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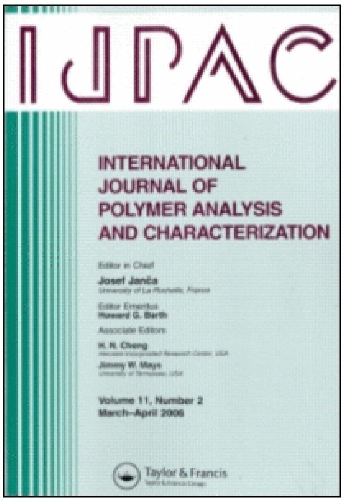

International Journal of Polymer Analysis and Characterization

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

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To cite this Article Voigt, D. , Eichhorn, K. -J. , Arndt, K. -F. and Prettin, S.(1997) 'Online Size Exclusion Chromatography-Fourier Transform Infrared Spectroscopy (FTIR): Investigation of Preferential Solvation Effects', International Journal of Polymer Analysis and Characterization, 3: 4, 333 — 349
To link to this Article: DOI: 10.1080/10236669708032773
URL: http://dx.doi.org/10.1080/10236669708032773

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Int. J. Polym. Anal. & Charact.,
1997 Vol. 3, pp. 333–349
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Online Size Exclusion Chromatography-Fourier Transform Infrared Spectroscopy (FTIR): Investigation of Preferential Solvation Effects

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(In final form 06 November 1996)

Light scattering investigations of alternating copolymers of maleic anhydride and styrene or methyl maleimide and styrene were carried out in tetrahydrofuran (THF) containing a small amount of water. A systematic decrease of the apparent molecular weight ($M_{w(\mathrm{app})}$) calculated from light scattering data is observed when the water content in THF is increased. It is assumed that strong interactions among polymer molecules exist in THF and that they are disrupted by addition of water. Simultaneously preferential solvation of the polar sequences of the copolymer molecule should be considered. This special form of solvation is characterized by both size exclusion chromatography/FTIR coupled technique (SEC/FTIR) and stationary FTIR experiments using low-molecular-weight model compounds with similar chemical structure as, for example, N-methyl succinimide.

Keywords: Preferential solvation, SEC-FTIR, maleic anhydride copolymer, maleimide copolymer, succinic acid, N-methyl succinimide

INTRODUCTION

Combinations of various liquid chromatographic techniques are frequently used for characterization of both the molecular weight distribution and the chemical heterogeneity in copolymers. The combination of

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*Corresponding author.

size exclusion chromatography and liquid adsorption chromatography (LAC) is described by Glöckner [1]. The importance of the liquid adsorption chromatography at critical conditions (LCCC) is being recognized for the investigations of copolymers or polymer mixtures [2-4]. This special chromatographic technique operates at the boundary between adsorption and size exclusion mechanisms and requires, in most cases, the use of solvent mixtures as eluents. It is known that the composition of these mixtures influences retention behavior of the particular solute components in a different way.

The change in the elution behavior can be attributed to both enthalpic interactions of the solute molecules with the stationary phase (LC column packing) and to differences in solvation of the solute molecules affecting their hydrodynamic volumes (molecular dimensions). Therefore the SEC separation process is influenced directly by changing the sample solvation. The separation process itself and the interpretation of the chromatographic results could be complicated by solvation effects especially in the oligomer region. Moreover, both the interactions among the dissolved macromolecules and the coil dimension of an isolated polymer molecule can be influenced strongly by the addition of electrolytes to the eluent [5]. Unfortunately, it is very difficult to distinguish the influences of various interactions (interactions among macromolecules; interactions among macromolecules and stationary phase or influences of preferential solvation by mixed eluent components) solely by chromatographic (SEC, LAC) or light scattering experiments. Effects of solvation, particularly of preferential solvation of macromolecules have also consequences for different characterization methods of the dissolved polymer molecules. Preferential solvation of copolymer molecules can also influence reactivity of macromolecules in solution [6-8]. Therefore the assessment of preferential solvation has practical importance from the point of view of polymer synthesis.

