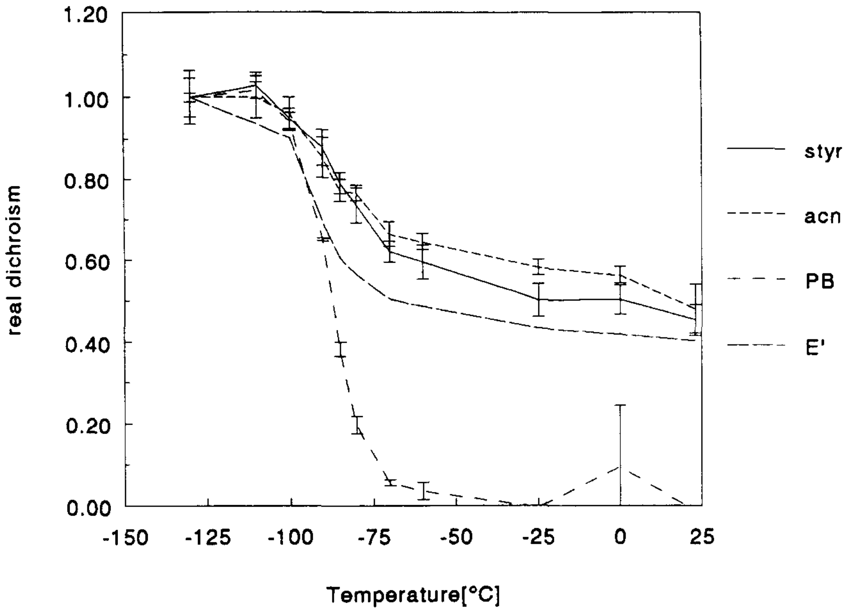

Figure 6 The normalized in-phase dynamic dichroic intensities of several bands

In *Figure 6* the normalized intensities of the in-phase dynamic dichroic bands were plotted as a function of temperature. For comparison the normalized storage modulus E' was also included in this figure. The dynamic intensities of the various absorption bands and the storage modulus at −130°C were used as reference values for the normalization.

The modulus shows a drop to about 40% of its glassy level in passing the glass transition of the PB-rubber at −85°C. Meanwhile, the dichroic intensities due to the PB-rubber disappear completely. The intensities of the bands specific for SAN decrease on the average to about 50% of their glassy level. The sharp drop of the PB-intensities confirms that indeed the glass transition of the PB-rubber is detected. At the glass transition the storage modulus of the rubber is known to show a sharp drop. Because the modulus of the SAN-matrix material remains high, the weak rubber-phase will share a larger part of the applied macroscopic deformation, while the SAN-phase is less deformed. This causes the total stress level in the material to be lower and the intensity of the dynamic SAN-bands to decrease. However, the observed decrease is smaller than the drop of the macroscopic modulus of the material. This indicates that the drop of the stress level in the SAN-phase is less that the drop of the macroscopically detected average stress level. This is in agreement with expectations since only the PB-rubber phase weakens at −85°C and not the SAN-phase.

The sharp drop in dynamic intensity in passing the glass transition has proven to be a general feature. While being unable to relax in the glassy state, segmental orientation is expected to relax nearly momentarily in the rubbery state due to the high mobility of the chain segments.

2D-correlation

As discussed in the previous paragraph, significant out-of-phase intensities are observed at −85°C only. This offers the opportunity to perform at this temperature a so-called synchronous and asynchronous correlation of the dynamic spectra, resulting in two-dimensional (2D) spectra as introduced and discussed in detail by Noda[4].

The so-called *synchronous correlation spectrum* shows to what extent the dynamic orientations detected at the different wavelengths occur simultaneously. A high synchronous intensity indicates a high level of synchronous orientation of the molecular segments involved. In contrast, the *asynchronous correlation spectrum* shows the extent to which the dynamic orientations detected at the different wavelengths occur a quarter period out-of-phase, i.e. the extent of decoupling of the motions of the corresponding molecular segments. Noda[4] has discussed that a high asynchronous correlation intensity can be used as a proof for the independent orientation of the molecular segments involved. Such independent behaviour shows that the environments of these segments are completely different, which can be an indication of heterogeneity of the material studied.

Figures 7 and *8* contain contour maps of the synchronous and asynchronous or 2D-correlation spectra calculated from the dynamic dichroic spectra at a temperature of −85°C.

