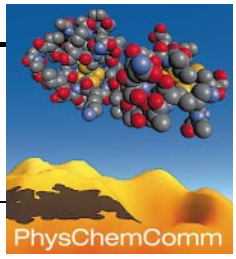

Paper

Application of generalized two-dimensional correlation theory to gel permeation chromatographic analysis

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This report demonstrates the promising potential for the application of generalized two-dimensional correlation analysis to time dependent GPC elution profiles, in analysis of complex dynamic variations in the sol–gel polymerization process.

In the polymerization process of octyltriethoxysilane (OTES), there exists a unique growth process, in which a microscopic transition occurs before macroscopic phase-separation.[1,2] That is, in this polymerization process, it has been proposed that the growth process occurs in two steps such that the monomer–monomer reaction occurs in the initial step and the cluster–cluster reaction in the second. The first stage of this reaction has been observed by time-resolved gel permeation chromatography[3] and, for the first time, analyzed by using the two-dimensional (2D) correlation theory.

The two-dimensional (2D) correlation theory, generalized by Noda,[4,5] has previously been successfully applied to IR, NIR, Raman, and other fields of spectroscopy.[6–9] The theory has been well established and can easily be adapted to analysis not only of spectroscopic methods but also of various other analytical methods. In this communication, we report the successful application of the 2D correlation analysis to a time-resolved GPC profile (2D GPC). It has been found that the 2D GPC correlation map can be used effectively to elucidate the details of complex dynamic variations in the time-dependent elution profiles.

For this study, an OTES–ethanol–1.0 M $HCl{\cdot}H_2O$ (1 : 1 : 0.4; weight ratio) solution was used as a reaction system at 25 °C. This reaction was sampled at intervals and a set of GPC traces (RI detector) obtained. This data set (E, t) constitutes a profile of the reaction in terms of elution time (E) and reaction time (t) and is illustrated by Fig. 1. The three GPC profiles, as shown in Fig. 1, include time-dependent variation of compositions (monomer, hydrolyzed monomers, dimer, trimer and higher polymerized precursors) in each profile. For $t = 0$, the distribution of monomer is very sharp, but after 60 s, the monomer molecules are hydrolyzed to produce a hydrolyzed monomeric precursor (band A) and polymerized precursors (bands C, D, E and F). The profile at 600 s shows that it is the higher polymerized precursors which are predominant.

The generalized 2D correlation analysis[4,5] was applied to these GPC profiles, in order to explore the potential of the technique for obtaining information on the relationship between the polymeric precursors, as well as between polymeric and monomeric (or lower polymeric) precursors. The synchronous and asynchronous 2D GPC correlation spectra are obtained directly from the set of time-dependent GPC traces by the 2D correlation method previously described.[4,5] More complete description of the 2D GPC correlation method is provided elsewhere.[10]

Synchronous 2D GPC spectrum

The synchronous 2D GPC spectrum is shown in Fig. 2(A). According to the 2D correlation theory, the intensity of a synchronous 2D correlation intensity spectrum $\Phi(E_1, E_2)$ represents the simultaneous or coincidental changes of GPC trace intensity variations measured at elution times E_1 and E_2

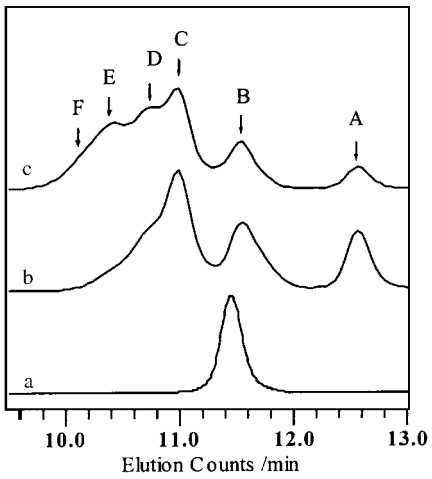

Fig. 1 Time-dependent GPC elution profiles obtained from the OTES–ethanol–1.0 M $HCl{\cdot}H_2O$ system (a: monomer ($t = 0$), b: 60 s, c: 600 s). A: monomeric precursor; B: monomer and monomeric precursor; C–F: polymeric precursor.