Numerous theoretical studies on the solvation properties of macromolecules in solution can be found in literature [9-14]. Investigations of preferential solvation of homopolymers like polystyrene [15,16], polymethacrylate or of copolymers on basis maleic anhydride in solvent mixtures [17-19] have been published. The characterization of intermolecular interactions between maleic acid or maleic acid amide copolymers and polyvinylpyrrolidone has been a subject of previous studies [20,21].

Investigations of preferential solvation effects were done using light scattering and viscosity measurements [22-24]. FTIR spectroscopy is useful to investigate interactions in solvent mixtures by analysis of frequency shifts and profiles of corresponding absorption bands [25-28].

Trathnigg *et al.*[29] proposed a method to quantify the preferential solvation of polyoxyethylene molecules by ethanol using a mixture of chloroform and ethanol as eluent for SEC measurements. The authors proved the dependence of preferential solvation on both the polymer sequences lengths and the end groups. Indications of preferential solvation were obtained from the presence of well-known chromatographic system peaks. [30-32] Fischer *et al.*[33] proposed a series of chromatographic experiments, which allow an indirect determination of preferential solvation by analysis of system peaks (vacancy peaks) using mixed solvents as eluent.

Irregularities observed during the molecular characterization of styrene-maleimide-copolymers [34] by viscosity measurements and light scattering experiments were the reason of our present work. In our preliminary SEC investigations of similar copolymers, we found first indications of preferential solvation of anhydride groups in copolymer chains by traces of water in the eluent [31]. We now present some results of light scattering measurements of alternating copolymers of maleic anhydride and styrene (MAn) and methyl maleimide and styrene (MIM) (90% imidization) in THF containing a controlled amount of water.

Sometimes effects of preferential solvation in copolymers could be too small for analyses with vibrational spectroscopy. Therefore we have first investigated low-molecular-weight substances with a chemical structure similar to polymer chain segments at which the solvation should occur. The main subject of this paper is the study of interactions of water with the model substance N-methyl succinimide using SEC with online FTIR spectroscopy.

EXPERIMENTAL

Materials

The styrene-maleic anhydride copolymer (MAn) 50/50 mol % was produced by Leuna-Werke AG (Merseburg, Germany). The apparent molecular weight ($M_{w(app)} = 6.8 \cdot 10^5$ gmol^{-1}) of the copolymer was determined by light scattering using pure THF as solvent. For all our experiments the dried copolymer was not additionally treated. The styrene-maleimide copolymer was prepared by imidization of MAn according to ref. [34]. The low-molecular-weight model compounds, succinic acid (SAc), N-methyl succinimide (SMI) and succinic anhydride (SAn), were of analytical grade (Aldrich–Chemie, Steinheim, Germany).

THF was dried over potassium hydroxide and freshly distilled over calcium hydride. Double-distilled water was used.

Light Scattering Measurements

The intensities of scattered light were measured by a modified SOFICA 42 photometer equipped with a He-Ne laser ($\lambda = 632$ nm). All light scattering experimental data were analyzed using the Zimm method. The solutions were purified prior to measurements by filtration through membrane filters (0.2 µm, RC 58, Schleicher-Schuell, Dassen, Germany).

Refractive Index Increment

Refractive index increments (RI) of polymer solutions and mixtures of THF/water were measured with a double beam differential refractometer (Model DRM-1020, Otsuka Electronics, Osaka, Japan) at 298 K and $\lambda =$ 632 nm. The instrument was calibrated using aqueous KCl solutions as standards. Five solutions of different concentration or different composition were measured for each RI-value. A range of the solvent mixtures was covered by the volume fraction of THF from $\varphi = 1.00$ to $\varphi = 0.90$. The refractive indices of these mixtures yield a linear relationship as a function of the water content. The refractive index increment of the solvent in the mixture, $dn/d\varphi$, is a constant for investigated range.

SEC

The SEC/FTIR coupled experiments were performed with modular chromatographic equipment consisting of an HPLC-pump type 64, refractive index detector and manual injection valve (Knauer, Berlin, Germany). A single Zorbax column PSM 60 S (6-µm silanized porous silica microspheres, Rockland Technologies, Inc., USA; 6.2 × 250 mm) was used. Ten thousand theoretical plates were calculated for this column. The injection volume was 20 µL. The sample concentration was c = 10 g/L.