Figure 7 shows a significant synchronous correlation amongst all SAN-bands and between most SAN-bands and the PB-bands. Asynchronous correlation (see *Figure 8*) is observed (ignoring the noise in the 750 $\mathrm{cm^{-1}}$ range) only for the combinations of the PB-absorption band at 970 $\mathrm{cm^{-1}}$ and a SAN-absorption band either at 1490 $\mathrm{cm^{-1}}$ or at 765 $\mathrm{cm^{-1}}$. However, no asynchronous correlation is observed amongst the SAN-bands. Note that no band can show an asyncronous autocorrelation[4]. These results prove that motion of the SAN and PB molecular segments is decoupled which confirms the heterogeneous nature (SAN/PB) of the ABS material studied.

CONCLUSIONS

It was demonstrated that rapid-scan 2D-i.r. spectroscopy can be successfully applied for studying the relation between microscopic molecular motions (via i.r. dichroic measurement) and macroscopic (via a dynamic mechanical experiment) mechanical behaviour. The experiments performed on ABS show that 2D-i.r. is capable of

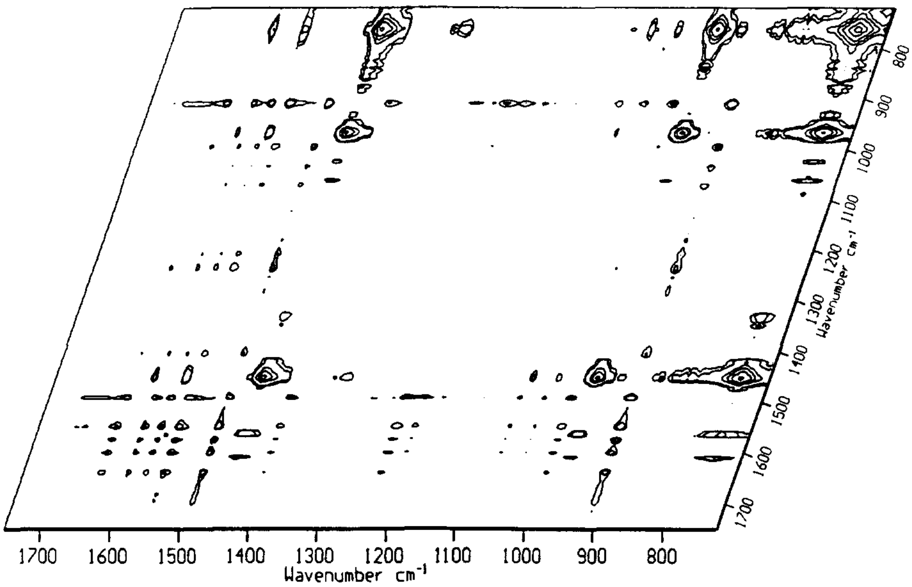

Figure 7 A contour map of the synchronous correlation of ABS at −85°C

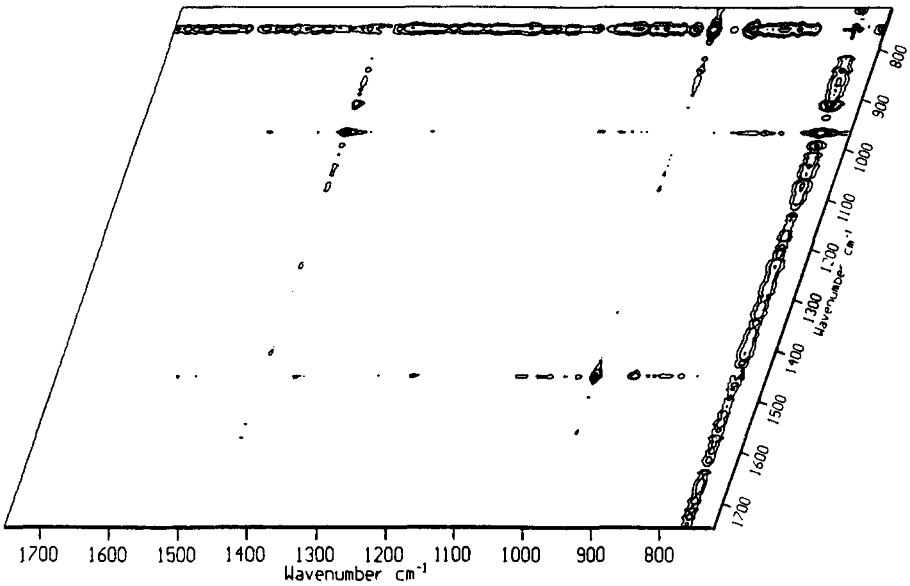

Figure 8 A contour map of the asynchronous correlation of ABS at −85°C

detecting on a molecular level which groups or molecular segments are involved in the macroscopically detected mechanical relaxation mechanisms in materials. Especially glass transitions induce large changes in the dynamic i.r.-spectra which can be easily attributed to specific groups.