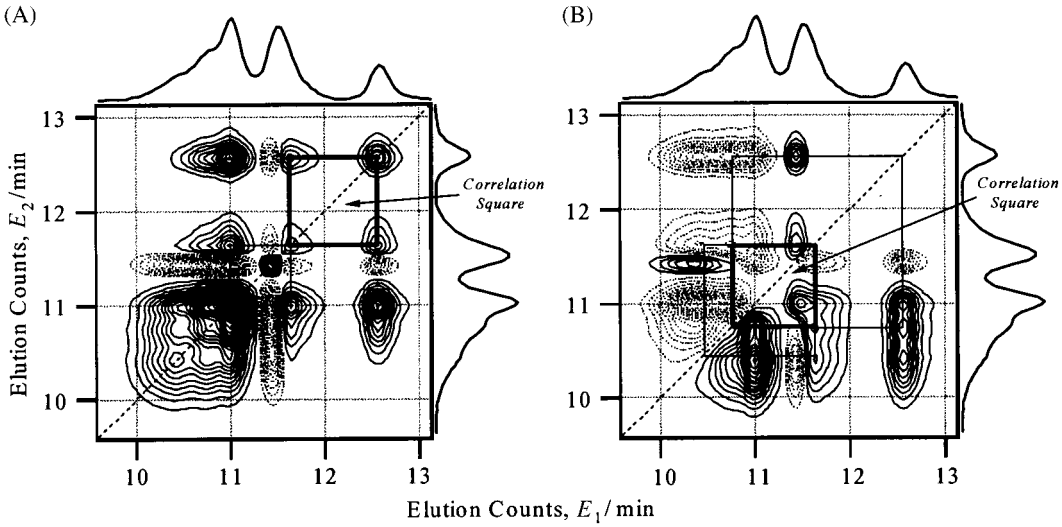

Fig. 2 (A) synchronous and (B) asynchronous 2D correlation maps of the OTES–ethanol–1.0 M HCl·H_2O system. Solid lines indicate positive peak, and broken lines indicate negative peak.

during the polymerization reaction. A synchronous spectrum is a symmetric spectrum with respect to the diagonal line corresponding to coordinates $E_1 = E_2$. Correlation peaks appear at both diagonal and off-diagonal positions.

The intensity of peaks located at diagonal positions mathematically corresponds to the autocorrelation function of refractive index intensity variations observed during the reaction. The diagonal peaks are therefore referred to as *autopeaks*, and the slice trace of a synchronous 2D spectrum along the diagonal is called the *autopower spectrum*. In Fig. 2(A), the autopeaks are located at (12.56, 12.56), (11.64, 11.64), (11.44, 11.44), (11.0, 11.0) and (10.44, 10.44) min. The magnitude of an autopeak intensity, which is always positive, represents the overall extent of GPC trace intensity variation observed at the specific elution count E. Thus, any regions in a GPC trace which change the trace intensity to a great extent under a given reaction process will provide strong autopeaks, while those remaining near constant develop little or no autopeaks. In other words, an autopeak represents the overall susceptibility of the corresponding GPC peak to change in intensity as the polymerization reaction is progressing.

Cross peaks located at the off-diagonal positions in a synchronous 2D spectrum represent simultaneous changes of spectral intensities observed at two different elution counts E_1 and E_2. In Fig. 2(A), the positive crosspeaks are found at coordinates (12.56, 11.64), (12.56, 11.0) and (11.64, 11.0) min, while negative crosspeaks are located at (12.56, 11.44), (11.64, 11.44) and (11.44, 11.0) min. Such a synchronized change, in turn, suggests the possible existence of a coupled or related origin for GPC trace intensity variations. It is often useful to construct a *correlation square*, joining the pair of cross peaks located at opposite sides of a diagonal line drawn through the corresponding autopeaks, to show the existence of coherent variation of GPC trace intensities at these spectral variables [*i.e.* the square made of (12.56, 12.56), (11.64, 12.56), (12.56, 11.64) and (11.64, 11.64) min in Fig. 2(A)].