The actual preparation of sample solution and the water content of the eluent is described in the corresponding figure legends. The flow rate was 0.2 mL/min. The coupling experiments were carried out at room temperature.

FTIR Spectroscopy

The IR spectra were collected on a modified IFS 28 FTIR spectrometer (Bruker, Karlsruhe, Germany) equipped with a Hg/Cd/Te detector and a rapid scan option. The spectroscopic behavior of the carbonyl group containing model compounds in binary and ternary solutions was studied in the course of stationary experiments at room temperature using a CaF_2.liquid cell (d = 0.069 mm). 250 scans/spectrum were co-added at a resolution of 1 cm^{-1}.

The SEC-FTIR coupled experiments were performed at room temperature using a #RA 4000—EXP reflecting flow cell (AABSPEC, Dublin, Ireland). The cell was mounted on a base plate in the sample compartment of the IFS 28 and connected with the LC column via stainless steel tubing. With this flow cell detection we have a "real-time detector" for SEC [35]. In our cell we used ZnS windows and elliptical Teflon spacers. The optimum cell thickness for our experiments in THF was 0.1 mm. That gives the cell volume of about 1.2 µL. The cell works in the transflection mode, so we had an optical path length of nearly 0.2 mm.

During the chromatographic run, the spectra were recorded online with 2s intervals. Eight scans were co-added for one spectrum at 40 kHz mirror velocity and at a spectral resolution of 8 cm^{-1}. The SEC-FTIR data were interpreted using the Bruker Opus-Chrom 2 software to calculate the Gram-Schmidt reconstructed chromatograms and the Chemigrams as described by Griffiths *et al.* [36].

RESULTS AND DISCUSSION

Light Scattering Measurements

The apparent molecular weights of MAn and MIM (90% imidization) determined in pure THF and in THF with various water contents are given in Table I. The value of apparent molecular weight, $M_{w(app)}$, determined in pure THF is much higher than the data obtained in the mixed

TABLE I $M_{w(app)}$ determined by light scattering as function of water content

Composition of Mixed Solvent (Volume Fraction THF)	$M_w(MAn)$ $[10^5\ g\ mol^{-1}]$	$M_w(MIM)$ $[10^5\ g\ mol^{-1}]$
1.00	6.8	6.0
0.99	4.9	4.5
0.98	4.1	4.7
0.97	3.2	3.8
0.96	3.0	3.8
0.95	2.7	3.3
0.94	2.7	2.2
0.93	2.4	1.7
0.92	2.5	1.5
0.91	2.1	1.8
0.90	2.1	1.3

solvent containing a small amount of water. The signs of the refractive index increments and the $dn/d\varphi_1$ (φ_1 volume fraction of THF in the mixed solvent) are positive. Therefore, the preferential solvation coefficient for THF is negative. That means, water is preferentially adsorbed on the copolymer molecules. The decrease of $M_{w(app)}$ with increasing water content could be caused either by changing the optical parameters of system due to preferential solvation or by suppressing intermolecular interactions leading to aggregation of macromolecules. It is evident that the light scattering experiments alone cannot give direct information about these phenomena.

Stationary FTIR Measurements

The presence of preferential solvation is evident from the shape and the frequency shifts of absorption bands in the case of N-methyl succinimide. Figure 1 shows the $\nu C = O$ absorption of N-methyl succinimide depending on water content of the solvent up to 10% (v/v). The adsorption intensity of the region about 1715 cm^{-1} decreased with increasing water content in THF. Moreover, a shift of the band 1705 cm^{-1} to lower frequencies and an increase of intensity with increasing water content was observed. The shift to lower frequencies and its dependence on water content (Fig. 2) indicates interactions among solute molecules and water via hydrogen bonding. Similar interactions should be expected if N-methyl succinimide is substituted by copolymers containing maleimide sequences in the main chain.