Performing 2D-i.r. experiments as a function of temperature offers, through thermal activation, the possibility to study the molecular mobilities in materials in detail. The overall picture emerging from the results on ABS presented is that the relaxation behaviour of the PB-rubber phase is entirely decoupled from the SAN-matrix. Thus the rubber is present as a separate phase in the material.

Using the *rapid-scan* mode of the *FT*i.r. spectrometer the required measurement times are reduced to an acceptable level of about 30 min per 2D-spectrum, compared to typically many hours for a step-scan instrument. Consequently, recording the 2D-spectra at various temperatures is becoming really practical in rapid-scan mode only. Meanwhile, the static pre-stress can be controlled and adjusted at regular intervals in order to assure reliable measurements.

Finally, contrary to the original step-scan set-up involving various lock-in amplifiers, the presently employed rapid-scan set-up is hardly more complicated than a standard *FT*i.r. spectrometer allowing for dichroic experiments.

ACKNOWLEDGEMENTS

Guido Struijk and Martin van Es are gratefully acknowledged for their part in the measurements, and Dr Maria Soliman is acknowledged for critically reading the manuscript. The management of DSM Research is acknowledged for their permission to publish this work.

REFERENCES

1. Noda, I., *J. Polym. Sci. Polym. Lett.*, 1983, **21**, 99.
2. Noda, I., Dowrey, A. E. and Marcott, C., *Mikrochim. Acta [Wien]*, 1988, **1**, 101.
3. Noda, I., Dowrey, A. E. and Marcott, C. *Applied Spectrosc.*, 1988, **42**, 203.
4. Noda, I., *Applied Spectrosc.*, 1990 **44**, 550.
5. Painter, P. C., Coleman, M. M. and Koenig, J. L., *The Theory of Vibrational Spectroscopy and its Application to Polymeric Materials.* Wiley, New York, 1982.
6. Palmer, R. A., Manning, C. J., Chao, J. L., Noda, I., Dowrey, A. E. and Marcott, C., *Applied Spectrosc.*, 1991, **45**, 12.
7. Manning, C. J. and Griffiths, P. R., *Applied Spectrosc.*, 1993, **47**, 1345.
8. Sonoyama, M., Shoda, K., Katagiri, G. and Ishida, H., *Applied Spectrosc.*, 1996, **50**, 377.
9. Noda, I., *J. Am. Chem. Soc.*, 1989, **111**, 8116.
10. Noda, I., Dowrey, A. E. and Marcott, C., in *Fourier Transform Infrared Characterization of Polymers*, ed. H. Ishida. Plenum, New York, 1987, pp. 33–59.
11. Socrates, G., *Infrared Characteristic Group Frequencies.* Wiley, Chichester, 1994.

APPENDIX: DETAILED DESCRIPTION OF THE RAPID-SCAN 2D-IR TECHNIQUE EMPLOYED

Basics of 2D-i.r. spectroscopy

I.r. dichroic measurements are a well-known tool for determining molecular orientation in materials. I.r. absorption occurs only when the electric field vector of the incident light and the absorbing dipole transition moment are aligned. By measuring the absorbance spectra in parallel and perpendicular directions $[A_{\parallel}(\nu)$ and $A_{\perp}(\nu)]$, using linear polarized light, the so-called dichroic difference spectrum $\Delta A(\nu)$ can be obtained:

$$\Delta A(\nu) = A_{\parallel}(\nu) - A_{\perp}(\nu) \qquad \text{(A1)}$$

The dichroic differences are a measure for the molecular orientation in the material. A positive dichroic difference is obtained when a transition moment is oriented along the parallel axis while a negative dichroic difference is obtained in the case of orientation along the perpendicular axis.