While the sign of autopeaks is always positive, the sign of cross peaks can be either positive or negative. The sign of synchronous cross peaks becomes positive, if the GPC trace intensities at the two elution times corresponding to the coordinates of the cross peak are either increasing or decreasing together, as functions of the sampling time during the observed reaction period. On the other hand, the negative sign of cross peaks indicates that one of the GPC trace intensities is increasing while the other is decreasing. The crosspeaks at (11.44, 11.0) and (11.64, 11.0) min arise from the fact that the band B is composed of two different components which have opposite directions in intensity change. The positive peak at (12.56, 11.0) min implies that the GPC trace intensity variations are both increasing, since the polymeric components are increasing in Fig. 1 (profiles c and d). The synchronous 2D GPC spectrum for this reaction has six cross peaks showing that every auto peak correlates with at least one other autopeak. Thus, it is found that the synchronous map makes a high resolution time-dependent GPC elution profile.

Asynchronous 2D GPC spectrum

Fig. 2(B) shows the asynchronous 2D GPC map $\Psi(E_1, E_2)$ obtained from the same time-dependent GPC profiles. The intensity of an asynchronous spectrum represents sequential, or successive changes of GPC trace intensities measured at E_1 and E_2. Unlike a synchronous spectrum, an asynchronous spectrum is antisymmetric with respect to the diagonal line. The asynchronous spectrum has no autopeaks, and consists exclusively of cross peaks located at off-diagonal positions. The positive crosspeaks in this OTES polymerization case are observed at (12.56, 10.96), (12.56, 10.74), (12.56, 10.42), (11.48, 11.0), (11.64, 10.74), (11.64, 10.42) and (11.0, 10.39) min. Likewise, negative crosspeaks are located at (12.56, 11.84), (12.56, 11.44), (11.64, 11.44) and (11.42, 10.39) min. By extending lines from the spectral coordinates of cross peaks to corresponding diagonal positions, one can construct asynchronous correlation squares.

An asynchronous cross peak develops only if the intensities of two GPC trace features change out of phase with each other, *i.e.*, are delayed or accelerated with respect to sampling time. This feature is especially useful in differentiating overlapped bands arising from GPC profiles of different origins. For example, different GPC trace intensity contributions from individual components of a complex mixture may be effectively discriminated. Even if bands are located close to each other, as long as the signatures or the pattern of sequential variations of trace intensities are substantially different, asynchronous cross peaks will develop between their GPC trace coordinates.

The sign of asynchronous cross peaks can be either negative or positive. The sign of an asynchronous cross peak becomes positive if the intensity change at E_1 occurs predominantly before E_2 in the reaction process. It becomes negative, on the other hand, if the change occurs after E_2. This rule, however, is reversed if the intensity of the corresponding synchronous peak at the same coordinate is negative, *i.e.*, $\Phi(E_1, E_2) < 0$. These

rules are all based on the well established theory of 2D correlation analysis.[4,5]

For example, we can obtain significant information from Fig. 2. The existence of the positive crosspeak at (11.48, 11.0) min in the asynchronous map, and of the negative crosspeak at the same position in the synchronous map, indicate directly that the monomeric components (E_1) change first and then the polymeric component (E_2) changes. In other words, these two events, the decrease of one and increase of the other, do not occur simultaneously but in a sequence with some time delay in between. The mechanism consistent with such observation calls for the existence of some intermediate species between the monomeric and polymeric forms. This conclusion is very reasonable and offers a solid support for the appropriateness of 2D GPC analysis. The asynchronous map definitely provides information on the order of events. We may conclude that the two-dimensional correlation analysis can be applied to the time-dependent GPC elution profiles, thereby providing detailed information on the complex reaction mechanism.

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