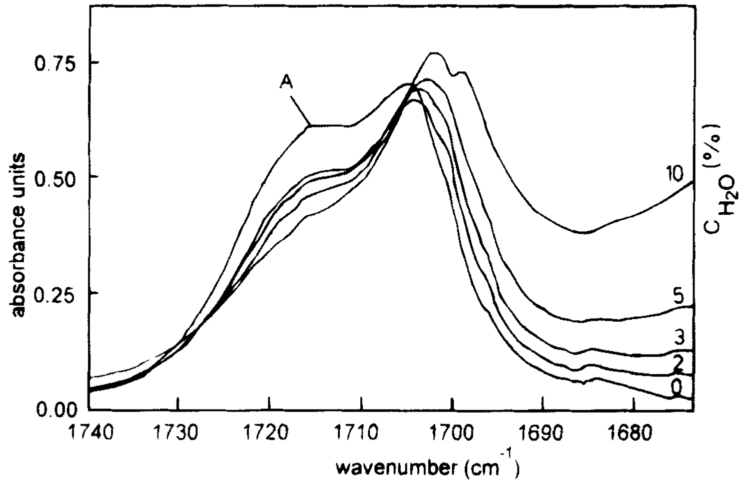

FIGURE 1 Shape of absorption band $\nu C = O$ of SMI as a function of water content (A: 0% water).

Online SEC-FTIR

The application of online SEC/FTIR is often complicated by the high-optical density of most eluents. The detection of the different components is only possible in regions of lower eluent absorption ("spectral windows"). For that reason, universal use of FTIR detection for identification in liquid chromatography is limited. In Figure 3, the different spectral regions are

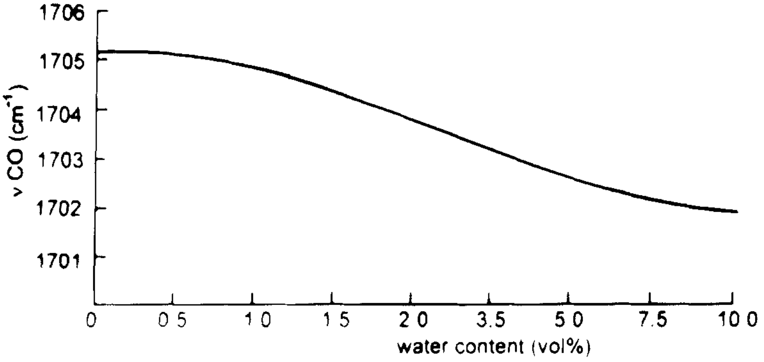

FIGURE 2 Shift of the ν C = O absorption of SMI as a function of water content.

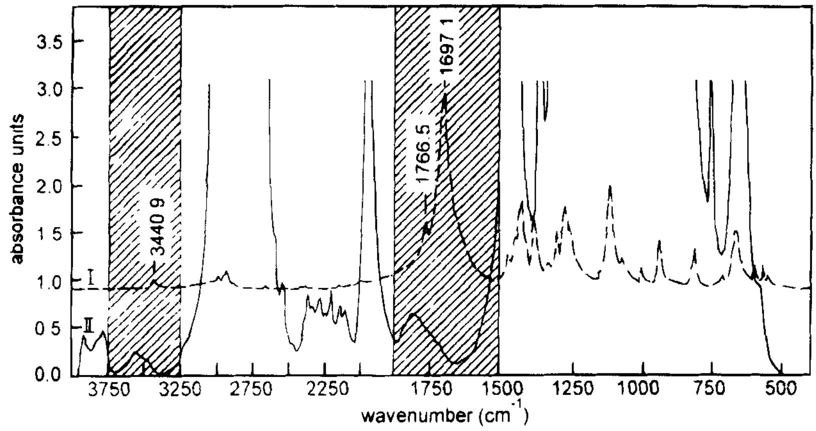

FIGURE 3 "Spectral window" regions of the model compound SMI (hatched area), spectrum of pure SMI as KBr pellet (I), spectrum of the pure solvent THF, d = 1.0 mm (II).

demonstrated for the system N-methyl succinimide (SMI) and THF. Only the regions of 1500–1875 cm^{-1} and 3250–3750 cm^{-1} are suitable for the detection of the SMI and water by their $\nu C = O$ and νOH or δOH vibrations.

In contrast to stationary solvent-solute systems, the preferential solvation is disturbed by the chromatographic separation process. The attractive forces among solute molecules and water that bring about solvation are affected by the entropically controlled size exclusion effects. Therefore, a smaller extent of preferential solvation in the SEC column was expected compared with the experiments in stationary systems. However, the solute-water complexes must be very stable if they are to be detected by the chromatographic methods. Three different chromatographic conditions were selected to indicate the presence of preferential solvation:

System A: SMI was dissolved in pure THF. Eluent contained 1% (v/v) water.