When the material is deformed a change will occur in the dichroic spectra. In the case of a small sinusoidal mechanical deformation $\epsilon = \epsilon_0 \sin(\omega t)$ these changes can be expressed as the sum of a static dichroic spectrum $\Delta\bar{A}(\nu)$ and a (small) dynamic dichroic spectrum $\Delta\tilde{A}(\nu)$:

$$\Delta A(\nu, t) = \Delta\bar{A}(\nu) + \Delta\tilde{A}(\nu, t) \qquad \text{(A2)}$$

$$\Delta\tilde{A}(\nu, t) = \Delta\tilde{A}_r(\nu)\sin(\omega t) + \Delta\tilde{A}_i(\nu)\cos(t) \qquad \text{(A3)}$$

in which $\Delta\tilde{A}_r(\nu)$ and $\Delta\tilde{A}_i(\nu)$ are the in-phase and the out-of-phase or quadrature dynamic dichroic spectra of the material in response to the mechanical modulation. The in-phase spectrum shows the dichroic effects induced by the mechanical deformation without any phase lag, while the out-of-phase spectra show dichroic effects with $\pi/2$ phase difference.

Sampling details

According to the Nyquist sampling criterion, a sinusoidal signal can be sampled by taking at least two samples during a period. Our basic idea of rapid-scan 2D-i.r. is to sample at least two i.r. spectra (we chose three), with the interferometer running in continuous mode, during one period of the mechanical deformation cycle. Modern fast *FT*i.r. spectrometer have the ability to collect typically up to 30–50 or more spectra per second. If three i.r. spectra are to be acquired during one period of the modulation, modulation frequencies up to 10–20 Hz can be applied, while using the rapid-scan technique. These frequencies are typical for step-scan 2D-i.r. instruments. However, in studying polymeric materials such high frequencies are not a prerequisite. The well-known 'time–temperature superposition' principle (see, e.g. the book by J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd edn, 1980, Wiley, New York) states that the results obtained using an angular frequency ω_1 at temperature T_1, can also be obtained by measuring with an angular frequency $\omega_2 < \omega_1$ at a temperature $T_2 < T_1$. The frequency shift with temperature depends on the activation energy of the process studied. Typical values from the book of Ferry are 3–5 K per decade in frequency. We therefore adopted measurement frequencies of about 0.1 Hz which impose less severe restrictions on the timing accuracy of the measurement system as will be discussed later.

Together with the i.r. spectra, the mechanical deformation signal is sampled with a separate A/D-channel, which serves as reference for the extraction of the dynamic infrared spectra. Schematically illustrated:

– – – – – – – – – – – – | – – – – – – – – – – – – – – mechanical period – – – – – – – – – – – – – – | – – – – – – – – –
– – | – – IR sampling – – | – – IR sampling – – | – – IR sampling – – | – – IR sampling – –

Spectrum acquisition in the rapid-scan mode is not instantaneous, but requires a measurement time t_s. Therefore, the i.r. intensities will vary during the acquisition of a single spectrum. The i.r. signals sampled contain the average intensities during the acquisition period. It can be easily shown that a sinusoidal intensity variation with angular frequency ω, amplitude A and arbitrary phase ϕ (depending on the moment of starting the i.r. acquisition):

$$\tilde{I}(t) = A\sin(\omega t + \phi) \qquad \text{(A4)}$$

is sampled during the time-interval $[t, t + t_s]$ as:

$$\begin{aligned} \tilde{I}(t, t + t_s) &= \frac{1}{t_s}\int_t^{t+t_s} \tilde{I}(t)\mathrm{d}t \\ &= \frac{A\sin(\omega t_s/2)}{\omega t_s/2}\sin(\omega t + \phi + \tfrac{1}{2}\omega t_s) \\ &= A'\sin(\omega t + \phi') \end{aligned} \qquad \text{(A5)}$$

i.e. a sinusoidal signal is sampled with reduced amplitude A', while the detected phase ϕ' is the central phase of the sampling interval:

$$\begin{aligned} A' &= A\frac{\sin(\omega t_s/2)}{\omega t_s/2} = A\,\mathrm{sinc}\,(\omega t_s/2); \\ \phi' &= \phi + \omega t_s/2 \end{aligned} \qquad \text{(A6)}$$

The detected amplitude A' is reduced by the sinc-function, $\mathrm{sinc}(x) = \sin(x)/x$, of $\omega t_s/2$. If $t_s \ll 1/\omega$ this reduction can be neglected. In the case of three spectra per period ($\omega t_s/2 = \pi/3$) the detected amplitude A' equals about 83% of the amplitude A of the actual intensity variations. This imposes no serious restrictions on the 2D-i.r. technique.