System B: Both the sample solvent and the eluent contained 1% (v/v) water. The sample was dissolved in the actual SEC eluent.

System C: The SMI was dissolved in a mixture of THF with 1% (v/v) water content. The eluent was pure THF.

The RI chromatograms of these three SEC runs are presented in Figures 4A–4C. Also, Figure 5 shows the RI-chromatogram of succinic acid. The

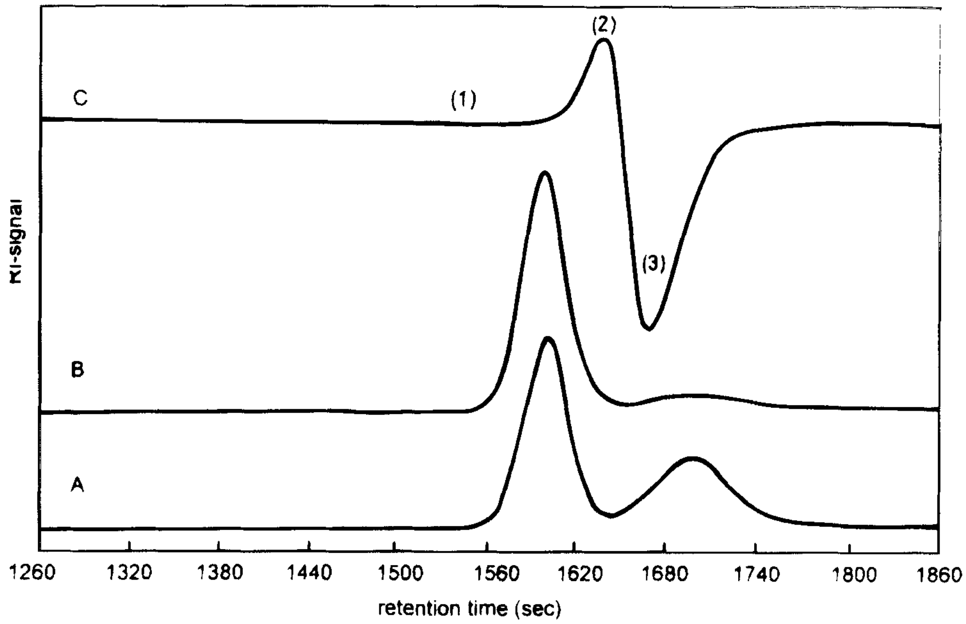

FIGURE 4 RI chromatograms of SMI at different chromatographic conditions (see text; A, C: sample size 0.2 mg, B: sample size 0.3 mg).

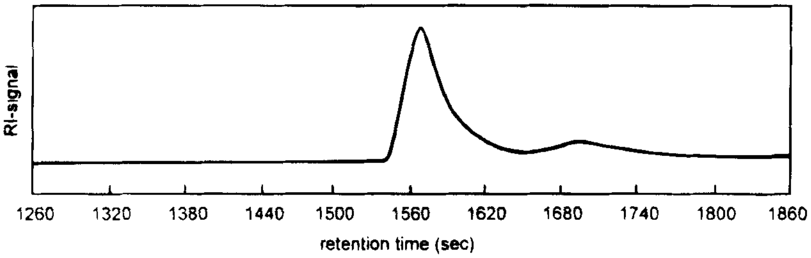

FIGURE 5 RI chromatogram of succinic acid (sample size 0.3 mg, sample solution and eluent with 1% water content).

sample preparation was similar to system B. The appearance of a second peak (Figs. 5 and 4B) at higher retention time is characteristic for all three systems.

Similarly to results observed in ref. [30] vacancy peaks (system peaks) were found during our earlier investigations [31,32] of aliphatic dicarboxylic acids in THF/water. The presence of system peaks indicates differences of the water content between bulk sample solvent and eluent due to preferential solvation.

Previous experiments were performed only under conditions similar to system B. It was possible to prove the water vacancy in the eluent and the water complexes of dicarboxylic acid directly by the described online experiments. The extent of preferential solvation can be calculated from the system peak area [30,32].

From Figures 4B and 5, it can be concluded qualitatively that the differences of water content are very small. The positive deviations from the base line of the chromatogram indicate smaller water content in the bulk solvent as compared with the eluent used. In this specific case (system B), the area of the vacancy of water correlates directly with solvate water of all of the solute molecules. It can also be seen that the system peak found for succinic acid (Fig. 5) is distinctly larger than that for SMI. Taking into account the chromatographic separation process, the interactions between water and the succinic acid must be stronger as compared with the interactions between SMI and water. For system C, a negative peak appears as expected (Fig. 4C). An excess of water is the reason for this because the water content of the sample solution is much higher than that of the eluent.

As described, an FTIR spectrometer was used as a real-time detector for SEC to obtain the IR spectra of the actual eluate present in the flow cell as an "infrared response" during the chromatographic run. It is well known that the IR spectra are calculated from measured interferograms via Fourier transformation algorithm. From interferograms collected during a chromatographic run, it is possible to construct functional group specific chromatograms in a way explained in detail, for example, by Griffiths and de Haseth [36]. A fast Fourier transform was performed and the resulting spectrum was divided into spectral regions of interest. The integrated infrared absorbance was calculated across each of the spectral regions to produce "IR chromatograms". The infrared absorbance within each region corresponds to the presence of a specific peak and hence a specific functional group. So the eluate can be identified by chemical class.

A more sensitive technique for real-time reconstruction of "IR chromatograms" from the interferometric data is the Gram-Schmidt vector orthogonization. According to ref. [36] it can be explained as a normalized subtraction routine, taking two vectors and removing from one any common components found in the other. Only if one interferogram has eluate information and the other is the eluent background, a positive peak in the Gram-Schmidt reconstructed chromatogram appears. The Gram-Schmidt reconstructed chromatogram for the system C is shown in Figure 6. (Figures 4C and 6 were obtained from two different chromatographic runs, which explains the difference in retention times of the two SEC curves caused by different flow rates.)

Analogously to Figure 4C, the "IR chromatogram" can be divided into three sections. The peak (3) at 1688 s has the largest area. Two small shoulders, (1) at 1584 s and (2) at 1630 s, appear in front of peak (3). It is impossible to identify peaks (1) and (2) only by interpreting the Gram-Schmidt and RI chromatograms. For interpretation of these sections in Figure 7 the chemigrams (obtained from the same run as the Gram-Schmidt-chromatogram) for three different spectroscopic regions of characteristic vibrations are presented: "carbonyl" $\nu C = O$ (1750–1690 cm^{-1}), "water 1" νOH (3500–3200 cm^{-1}) and "water 2" δOH (1690–1619 cm^{-1}).

The "carbonyl" chemigrams explain the origin of the peaks (1) and (2). It could be seen that these peaks can be assigned to carbonyl groups containing compounds. Furthermore from the "water 1" and "water 2"

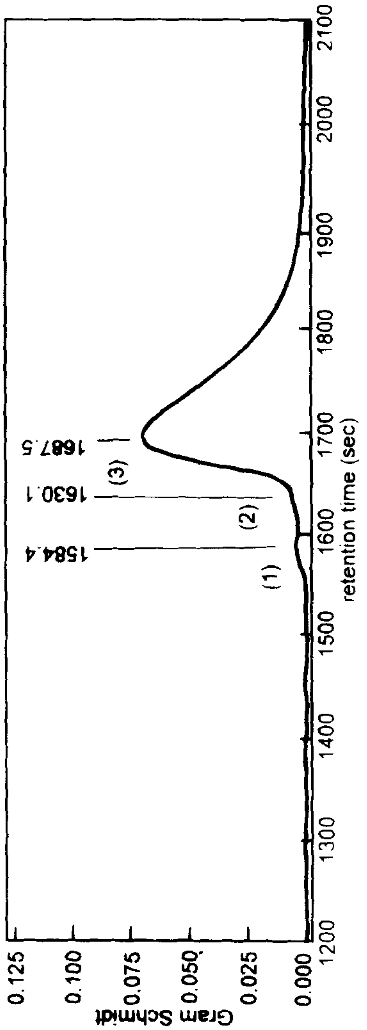

FIGURE 6 Gram-Schmidt reconstructed chromatogram of system C.