An additional complication might arise if the material displays a non-linear response. In that case higher harmonics of the basic sine wave may be present in the i.r.-signal which is being sampled:

$$\tilde{I}(t) = \sum_{i=1}^{\infty} A_i \sin(i\omega t + \phi_i) \quad \text{(A7)}$$

The higher harmonics ($i > 1$) will also be sampled and have an effect on the detected signal. However, these components are suppressed by the action of the sinc-function in equation (A6). In the case that three i.r. spectra are acquired per mechanical period the detected amplitude A_2' of a possible second harmonic ($i = 2$), for which $\omega t_s/2 = 2\pi/3$, is reduced to about 41% of its amplitude A_2 in the actual signal and therefore suppressed by at least 50% in comparison with the basic harmonic ($i = 1$). Similarly, the more important third harmonic ($i = 3$), in which case $\omega t_s/2 = \pi$, is completely suppressed since its period time is equal to the sampling time. Even higher harmonics will again have a minor contribution. Moreover, in the range of mechanical deformations studied (< 1%), most polymeric materials show to a large extent linear behaviour. Therefore, higher harmonics if present will be weak and well suppressed as described above. It is concluded that at most minor disturbances due to nonlinear effects are to be expected in the rapid-scan 2D-i.r. results. A further improvement is possible by increasing the number of i.r. spectra acquired per period of the mechanical signal (e.g. six is clearly profitable).

Spectra acquisition and data processing

In principle the scanner in the i.r. spectrometer and the mechanical modulation can be driven asynchronous. In that case a series of i.r. spectra, e.g. a few hundred, with the simultaneous values for the mechanical deformation have to be acquired. By performing Fourier or regression analysis on the sampled mechanical signals and the i.r. spectra, the static and the dynamic (both in-phase and out-of-phase) i.r. intensities can be obtained. Such a routine requires a nonlinear iteration to determine the mechanical reference signals from the sampled mechanical data points, and will be rather complicated and time consuming because of the large number of spectra involved.

However, if the scanner in the i.r. spectrometer and the mechanical modulation frequency are matched, such that exactly three infrared spectra are acquired during one mechanical period, the data acquisition is much simplified for two reasons.

Firstly, since every three spectra are collected at the same phase of the mechanical deformation it is allowed to add the i.r. spectra of subsequent periods to the first three spectra acquired. Therefore, after the measurement series is finished three averaged result spectra are obtained which contain all the necessary information, with a much better signal to noise ratio. From this it is also concluded that the frequency match of the scanner and the mechanical modulation is not very critical since a slight mismatch will result in averaging of the spectra over a slightly larger acquisition period, leading to a slightly lower amplitude A'. In our case, we have experienced that a timing mismatch of up to 10% of the i.r.-sampling time over 30 mechanical periods (5 min), i.e. 0.3% mismatch in frequency is acceptable. In practice using quartz driven signal generators a much better match and stability (< 0.1%) can be obtained.

Secondly, since the frequencies of the i.r. spectrum collection and the mechanical deformation are matched, i.e. the mechanical frequency is known, a least squares analysis is sufficient for determining the phase ϕ and the amplitude of the mechanical signal. Note that it is not necessary to start the i.r. sampling at zero phase of the mechanical deformation cycle!

Next, if the analysis of the mechanical signal has been performed both the frequency and the phase ϕ are used for generating the sine and cosine waves of the mechanical modulation, which serve as reference for the Fourier or regression analysis of the i.r. spectra. Since only three spectra are involved this analysis is easy and can be performed very fast using standard macro features available in the OPUS™ i.r.-software.

Finally, the calculated static and dynamic (in-phase [r] and out-of-phase [i]) infrared intensities $\bar{I}(\nu)$, $\tilde{I}_r(\nu)$ and $\tilde{I}_i(\nu)$, respectively, can be converted to the static and dynamic absorption spectra $\bar{A}(\nu)$, $\tilde{A}_r(\nu)$ and $\tilde{A}_i(\nu)$, respectively, using the following equations and the source spectrum $I_{\mathrm{source}}(\nu)$ measured with no sample mounted:

$$\bar{A}(\nu) = -\log\left(\frac{\bar{I}(\nu)}{I_{\mathrm{source}}(\nu)}\right) \quad \text{(A8)}$$

$$\tilde{A}_{r,i}(\nu) = -\frac{\tilde{I}_{r,i}(\nu)}{\bar{I}(\nu)} \quad \text{(A9)}$$