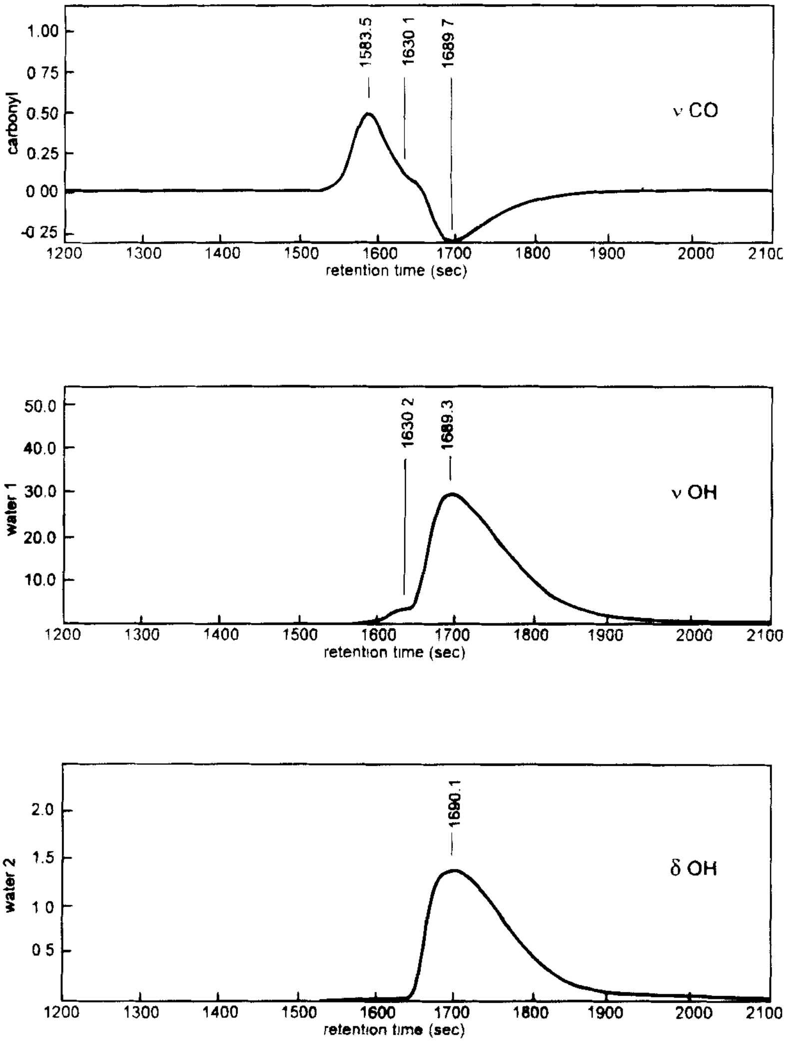

FIGURE 7 Chemigrams obtained for three different regions of absorption (νC = O, νOH, δOH).

chemigrams, it is clearly visible that the two peaks are influenced by different amounts of water. Definitively it can be concluded that the peak (3) was produced by water. Note the different scaling of the ordinates in Figure 7.

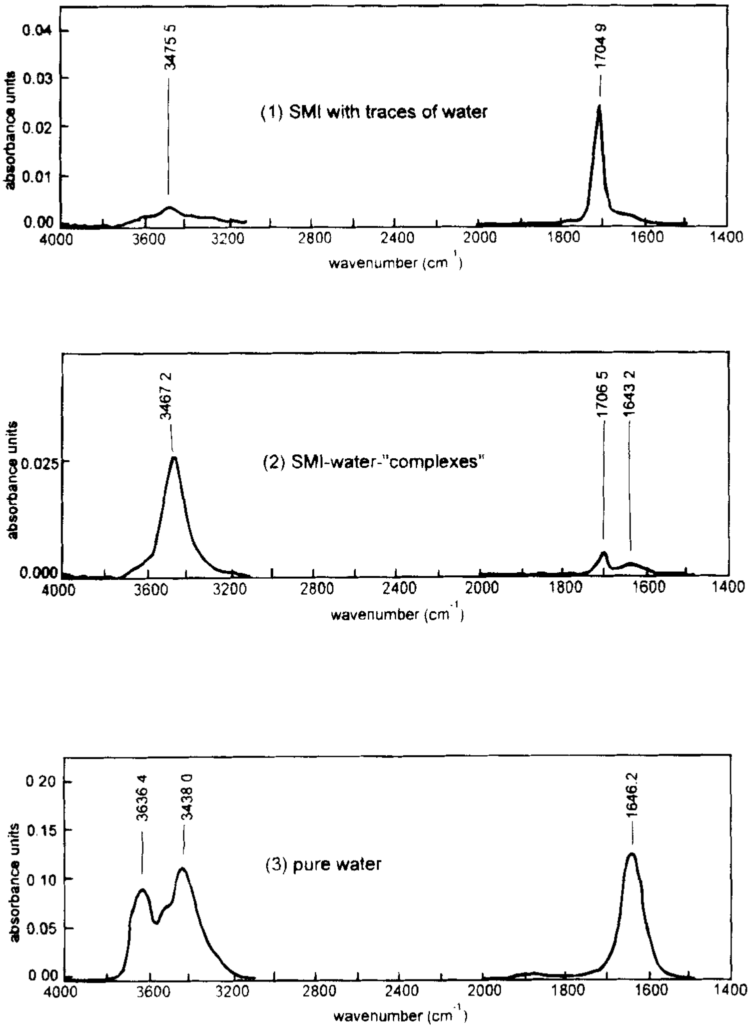

FIGURE 8 IR spectra extracted from the Gram-Schmidt-chromatogram peaks (1), (2) and (3).

The negative value at 1690 s in the "carbonyl" chemigram is caused by an insufficient base-line correction due to the relatively high water content in THF. The infrared spectra extracted from Gram-Schmidt-chromatogram at the maxima of the three peaks are presented in Figure 8.

SMI was clearly identified in peaks (1) and (2) by its typical νC = O bands near 1700 cm^{-1}. The νOH and δOH regions demonstrate that the water content increases from peak (1) up to peak (2). The shape of the νOH bands is comparable to those which were obtained by stationary measurements for low-water content in THF/SMI solution. The spectrum of peak (1) indicates a very low water content in the vicinity of the solute molecules (solvated water). The single νOH band at 3475 cm^{-1} and the ν C = O band at 1705 cm^{-1} could be related to remarkable interactions of the water molecules with the SMI molecules. The peak (2) was produced by another type of SMI-water association called SMI-water "complexes". In this case, the νOH and νC = O bands appear at 3467 cm^{-1} and 1707 cm^{-1}, respectively. The spectrum of peak (3) is typical for water dissolved in THF. The same band structure in the νOH region was found in the stationary experiments.

CONCLUSIONS

Light scattering measurements on alternating copolymers of maleic anhydride or methyl maleimide and styrene show a strong dependence of the M_w values on the water content in the solvent tetrahydrofuran. The results suggest that these effects arise from preferential solvation and complicate the molecular characterization of the copolymers.

With SEC/FTIR online experiments, the correlation of the water vacancy peak with preferential solvation of N-methyl succinimide as a model compound for the methyl maleimide segment could be explained. The water-solute-complexes formed in the sample solution are stable enough during the SEC-separation process if dry THF is used as eluent. Only by FTIR online detection it was possible to detect the different water content in the effluent along the chromatographic run and especially within the solute components. The peaks in the RI and Gram-Schmidt reconstructed chromatograms could be identified by chemigrams and by extracted IR spectra.

We expect that the effects of preferential solvation of polymer molecules will be much smaller than the investigated low-molecular-weight compounds. This assumption could be confirmed by first SEC-FTIR online experiments with copolymer as the solute. The results compared with light scattering experiments, and will be published in a following paper.

Acknowledgements

The authors would like to thank Mrs. Ch. Meißner, Mrs. Ch. Möller and Mrs. G. Adam for LS and FTIR measurements. Prof. Dusan Berek (Polymer Institute, Slovak Academy of Science, Bratislava) is gratefully acknowledged for the helpful discussion. Part of this work was supported by the Deutsche Forschungsgemeinschaft.

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